SYMPOSIUM

April 10 - April 26, 2023

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SESSION CH01.01: Synchrotron/X-Ray/Spectroscopy Techniques for Batteries

Session Chairs: Rosa Arrigo and Akihiro Kushima
Monday Morning, April 10, 2023
Moscone West, Level 3, Room 3022

8:15 AM *CH01.01.01
Synchrotron-Based X-Ray Characterization of Li-Ion Battery Degradation Mechanisms Johanna N. Weker; SLAC National Accelerator Lab, United States

Synchrotron-based X-rays are a powerful characterization tool that can probe across many relevant length scales (from atomistic to millimeter) with different techniques that are sensitive to distinct features such as microstructure, chemistry, and morphology. Because of the high flux available and penetrating power of X-rays, batteries can be probed under realistic conditions, which enables us to understand and overcome failure mechanisms of the generation battery materials. I will discuss our multimodal approach combining information from high resolution transmission X-ray microscopy, X-ray diffraction, and X-ray absorption spectroscopy to study a range of different battery chemistries. Specifically, I will present recent work on using X-ray microscopy to study nanoporous architectures for alloying anode to accommodate their large volume changes. I will also demonstrate the value in X-ray tomography at multiple length scales (from nm to micron) to characterize the degradation of $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ cathodes from fast charging.

8:45 AM CH01.01.02
Structure-Dynamics Investigation of Electro-Responsive Redox-Polymer by *In Situ* Neutron Reflectometry Hanyu Wang[1], Riccardo Candeago[2], Mathieu Doucet[1], Jim Browning[1] and Xiao Su[2]; [1]Oak Ridge National Lab, United States; [2]University of Illinois at Urbana-Champaign, United States

Heavy metal contamination has been a major health and environmental hazard on the global scale. The development of smart materials for water purification and environmental remediation has received intense attention. In recent years, redox-active materials have been demonstrated to be an attractive platform for separations due to their molecular selectivity and electronic tunability. The main features of these systems are the fast electron transfer and redox processes at moderate potentials, which allow reversible adsorption and desorption of ionic components. Furthermore, due to the selective performance differences among these redox-polymers, a promising platform for electrochemical separations can be built by tailoring polymer structures for targeted metal recovery processes, depending on the stream compositions. Our planned study aimed to combine the electrochemical characterization with a simultaneous, non-destructive *in situ* or *operando* characterization technique, so to correlate oxidation states of the redox-active centers with migration of ions and solvent in the polymer film. Neutron reflectometry (NR) is the ideal candidate for investigating thin-film systems in a non-destructive and non-invasive fashion. Liquids Reflectometer (LR) at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL) measures the surface and interfacial structures of the thin films in a horizontal sample geometry on length scale of 0.5 nm to 350 nm, and tracks changes of layer thickness, scattering length density (SLD), and roughness as a function of depth. The unique sample environment at LR offers the capability to conduct *in situ* electrochemistry to probe the morphological and structural changes of redox-polymer interfaces during operation as a function of chemical and electrochemical gradients over time. Electrochemical *in situ* NR experiments studied the equilibrium of swelling/deswelling of the poly(vinyl ferrocene) (PVFc) in presence of ReO_4^- with H_2O and D_2O (Figure 1 a and b, reflectivity curve; Figure 1 c, corresponding scattering length density profile). The NR data revealed high uptake capacities when applying voltages beyond the oxidation potential for ferrocene, showing promising results for implementation in real conditions. Dynamic data was collected too (Figure 1 d). After data analysis, we were able to track the capture or the release of the target ions (e.g., ReO_4^-) as the electrochemical process happens (Figure 1 e). This study will allow us to answer questions such as: what is the role of solvation in determining selectivity? What roles do uptake kinetics, diffusion limitations in the film play for selectivity? Answering these questions will be critical for creating new, more selective separation systems through the rationally design of the polymer structure and operating conditions.

9:00 AM CH01.01.03
Advanced *In Situ* X-Ray Analysis for Understandings on Chemo-Mechanistic Dynamics in Lead-Acid Batteries Seongjun Kim, Mark Wolfman,

Tiffany Kinnibrugh, Jaejin Kim, Alan Kastengren, Paul Fenter and Tim Fister; Argonne National Laboratory, United States

Since developed in 1859, the lead-acid batteries have been loved as secondary power source for various vehicles because of its cheap price and easy production process. Although the lead-acid battery is inferior in terms of specific energy and power density from the high atomic weight Pb compared to state-of-art lithium-ion batteries (LIB), this classical system has still loved worldwide all times because of its bold economic advantages. High powder density and simplicity of manufacture solidifies their status in the battery market. In addition, it is noteworthy that the almost every component after use can be recycled and long storage time in the perspective of energy sustainability.
Climate change is becoming a global issue that all humans must be concerned about. The internal combustion (IC) vehicle is one of the largest sectors that occupies the cause of air pollution and global warming. Accordingly, the hybrid electric vehicle (HEV) was designed to reduce fuel consumption along with development of full elective vehicles (FEV). The HEV consists of electric motor and IC engine, which needs high power whenever the start-stop system turns on and off. Therefore, the high-power lead-acid battery being used in conventional IC vehicles is still a good option for HEV system. However, the lead-acid battery should overcome some major problems in order to compete other types of batteries. Deep discharge cause facilitation of rapid sulfation, also the irreversible crystallization of lead sulfate ($PbSO_4$) can decrease the battery lifespan and performance. In other words, examining the structure transformation of two active materials, positive active material (PAM) and negative active material (NAM), is important to enhance the battery capacity and cycle life. The internal morphological variation can lead to change porosity and surface area in the electrode, which is crucial parameter to determine the performance. However, the existing post-mortem analysis such as scanning, and transmission electron microscopy (SEM and TEM) do not show the real-time changes during cycling.
Synchrotron x-ray computed tomography (XCT) is a promising technique to investigate two- or three-dimensional (2D or 3D) morphological transformation. Through in situ or in operando measurement, the morphology changes by phase transition during cycling can be identified in real-time. Images obtained from the XCT can be reconstructed to the 2D slice image, which is able to reassemble to the 3D images. The porosity and particle evolution by the different state of charge (SOC) is interpreted by the techniques. Additionally, the other synchrotron x-ray techniques such as diffraction (XRD) and transmission x-ray microscopy (TXM) support the intrinsic chemo-mechanical dynamics in the lead-acid batteries.
This presentation will provide much interest in the lead-acid batteries and information on the mechanism analysis using various synchrotron x-ray techniques. The application of in situ and operando x-ray measurements enable to enhance general comprehensions on the battery chemistry beyond not only lead-acid but other types of batteries.

9:15 AM CH01.01.04
Ultrafast Dark-Field X-Ray Microscopy – A New Tool for Analysis of Multiscale Dynamics Leora E. Dresselhaus-Marais; Stanford University, United States

Defects and structural distortions dominate the dynamics of metals and functional materials. But many processes – from fracture to phase transitions – have dynamics that rely on multiscale dynamics that are difficult to reconcile between mm-A lengthscales and ms-ps timescales. Dark-field X-ray microscopy (DFXM) can now directly image defects in single- and poly-crystals, resolving distortions deep beneath the surface over a wide field of view, with high sensitivity to strain and inclination in the lattice. We have developed time-resolved DFXM over the past 5 years for multiscale analysis of dynamics, and recently extended this to ultrafast timescales at X-ray free electron lasers. I will present the new DFXM toolbox we have developed and demonstrate how they inform important multiscale structural dynamics relevant to mechanics and thermal engineering. Our DFXM experiments can now collect movies of mesoscale phonon-defect interactions and deformations *in-situ* over ms-fs timescales, offering key opportunities to inform models yet untested.

9:30 AM CH01.01.05
High-Resolution Kinetic Studies of Battery Degradation Using Laboratory X-Ray Microscopy Kristina Kutukova[1], Victor Shapovalov[2] and Ehrenfried Zschech[1]; [1]deepXscan GmbH, Germany; [2]The Smart Materials Research Institute, Southern Federal University, Russian Federation

Advances in the design of new materials for efficient and durable energy storage and conversion systems are critical to current and future energy technologies. Performance and lifetime of batteries strongly depend on the 3D morphology of hierarchically structured materials and on morphology changes during operation. Morphological changes, i.e., particle fracture and surface deterioration, are among the most prominent sources of electrode degradation and eventual irreversible capacity loss. Advanced characterization techniques are needed to gain a deep understanding of the degradation mechanisms that affect performance and limit the lifetime of energy storage and conversion systems.

The potential of X-ray microscopy (TXM) and nano-XCT studies as a non-destructive method for characterizing kinetic processes in 3D-structured systems has been demonstrated mainly at synchrotron radiation beamlines. In this talk, we are presenting a customized solution for a laboratory nano-XCT tool with an integrated operando cell, and we are demonstrating its applicability for the study of kinetic processes in electrode materials, that cause degradation of batteries at the nanoscale, using a photon energy of 8 keV (Cu-Ka radiation). For laboratory nano-XCT tools, the selection of the material for the windows is particularly important because of the lower brilliance of the X-ray sources compared to synchrotron radiation sources. Ideally, the windows for an electrochemical *operando* cell must be transparent for photons in the selected energy range, it has to be rigid, nonpermeable to gases and moisture and electrically conductive. Glassy carbon, widely used in a variety of electrochemical and electrocatalytic applications, fulfils these requirements. It acts simultaneously as a current collector and a window. Glassy carbon is suitable for applications with most electrode compositions for Li- and Na-ion batteries. However, the thin glassy carbon windows are extremely fragile and require proper structural support from the cell enclosure.

A special custom-built electrochemical cell with glassy carbon windows/current collectors was designed and integrated into a TXM tool. The design of the electrochemical cell allows X-rays to pass through the sample at a wide range of angles, which allows limited-angle X-ray tomography to image the 3D morphology of the porous material and the evolution of defects like microcracks during battery cycling.

We demonstrate the capability of laboratory nano-XCT for the non-destructive imaging of microcracks in particles of $Na_{0.9}Fe_{0.45}Ti_{1.55}O_4$ (NFTO) cathode material in Li-ion batteries [1]. Many particles of the as-prepared cathode material show already initial microcracks. These microcracks start to grow at the first charge/discharge cycle. Further charging/discharging results in division of large particles into smaller ones. Chemo-mechanical stress caused by the supposed electrochemical substitution of Na by Li ions might accelerate the processes of microcrack formation and propagation. A notable observation is that the probability for formation and growth of microcracks is higher for large particles with low density than for the more dense and finer particles. A possible reason for the higher fracture susceptibility of large particles (especially at higher current densities) might be the state-of-charge (SOC) heterogeneity. The impact of the morphology on the degradation of battery materials, particularly the size- and density-dependence of the fracture behavior of the particles, is revealed based on a semi-quantitative analysis of the formation and propagation of microcracks in particles.

This study opens new perspectives for the nondestructive characterization of novel electrode materials for batteries. In-situ and operando X-ray microscopy allows kinetic studies of morphology changes and defect evolution during battery cycling with about 100nm resolution.

[1] V. Shapovalov, K. Kutukova, et al., Crystals (2022) 12, 3.

9:45 AM BREAK

10:15 AM CH01.01.07
Revealing and Controlling Dynamic Lithium Insertion Pathway at High Rate via *In Situ* XRD and X-Ray Microscopy Bonho Koo[1], Jinkyu Chung[1], Juwon Kim[1], Hyejeong Hyun[1], Dimitrios Fraggedakis[2], Jian Wang[3], Namdong Kim[4], Markus Weigand[5], Tae Joo Shin[6], Daan Hein Alsem[7], Norman J. Salmon[7], Martin Z. Bazant[2,2] and Jongwoo Lim[1]; [1]Seoul National University, Korea (the Republic of); [2]Massachusetts Institute of Technology, United States; [3]Canadian Light Source, Canada; [4]Pohang Accelerator Laboratory, Korea (the Republic of); [5]Helmholtz-Zentrum Berlin, Germany; [6]Ulsan National Institute of Science and Technology, Korea (the Republic of); [7]Hummingbird Scientific, United States

Lithium-ion insertion kinetics fundamentally hinges upon phase transformation behavior during (dis)charging. At high c-rates, kinetic hysteresis is amplified and phase evolution becomes heterogeneous and unpredictable. For instance, discharging becomes more sluggish than charging for most of the battery electrodes. In addition, single-phase $LiNi_xMn_yCo_zO_2$ (NCM) undergoes phase separation behavior. Here, we developed an operando soft x-ray microscopy to track the lithium transport and phase evolution on the surface and bulk of individual battery particles over a wide range of cycling rates (0.01 – 10C). Our result unambiguously reveals that dynamic asymmetry between fast charging and discharging originates from auto-inhibitory Li-rich and autocatalytic Li-poor surface domains, respectively. In addition, we developed synchrotron-based operando fast XRD to track phase evolution during fast cycling. We electrochemically manipulate the lithium-ion concentration distribution within NCM particles to effectively promote solid-state lithium diffusion. Our method succeeded in redirecting the unwanted phase separation at a fast rate to solid-solution behavior. Our work lays the groundwork for developing high-power applications and ultrafast charging protocols.

10:30 AM CH01.01.08
Solid-State Synthesis and Electrochemical Electrode Reactions Investigated by *In Situ* X-Ray Diffraction Matteo Bianchini[1,2,3], Damian Goonetilleke[2], Marie Duffiet[2], Torsten Brezesinski[2] and Jürgen Janek[2,4]; [1]University of Bayreuth, Germany; [2]Karlsruhe Institute of Technology, Germany; [3]BASF SE, Germany; [4]Justus-Liebig-Universität Giessen, Germany

In situ diffraction studies can capture transient crystalline phases forming during chemical reactions. Whether the reaction is a chemical solid-state synthesis, or an electrochemical intercalation process within typical layered compounds used as battery electrodes, proper sample environments can nowadays be developed to perform *in situ* diffraction experiments. Furthermore, *operando* studies, in the case of batteries, can be used to capture the materials' evolution during the realistic functioning of the device.
In both cases, the time-resolved nature of the experiments allows to obtain a greatly increased amount of information. For example, in the synthesis of inorganic materials, reactions often yield non-equilibrium kinetic byproducts instead of the thermodynamic equilibrium phase [1]. To rationalize that, the competition between thermodynamics and kinetics occurring during the process need to be investigated in real time. Fully determining the reaction pathway potentially is a key requirement to achieve the rational synthesis of target materials [2, 3]. In this presentation, recent examples from our work applying *in situ* synchrotron XRD to understand the synthesis of relevant industrial compounds such as $LiNiO_2$ [4] and $LiCoO_2$ (2022, unpublished) will be reported and compared. The use of neutrons as possible probes with Li sensitivity for such reactions will also be demonstrated.
In addition, a recent example of the use of *in situ* (and *operando*) XRD to the $LiNi_{1-y}Mn_yO_2$ ($y = 0, 0.05, 0.1, 0.17, 0.25$) series of positive electrode materials will be reported [5], where we have ensured a fair comparison of the samples by obtaining an equal amount of delithiation of all samples during charge. We found in particular a significantly decreasing anisotropy (difference in the variations of the *a* and *c* unit cell parameters) in the crystallographic lattice change of the materials with increasing y, signifying that Mn-containing compounds yield lower mechanical strain to the cathode composites.

References:
[1] M. Aykol et al., *Science Advances*, **2018,** 4 (4), 148.
[2] Z. Jiang et al., *Journal of Materials Chemistry C,* **2017**, 5 (23), 5709-5717.
[3] M. Bianchini, J. Wang et al., *Nature Materials*. **2020**, 19 (10), 1088-1095.
[4] M. Bianchini et al., *Journal of Materials Chemistry A*, **2020**, 8(4), 1808-1820.
[5] D. Goonetilleke et al. *Journal of Materials Chemistry C,* **2022,** https://doi.org/10.1021/acs.jpcc.2c04946

10:45 AM CH01.01.09
Excitonic and Surface Effects in X-Ray Absorption Spectra of Fluoride Salts Ana Sanz-Matias[1], Subhayan Roychoudhury[1], Xuefei Feng[1], Feipeng Yang[1], Li Cheng Kao[1], Kevin R. Zavadil[2], Jinghua Guo[1] and David Prendergast[1]; [1]LBNL, United States; [2]Sandia National Laboratories, United States

Due to the practice of employing electrolytes with fluorine-containing species (salt, solvent, or additives) that electrochemically decompose and deposit on the electrodes, fluoride salts may appear as evolving components of electrochemical interfaces in Li-ion batteries and emergent multivalent ion cells. We explore fluorine K-edge XAS of mono- (Li, Na, and K) and di-valent (Mg, Ca, and Zn) fluoride salts from a theoretical standpoint and discover a surprising level of detailed electronic structure information about these materials despite the relatively predictable oxidation state and ionicity of the fluoride anion and the metal cation. Given ultimate applications to evolving interfaces, some understanding of the role of surfaces and their terminations in defining new spectral features is provided to indicate the sensitivity of such measurements to changes in interfacial chemistry.

11:00 AM CH01.01.10
X-ray Diffraction Tomography for Investigating Li-Ion Batteries Under Operating Conditions Dorota Matras[1,2], Thomas Aston[3], Marta Mirolo[4], Isaac Martens[4], Jakub Drnec[4], Olof Gutowski[5], Simon Jacques[6], Jawwad Darr[3], Andrew Beale[3,6], Paul Quinn[2] and Antonis Vamvakeros[6]; [1]Faraday Institution, United Kingdom; [2]Diamond Light Source, United Kingdom; [3]University College London, United Kingdom; [4]European Synchrotron Radiation Facility, France; [5]Deutsches Elektronen-Synchrotron, Germany; [6]Finden ltd, United Kingdom

Li-ion batteries (LiBs) have become the preferred energy storage device choice for a variety of applications ranging from portable devices to (hybrid) electric vehicles, due to their relatively large energy density and life-cycle when compared to other competitive technologies. LiBs are though complex multi-component material systems and their performance directly depends on numerous parameters such as electro-chemical stability of the cell components and uniform current and temperature distributions for the desired operating conditions (voltage/current density), all of which are interlinked. A non-uniform current/charge distribution can have a negative impact on the performance of LiBs as it can lead to decreased capacity and power output, local temperature gradients and even to overcharge/overdischarge. Understanding how the local chemistry of the various system components is related to spatial gradients in the state of charge (SoC) and indeed capacity fade, is essential in order to optimise cell performance and design LiB materials with enhanced properties. However, investigating the evolving chemistry and the Li distribution in real-time is crucial to avoid relaxation problems coming from *ex situ* cell/material characterisation measurements.
Over the past decade, several studies focusing on *in situ*/ *operando* investigation of commercial LiBs, but most have been performed with conventional X-ray absorption-contrast computed tomography which provides limited/no chemical information in the reconstructed images [1]. In contrast, combining

scattering or spectroscopic techniques with tomography enables the extraction of local chemical and physical information within the interiors of intact materials and devices.
In this work, X-ray diffraction computed tomography was employed to study the state-of-charge induced chemical heterogeneities in commercial cylindrical LiBs in a spatially-resolved manner. More precisely, the (de)lithation processes under operating conditions and the effect of cycling rate on the heterogeneities within both electrodes were investigated. In both these studies [2,3], we were able to identify regions of uneven Li distribution which is bound to have an effect on the current and temperature distribution, potentially leading to capacity loss and/or cell failure. Finally, the obtained results demonstrated the importance of this chemical imaging technique as an invaluable diagnostic tool for real-word commercial batteries. This technique can applied for a variety of different experiments related to battery degradation mechanisms, such as *in situ/operando* abusing testing to capture internal temperature gradients through the crystallographic behaviour of both electrodes.
[1] Pietsch, Wood, Annual Review of Materials Research, 47, 451, 2017.
[2] Vamvakeros et al., Small Methods, 5, 2100512, 2021.
[3] Matras et al., Journal of Power Sources 539, 231589, 2022.

SESSION CH01.02: Spectrometry and Spectroscopy Techniques for Energy Materials
Session Chairs: Rosa Arrigo and Junjie Niu
Monday Afternoon, April 10, 2023
Moscone West, Level 3, Room 3022

1:30 PM *CH01.02.01
On Chip Electrochemistry Mass Spectrometry for Multiple Li Chemistries—from Batteries to N_2 Fixation Daisy Thornton[1], Bethan Davies[1], Artem Khobnya[1], Soren Scott[1], Ainara Aguadero[2], Mary Ryan[1] and Ifan E. Stephens[1]; [1]Imperial College London, United Kingdom; [2]ICMM, Spain

Gas evolution is ubiquitous in electrochemical energy conversion and storage; for instance in water electrolysis O_2 and H_2 evolution are desired, while in batteries, the same reactions are largely undesired and parasitic. On chip electrochemistry mass spectrometry offers much higher sensitivty than the prior state-of-the-art methods, typically based on differential electrochemistry mass spectrometry (DEMS).

In this contribution I will discuss how we have recently translated on chip electrochemistry mass spectrometry from aqueous systems to non-aqueous systems, both for probing (a) parasitic reactions in Li ion batteries and (b) ammonia production during Li mediated N_2 reduction.

The method allows quantitative pmol/s sensitivity to O_2, N_2, C_2H_4, CO_2 and NH_3 , all in real time. We have detected these products under conditions milder than previously reported. In this contribution I will discuss the mechanistic implications of our findings.

2:00 PM CH01.02.02
Highly Reliable Electrochemical Characterization of Electrode/Electrolyte Interface in Sub-Second Time Based on Impulse Response Analysis
Inyeol Yun, Jinpyeo Jeung and Yoonyoung Chung; Pohang University of Science and Technology, Korea (the Republic of)

Electrochemical analysis on electrode/electrolyte interface (EEI) is utilized in numerous research areas, such as batteries, skin electrodes, and biochemical sensors. Contact impedance, the most intuitive indicator of the electrochemical reaction between electrode and electrolyte, was generally extracted through electrochemical impedance spectroscopy (EIS). However, the EIS is too time-consuming to be implemented at the industry level [1]. Also, the long measurement latency leads to low reliability in time-variant measurement conditions, such as a human body and a microfluidic channel. Therefore, a contact impedance extraction method with a short measurement latency is required for ultrafast electrochemical analysis of EEI.
In this study, we propose a novel approach to extract contact impedance in an extremely short period (<1 sec) through an impulse response analysis. Our approach only measures an instantaneous response of EEI to an impulse input, and then extracts the contact impedance by analyzing the response with a unique algorithm. The extracted contact impedance exhibits a slight deviation of 6.4% with conventional EIS despite of its significantly short measurement latency. The ultrafast measurement enables to reliably extract contact impedance even on human skin, which has inhomogeneous characteristics with time. Furthermore, we demonstrated the impulse response analysis in a dynamic measurement condition which moves at high speed (500 mm/s) on a linear rail. The deviation rate of the impulse response analysis exhibits 5 times lower than EIS, which suggests that the impulse response analysis has robust characteristics in time-variant environments. The superiority and practicality of impulse response analysis will be of great help to numerous electrode-related research areas as well as the industry site by providing a concise and quantitative analysis of EEI.

[1] N. Meddings, M. Heinrich, F. Overney, J-S. Lee, V. Ruize, E. Napolitano et al., " Application of electrochemical impedance spectroscopy to commercial Li-ion cells: A review," Journal of Power Sources, vol. 480, no. 228742, Dec 31 2020.

2:15 PM CH01.02.04
Understanding Chemo Mechanical Interfacial Degradation Mechanisms in all Solid-State Batteries Using XRD-CT Partha P. Paul[1,2], Ji Hu[3], Robert Young[3], Alex Rettie[3], Marco DiMichiel[1] and Philip Withers[2]; [1]European Synchrotron Radiation Facility, France; [2]The University of Manchester, United Kingdom; [3]University College London, United Kingdom

As the transportation sector rapidly transitions from gasoline-driven to rechargeable battery-powered vehicles, there is an urgent need to develop more energy-dense batteries, with stable operation over long-term cycling. Using a solid-state electrolyte (SSE) offers the chance to exploit the significantly higher energy density of Li metal as an anode, compared to traditional intercalation anodes. However, interfacial stresses due to the non-uniform solid-solid contact at the anode/electrolyte interface can generate voids and cracks over cycling, as well as induce lithium plating [1]. Additionally, deleterious chemical and electrochemical reactions at the interface can exacerbate the interfacial instability, leading to crack propagation, metallic Li filling the voids, and eventually catastrophic failure of the battery [2]. Thus, understanding the nature of interfacial degradation mechanisms (chemical, electrochemical and morphological) is critical to achieving stable cycling with all solid-state batteries (ASSBs).
In this work, we employ synchrotron XRD-CT (X-ray diffraction computed tomography) to understand interfacial degradation in ASSBs under in-situ conditions. Specifically, we focus on the anode – SSE interface in symmetric Li | SSE | Li cells. We focus our study on the popularly used argyrodite (LPSCl) SSE. We scan the cells in the pristine, cycled and burned (cycled to failure) conditions. Using microcomputed X-ray tomography, we map and contrast the extent of cracking at the Li | LPSCl interface in Swagelok cells. Then, we scan the cells using XRD-CT to chemically map various species across the interface, including Li, LPSCl and Li_2S.
After registering the datasets together, we overlay the morphological microCT volume with the XRD-CT map, to correlate the presence of deleterious

interfacial products such as Li_2S. Additionally, we map the strains in the various chemical species, to correlate regions of strain heterogeneity with the size and extent of cracking, as well as the quality of interfacial contact between the SSE and Li anode in that region. We also investigate the effect of heat treatment of the SSE prior to cycling on the grain size, and correspondingly the extent of strain heterogeneities and cracking in argyrodite SSEs after moderate cycling. The non-destructive and fast nature of synchrotron X-ray characterization provides an ideal avenue to pursue *operando* characterization. Such non-destructive and multimodal characterizations are essential to understanding the interplay between various degradation modes, in turn informing strategies to mitigate them and enhance their cycling stability.

[1] Paul, P. P., Chen, B. R., Langevin, S. A., Dufek, E. J., Weker, J. N., & Ko, J. S. Interfaces in all solid state Li-metal batteries: a review on instabilities, stabilization strategies, and scalability. Energy Storage Materials 2022, 45, 969-1001.
[2] Hao, S.; Daemi, S. R.; Heenan, T. M. M.; Du, W.; Tan, C.; Storm, M.; Rau, C.; Brett, D. J. L.; Shearing, P. R., Tracking lithium penetration in solid electrolytes in 3D by in-situ synchrotron X-ray computed tomography. Nano Energy 2021, 82, 105744.

2:30 PM CH01.02.05
Tracking Electrochemical Active Material Transport with Simultaneous Neutron and X-Ray Tomography Jacob LaManna[1], Michael C. Daugherty[1], Youngju Kim[1,2], Daniel Hussey[1], Eli Baltic[1] and David Jacobson[1]; [1]NIST, United States; [2]University of Maryland, United States

In situ tracking of electrochemical active species is critical to understanding the complex transport mechanisms in electrochemical devices such as fuel cells, electrolyzers, and batteries. Many probes available to track electrochemical processes often require significant modifications to the devices to allow probe access to the reaction sites. These modifications can strongly influence the reaction by altering mass and charge transport, thermal gradients, and mechanical stresses. Additionally, the layered materials in electrochemical devices are not flat and can have a wavy interface which requires three-dimensional analysis to fully capture these interfaces. Two penetrating nondestructive probes that resolve three-dimensional structures are neutron tomography and X-ray tomography. Neutrons excel at detecting hydrogen and lithium while X-rays of sufficient energy to penetrate larger samples are sensitive to solid structures and high-Z components. The NIST-NeXT system combines these two probes together for truly simultaneous neutron and X-ray tomography that can gain greater information about the sample than either mode on its own. Recent advances in how NIST-NeXT data are analyzed has significantly reduced the acquisition time of a tomography scan. This reduction will produce scan times in the <15 minute range which is critical for tracking performance evolution in electrochemical devices. This talk will give an overview of the NIST-NeXT system with example studies from fuel cells, electrolyzers, and lithium-ion batteries to demonstrate the system's unique characterization capabilities for electrochemical devices.

2:45 PM CH01.02.06
Nano-FTIR Spectroscopy of the Solid Electrolyte Interphase Layer on a Thin-Film Silicon Li-ion Anode Andrew Dopilka[1], Yueran Gu[1,2], Jonathan M. Larson[1], Vassilia Zorba[1,2] and Robert Kostecki[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

Si anodes for Li-ion batteries are notorious for their large volume expansion during lithiation and the corresponding detrimental effects on cycle life, however, the calendar life is the main roadblock for widespread adoption. During the calendar life aging, the origin of the impedance increase and capacity fade is attributed to the instability of the solid electrolyte interphase (SEI).[1] In this work, nano-FTIR spectroscopy and XPS depth profiling is used to characterize the structure and composition of the SEI on Si thin film electrodes that underwent an accelerated calendar aging protocol.
Nano-FTIR spectroscopy is a novel scanning probe technique in which a metallically coated atomic force microscope (AFM) tip is illuminated with a broadband infrared light source.[2] By operating the AFM in constant tapping mode, the background from the scattered light can be separated from the near-field response with lock in amplification. The result is FTIR spectra with high spatial resolution (ca. 20 nm) that match well with standard far-field and ATR-FTIR references.[2–5] Nano-FTIR is an ideal method to study the SEI because of its high spatial resolution, ultrahigh sensitivity, and specificity for identifying inorganic and organic SEI compounds.
We first evaluate the structure and composition of the SEI after different washing procedures with dimethyl carbonate (DMC). We find that brief washing (< 5 seconds) results in large chemical and topographic changes to the surface of the Si electrodes in comparison to non-washed electrodes. While the non-washed electrode is homogenous in terms of topography, IR imaging and nano-FTIR spectra, the washed electrode displays heterogeneity on multiple length scales demonstrating how brief washing can disrupt the delicate SEI layer and potentially result in misleading conclusions. This is further supported by XPS depth profiling experiments showing that the SEI layer thickness also decreases with increased washing time.
After establishing the undesirable effects of washing on the SEI layer, we focus on characterizing the initial SEI formation (non-washed) to compare it to the SEI after the accelerated calendar aging protocol which invovles a 12 hour hold at 0.05 V. From the characterization on the initial SEI formation, we identify Li ethylene dicarbonate (LiEDC), polyethylene oxide (PEO) and LiF as the major components of the SEI layer. After the accelerated aging protocol, we find that the amount of PF_6^- reduction products is much higher than the initial SEI suggesting that there is accumulation of salt related decomposition products during the aging process. Based on this result, we propose that PF_6^- mass transport into the SEI layer is a major source of parasitic reactions and could be prevented by increasing the fraction of the inorganic scaffold (e.g. LiF) in the SEI or improving the Li^+ transference number of the polymer like SEI species.

Acknolwedgements
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3:00 PM CH01.02.07
Improving the Accuracy and Reproducibility of Raman Spectroscopy for Graphitic Particles Andrew Pollard, Piers Turner, Keith R Paton, Elizabeth Legge and Konstantinos Despotelis; National Physical Laboratory (NPL), United Kingdom

As a key component of energy storage devices, electrodes containing graphitic particles must be accurately characterised to determine their material properties, properties which will affect the final performance of the device itself. Raman spectroscopy has long been a 'go-to' technique for measuring

carbon materials, as the resulting Raman spectra reveal many of the material properties, such as the level of disorder, strain, doping, particle lateral size and thickness. However, although this technique has been used for many decades, there are still glaring issues with reproducibility, as well as the quantification of the Raman peak metrics in relation to the material properties. As a non-destructive and rapid technique, these issues become a crucial barrier, when trying to use this technique for both academic research and as an industrial quality control tool.
Towards this effort, firstly we report the results of an international interlaboratory study (ILC) conducted under VAMAS. This study compared Raman spectroscopy data for an idealised graphitic material, that is a graphene layer grown using chemical vapour deposition, gathered from 17 participants across academia, industry (including instrument manufacturers) and National laboratories and will be used as the basis for the international standard ISO/TS 21356-2. By comparing reported Raman metrics with the measurements of the same regions made by the lead participant, variations in the reported peak intensity ratios and peak fits could be explored for both instrumentation and data analysis. Due to a lack of relative intensity calibration, the relative difference reported in the 2D- and G peak intensity ratios (I_{2D}/I_{G}) was up to 200%. It was also shown that the standard deviation for Γ_{2D} values reported by different software packages, was 15× larger for Lorentzian fit functions than for pseudo-Voigt functions. This study has shown that by adopting a relative intensity calibration and consistent peak fitting and data analysis methodologies, these large, and previously unquantified, variations can be significantly reduced, allowing more reproducible and comparable measurements of graphitic materials using Raman spectroscopy.
Secondly, we assess how Raman metrics measured for graphitic particles in powder form can be used to determine impurities and the limits of detection, namely for larger and undesired graphite particles that, in this case, have been deliberately added to a more homogeneous powder of smaller particles. When a sufficiently large number of spectra are acquired, it is found that by processing and classifying individual spectra, rather than the averaged spectrum, a reasonable estimate of the fraction of unexfoliated material can be obtained. These results highlight the care that must be taken when interpreting results of Raman spectroscopy measurements.

3:15 PM CH01.02.09
Probing Silicon Anodes in Lithium-Ion Batteries Using *In Situ* FTIR Spectroscopy Nathan R. Neale, Trevor R. Martin, Jaclyn Coyle and Maxwell Schulze; National Renewable Energy Laboratory, United States

We have been exploring the intrinsic chemical and electrochemical reactivities of silicon nanoparticles (Si NPs), the electrode binder and finished 3D electrodes using both ex situ and in situ attenuated total reflectance-infrared Fourier transform (ATR-FTIR) spectroscopies. We will first detail ex situ FTIR results that probe the solid reaction products from the chemical reaction of aprotic battery electrolyte and three purported components of the Si-based anode solid-electrolyte interphase (SEI): SiO_2 nanoparticles (NPs), lithium silicate (Li_xSiO_y) powders and Si NPs. We use FTIR and classical molecular dynamics/density functional perturbation theory to assess the solid products remaining with these model materials after exposure to electrolyte. These species represent the initial stages of SEI growth and predict they likely drive subsequent chemical and electrochemical reactions by controlling molecular interactions at the Si active material interface.
Additionally, we will present studies on poly(acrylic acid) (PAA), a commonly used binder for fabricating Si anodes, that show the evolution of PAA occurs via a cross-linking reaction during electrode curing. We will relate its chemical change to the final electrode properties and performance as well as local electrolyte structure in the 3D electrode. These studies are made possible using two types of in situ ATR-FTIR spectroscopy: thermal ATR-FTIR to probe the PAA cross-linking reaction, and ATR-FTIR spectroelectrochemistry of three-dimensional composite electrodes, a unique technique that probes the solvation dynamics of lithium ions at the silicon anode interface under electrochemical polarization. These latter studies reveal that PAA acts as an interfacial material that conducts lithium-ions, limits solvent molecule access to the Si surface, and stabilizes the electrode against parasitic lithium inventory loss at high state of charge for an extended period.

3:30 PM CH01.02.10
Operando Electrochemical XPS at the Electrode-Electrolyte Interface Roxy Lee and Robert Palgrave; UCL, United Kingdom

A major challenge in the development of reversible batteries is the huge irreversible capacity loss incurred during the first cycle, which is primarily due to electrolyte decomposition on the anode surface to form a solid electrolyte interface (SEI) layer. Thus, an in situ study on the behaviour of species at the electrode-electrolyte interface, in addition to proper characterisation of the SEI layer, is of great interest. One such emerging area with great prospect is that of in situ electrochemical X-ray photoelectron spectroscopy (XPS). A wealth of information for the top ~5 nm of a sample can be obtained using XPS, including identification and quantification of elemental surface composition, determination of oxidation state and local chemical environment. Additionally, the high-vacuum requirement of traditional lab-based XPS studies can be overcome using ionic liquid (IL) electrolytes, due to their negligible vapor pressure. Further beneficial properties of IL electrolytes, including a large electrochemical window, superior thermal stability and potential for greener chemistry make them exciting alternatives to organic electrolytes.

In this contribution, we demonstrate the unique information that can be obtained from operando electrochemical XPS. Cyclic voltammetry (CV) measurements were performed in tandem with XPS analysis, with the X-ray beam focussed on the electrode-electrolyte interface of the working electrode (WE) in a three-electrode electrochemical cell, for a variety of different systems containing IL electrolytes. We report on the binding energy shifts of characteristic signals from the electrode and electrolyte species with the applied electrochemical potential, and the evidence of electrochemical decomposition products as evidenced by the formation of new species. The techniques presented here may be applied to an extensive range of systems containing IL electrolytes and may bring new insights into complex electrochemical reactions at the electrode-electrolyte interface, ultimately helping us to design and develop reversible batteries for the future.

3:45 PM CH01.02.11
Understanding the Active Surface of a MnO_x@Ag Fuel Cell Catalyst Using Operando X-Ray Absorption Near-Edge Spectroscopy Johanna Schroeder[1,2], José A. Zamora Zeledón[1,2], Gaurav A. Kamat[1,2], Melissa E. Kreider[1,2], Lingze Wei[1,2], Dimosthenis Sakoras[2], Alessandro Gallo[2], Michaela Burkes Stevens[2] and Thomas Jaramillo[1,2]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States

The global drive toward the sustainable generation of fuels and the use of sustainable fuels is accelerating as the challenges posed by climate change become increasingly apparent. Hydrogen fuel cells or metal-air batteries using renewable electricity represent uniquely promising technology areas for this purpose.[1] The optimization of the kinetically hindered oxygen reduction reaction (ORR) is thereby one of the key components for a widespread use of such renewable energy conversion and storage technologies. Current state-of-the-art catalysts for hydrogen fuel cells are composed of expensive platinum. However, to reduce the material costs and increase the sustainability of the catalyst material, non-Pt group metals and non-critical raw material are of high interest. Due to stability limitations, non-Pt group metals are currently only employed in alkaline media. Bimetallic silver (Ag) catalysts are very promising non-critical raw materials for the ORR.
In our recent work Zamora Zeledón *et al.*[2] presented ultra-thin Mn films (maximum 1 nm) deposited on top of Ag bulk material prepared by physical vapor deposition that are substantially more active under ORR conditions at 0.8 V_{RHE} than single metal Ag and Mn thin films. Herein, we used operando X-ray absorption near-edge spectroscopy (XANES) to understand the surface dynamics of the highly active MnAg thin films. Applying a potential of 1.2 V_{RHE}, above the onset of electrochemical oxygen reduction, the pre-edge features in the Mn K-edge indicate a mixture of MnO_2 and Mn_2O_3 in oxygen and nitrogen saturated electrolyte. At 0.8 V_{RHE}, a potential within the ORR window, the Mn is more reduced. Notably, shifts in both the main edge and distinct

pre-edge features indicate that at 0.8 V_{RHE} the Mn is more reduced during ORR, namely, in oxygen vs. nitrogen saturated electrolyte. In terms of reversibility, consecutively applying 1.2, 0.8, and again 1.2 V_{RHE} revealed a non-reversible oxidation state change in oxygen in contrast to nitrogen saturated electrolyte. This could be explained by stability changes and a possible MnAg reconstruction. By coupling operando X-ray absoprtion spectroscopy (XAS) and electrocatalysis we are able to correlate activity changes to distinct changes in oxidation state. Those insights gained from operando XAS offer new directions for in situ stabilization or enhancement of electrocatalytic materials.

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SESSION CH01.03: Advanced Microscopy in Battery Research I
Session Chairs: Akihiro Kushima and Junjie Niu
Tuesday Morning, April 11, 2023
InterContinental, Fifth Floor, Ballroom C

10:30 AM *CH01.03.01
***In Situ* TEM Diagnosis Guided Designing of Electrode Materials for Better Battery** Chongmin N. Wang; Pacific Northwest National Laboratory, United States

Electron microscopy-based diagnosis, in particular in-situ TEM, appears to be one of the essential methods for gaining insights as how an electrode material failure, which can be used to guide battery materials development for creating new materials with enhanced battery performance. In this presentation, I will highlight recent progress on the development of in-situ TEM techniques, featuring integration of environmental electron microscopy with force and electrochemical process, which enable direct observation of structural evolution, phase transformation, coupling of electrochemi-mechanical effect and their correlation with mass and charge transport, providing insights as how active materials evolve that leads to fading and eventual failure of a battery. In particular, I will cover the current understanding of the interfacial process in an electrochemical cell and its correlation with the process such as Li dendrite growth, mossy Li formation, and cathode-air interfacial reaction. In perspective, the presentation will target to check what need to be done in terms of in-situ TEM to tackle the challenging science questions for advancing energy storage research.

11:00 AM CH01.03.02
Advanced Electrode Design with Homogenous Electric Field Distribution to Study the Electrochemical Li Deposition on Carbon Electrodes by Means of *In Situ* TEM Xin Wei, Michael Noyong and Ulrich Simon; RWTH Aachen University, Germany

A detailed understanding of the early stage Li dendrite formation as well as of the solid electrolyte interphase (SEI) formation at the electrode/electrolyte interface is indispensable in mitigating the degradation in battery performance and the safety issues for Li batteries, as well as in developing other energy materials. *In situ* electrochemical transmission electron microscopy (ec-TEM) is a powerful tool to investigate the Li deposition process in its very early stage during the electrochemical cycling of Li battery materials. It has been demonstrated so far that real-time observation of electrochemically induced Li nucleation, growth, and dendrite formation can be achieved with high spatial resolution on the glassy carbon as well as on metal (platinum or gold) electrodes *in situ* by using meanwhile commercially available microscale ec-TEM liquid cells. However, the so far reported ec-TEM cells feature inhomogeneous electric field distribution along the electrodes, which may cause unreliability of the measurement and set tight limits for the interpretation and the quantitative analysis. Thus, this persuasive characterization technique is still kept far from a “close to real” application scenario.
Here, we report an advanced electrode design enabling a homogenous electric field distribution for further microscopic quantitative characterization of the early-stage Li deposition in a closer approximation to the actual battery scenario. Similar to the commercially available chips, the designed ec-TEM chips are equipped with a semicircle carbon electrode as the working electrode surrounding two platinum wires in the same shape as reference and counter electrodes. The design is based on COMSOL 3D simulations, which demonstrate the electric field distribution and allow for a quantitative comparison of the designed chips with the commercially available ones. Experimental investigations on metal deposition from liquid electrolytes (Li and other reference materials) using the designed ec-TEM chips were performed and these analyses demonstrated the advancement and feasibility of the newly designed electrode configuration to approach true battery conditions. These designed ec-TEM chips facilitate the quantitative electrochemical characterization combined with the *in situ* TEM technique not only relevant for Li battery research but for any kind of electrochemical processes, where the deposition of active compounds from liquid electrolytes represents an elementary mechanistic step in the overall process.

11:15 AM CH01.03.03
New Frontiers in Electrochemical Device Characterization Enabled by AI-driven X-Ray Microscope Reconstruction Technologies Stephen Kelly, Hrishikesh Bale, Yulia Trenikhina and William Harris; Carl Zeiss RMS, United States

A clean energy future will rely heavily on electrochemical energy storage and conversion devices like batteries and fuel cells to shift away from carbon-based energy sources. These electrochemical devices are generally closed off from the outside world and operate under highly non-ambient conditions (e.g., liquid electrolytes, air-free or controlled gas environments, elevated temperatures, liquid / gas flows). The performance of these devices is largely driven by the 3D microstructures of the internal components and their evolutions. For example, the weaves of the gas diffusion layer in a polymer electrolyte fuel cell control the gas flow to the catalyst and electrolyte layers; breached layers in batteries due to lithium dendrite growth can lead to catastrophic failures and safety concerns. As such, imaging the internal microstructures and processes in these devices is important for observing and measuring device construction details and understanding how defects are distributed and change performance during operation. In particular, 3D imaging allows for analysis of features and parameters that can only be fully understood in 3D like porosity and tortuosity, and can also provide realistic microstructural input for 3D modelling and simulation approaches.

Within this scope, X-ray microscopy provides a unique method to image electrochemical devices because of the non-destructive nature of the technique. Modern X-ray microscopes also enable high resolution imaging inside relatively large objects – critical for in situ imaging of closed-form electrochemical devices like batteries and fuel cells. Advances in tomographic image reconstruction have allowed researchers to increasingly maximize the impact of X-ray microscopy data through higher image quality and enabling faster data acquisition schemes. Recently, artificial intelligence (AI) has been incorporated into these algorithms, dramatically increasing the performance and capability of the technique. Here, we apply multiple novel reconstruction technologies that leverage AI to dramatically improve the performance of laboratory-based X-ray microscopes, showing examples across multiple fields of electrochemical device research.

We show how AI-powered tomographic reconstruction can reveal new levels of detail in lithium-ion batteries and polymer-electrolyte fuel cells, and enable up to 10 times faster data collection at both the micrometer and nanometer length-scales. We additionally show how these technologies can be used to generate massive 3D images that allow researchers to evaluate, measure, and simulate the performance of these devices with the needed micrometer resolution across truly meaningful length scales of many millimeters of device volume. We additionally show how these technologies can be used to generate massive 3D images up to 100 times faster than conventional approaches allowing researchers to evaluate, measure, and simulate the performance of these devices with unprecedented precision and representivity. These capabilities shift the paradigm in volume analysis for electrochemical devices and give researchers unprecedented insight into the detailed microstructures that drive device performance, enabling new levels of understanding and helping to power the drive to a clean energy future.

11:30 AM CH01.03.04
The Impact of 3D Microscopy Strategies on Computational Analysis for Battery Research Yulia Trenikhina[1], Stephen Kelly[1], Sarah Reeb[2], Cheryl Hartfield[3] and William Harris[3]; [1]Carl Zeiss X-ray Microscopy, United States; [2]Math2Market, Germany; [3]Carl Zeiss Microscopy, LLC, United States

Rapidly progressing global warming and pricing of natural fuels are well-known reasons to search for renewable energy sources. Many nations are addressing global climate change by implementing legislation that favors electric vehicles (EV) and related infrastructure development. The idea of a greener vehicle with no harmful CO2 emission is attractive for most drivers. However, multi-hour charging times and limited distance range are the downsides that keep many car shoppers away from EVs.
Striving for the electrification of transportation sets up new, challenging EV battery standards. Fast charging ability (“fueling time”) and battery capacity (vehicle’s distance range) are the key metrics for Lithium-Ion Battery (LIB) performance. LIBs with graphite anode suffer from rapid capacity fade and Li plating at high charging rates. Degraded battery capacity limits the range of applications, and Li plating becomes a safety concern once conductive paths between anode and cathode are formed. Overpotentials in intercalation electrodes cause both of these effects during fast charging. Li ions diffusion limitation at high charging current is one of the problems that results in electrode polarization that causes overpotentials. There are two pathways to improve Li ion diffusion: to increase the rate of interfacial reactions and to reduce the tortuosity of Li ions paths. The first approach involves altering electrolyte composition and SEI properties. The second approach is concerned with the electrode architecture. The electrode microstructure is the result of a multi-step manufacturing process that is concerned with uniform distribution of the electrode components (active particles, binder and conductive additive) and constant thickness. These microstructures call for characterization methods that cover several orders of magnitude in the length scale from a nm up through micrometers and beyond. Particularly important parameters for fast charging performance are particle connectivity and size, electrode tortuosity, and surface area and, due to the nature of the parameters, only 3D techniques enable adequate characterization.
3D FIB-SEM tomography presents a powerful approach to 3D microstructural characterization of battery electrodes and, when combined with computational modelling packages, enables robust analysis, modelling, and design workflows for fast-charging applications. However, because FIB-SEM tomography operates on the slice-and-view principle, care must be taken in acquiring and analyzing the data to ensure accurate results.
In this study we explore how the 3D FIB-SEM tomography parameters such as slice thickness, slice thickness variation, slice-to-slice alignment, and signal-to-noise level influence resulting electrode microstructure characterization parameters. We control slice thickness, regularity, and alignment by using advanced FIB-SEM acquisition software like Atlas 3D that allows for nm precision. Then, tomography data is plugged into simulation software for the quantitative analysis and battery performance prediction by comparing the cell overpotential to the open-circuit voltage at different charge rates. This approach links electrode manufacturing parameters directly to the estimation of available capacity at various charging rates. Computational simulation of the battery performance based on realistic electrode properties provided by 3D FIB-SEM tomography reduces the need for battery assembly, testing and post-mortem analysis and streamlines the electrode architecture design for fast-charging applications. This work investigates the interplay between data collection approaches and computational output within this framework and provides guidance for ultimate success.

11:45 AM CH01.03.05
Formation and Impact of Nanoscopic Oriented Phase Domains in Electrochemical Crystalline Electrodes Revealed by Collocated 4D-STEM and EELS Mapping Wenxiang Chen, Xun Zhan, Renliang Yuan, Saran Pidaparthy, Arghya Patra, Kim Ta, Zhichu Tang, Hong Yang, Andrew Gewirth, Paul V. Braun, Elif Ertekin, Jian-Min Zuo and Qian Chen; University of Illinois Urbana Champaign, United States

We study the structural and compositional changes in primary cathode nanoparticles in the electrochemical phase transformation. We map the formation of oriented phase domains and the associated development of strain gradients quantitatively during ion insertion. A collocated four-dimensional scanning transmission electron microscopy and electron energy loss spectroscopy approach, coupled with data mining, enables the research. Results show that in the spinel cathode nanoparticles their phase transformation upon Mg^{2+} insertion leads to the formation of domains of similar chemical identity but different orientations at the nanoscale. The domain formation process follows the nucleation, growth and coalescence process, different from the conventional diffusion- or reaction-limited mechanisms. Furthermore, electrolytes have significant impacts on the transformation microstructure (‘island’ versus ‘archipelago’). Large strain gradients built up from the development of phase domains across their boundaries change the chemical diffusion coefficient in the cathode nanoparticles by a factor of ten or more. Our findings provide critical insights into the microstructure formation mechanism and its impact on ion insertion, suggesting another dimension of transformation structure control for energy storage materials.

SESSION CH01.04: Advanced Microscopy in Battery Research II
Session Chairs: Akihiro Kushima and Chongmin Wang
Tuesday Afternoon, April 11, 2023
InterContinental, Fifth Floor, Ballroom C

1:30 PM *CH01.04.01
Multi-Modal *In Situ* Liquid-Electrochemical Microscopy for Energy Applications Daan Hein Alsem[1], Tyler Mefford[2], Jongwoo Lim[3], Rui Filipe Serra Maia[4], Aram Yoon[5], Pawan Kumar[6], Deep M. Jariwala[7], See Wee Chee[5], William C. Chueh[2], Norman J. Salmon[1] and Eric A. Stach[7,1]; [1]Hummingbird Scientific, United States; [2]Stanford University, United States; [3]Seoul National University, Korea (the Democratic People's Republic of); [4]CoLAB NET4CO2, Portugal; [5]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany; [6]imec, Belgium; [7]University of Pennsylvania, United States

In-situ liquid cell electron and x-ray microscopy has enabled the dynamic studies of electrochemical reactions in energy materials and is capable of, at the nanoscale, produce relationships between performance and the structure and chemical composition of these material systems. These fundamental relationships are critical to the development of better performing batteries, catalysts, and other energy materials. Together with the rapid increase of research in energy materials systems over the last decade and a half, in-situ liquid-electrochemical techniques have developed into more mature and more widely used characterization methods.

Here we will demonstrate how in-situ liquid-electrochemical transmission electron, X-ray synchrotron and scanning electron microscopy methods were used to study dynamics and structural changes of lithium-ion insertion/extraction in micron-scale Li_xFePO_4 battery particles, electrocatalytic behavior of β-Co(OH)2 platelet particles, and electrochemical oxidation of copper nanoparticles under electrolytic reduction conditions. These studies all yielded new insights into these materials systems that can directly provide guidance for development of improved energy systems.

New scientific hardware and method development has been crucial in enabling the exponential growth of in-situ nano-scale liquid cell microscopy/spectroscopy of electrochemical systems. Therefore, we will also discuss best-practice hardware and method design and development for these in-situ liquid-electrochemical microscopy experiments. Examples are how the potentiostat and holder connections should carefully consider different ground potentials and how the incorporation of real bulk-scale reference electrodes in these in-situ systems can yield quantitatively higher fidelity data. We will also show how heating the sample or illuminating the sample with light during these in-situ electrochemical experiments is starting to expand the new frontier of what can be achieved with these in-situ microscopy techniques.

2:00 PM CH01.04.02
Atomic Fortune-Telling—Forecasting the Future for *In Situ* Experimentation Steven R. Spurgeon[1,2]; [1]Pacific Northwest National Laboratory, United States; [2]University of Washington, United States

Mastery of dynamic materials and chemical processes depends on our ability to describe not just the present state of a system, but how it will evolve in the future. To better control phenomena ranging from radiation-induced defects to order-disorder phase transitions, we must both harness and anticipate how multi-modal data streams may change during a reaction. Surprisingly, there are few examples of machine learning-based forecasting models for transmission electron microscopy, one of the cornerstone platforms for in situ experimentation at high spatial and chemical resolution. Here I will describe our recent development of long short-term memory (LSTM) models, a kind of recurrent neural network, to predict phase transition points during in situ imaging and electron energy loss spectroscopy (EELS). I will describe how such models can be integrated into emerging automated microscopes to guide long-latency control parameters, laying the groundwork for *anticipatory* direction of complex reactions. Together, these developments show how artificial intelligence unlock richer, more controlled, and informative studies of dynamic processes in materials and chemical systems.

2:15 PM *CH01.04.03
Ionic Gradients at Active Battery Interfaces Revealed Through Time-Resolved Cryo-EM Nikita S. Dutta, Sang-Don Han, Mowafak Al-Jassim and Katherine L. Jungjohann; National Renewable Energy Laboratory, United States

Characterizing the structural and chemical evolution of battery interfaces during cycling and aging is critical to realizing longer device lifetimes. Cryogenic electron microscopy (cryo-EM) has greatly advanced our ability to study such interfaces at high spatial resolution without damaging sensitive organic or lithium-containing components. The temporal resolution, however, is limited by time-consuming traditional sample preparation techniques that allow structural changes to occur between electrochemical cycling and the later ex-situ freezing process. Here, we demonstrate a method to freeze active battery interfaces *in situ* on sub-second timescales, allowing the native structures and chemistry that arise at different points in cycling to be captured for cryo-EM study. We apply this technique to study the role of ionic gradients at charged nanostructured interfaces on formation and evolution of the solid-electrolyte-interphase (SEI) on silicon anodes. This allows us to capture diffuse features that form at the active interface, which otherwise relax too quickly to be studied with ex-situ sample preparation techniques. We discuss the potential to expand this technique to other electrochemical systems and advance characterization of broader energy materials.

2:45 PM CH01.04.04
***In Situ* and Ex-Situ 4D-STEM Characterization of Low *q* Scattering in Conductive Polymers Used for Li-Ion Battery Anodes** Hadas Sternlicht[1], Tianyu Zhu[2], Benjamin Savitzky[1], Chen Fang[2], Colin Ophus[1], Gao Liu[2] and Andrew M. Minor[1,3]; [1]National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory, United States; [2]Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, United States; [3]University of California, Berkeley, United States

Characterization of soft materials, such as polymers, using conventional transmission electron microscopy (TEM) techniques typically applied to harder materials (metals and ceramics), normally results in beam damage, while essentially providing no structural information. Four-dimensional scanning TEM (4D-STEM) captures the complete reciprocal space information while allowing for the practical evaluation of applied dose, addressing the challenges associated with the characterization of soft materials.

Conductive polymer binders provide electronic conductivity and mechanical support for Si-based composite anodes in Li-ion batteries. They moderate volume changes during electrochemical cycling and provide improved capacity retention. Promising polymer binders include poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester), abbreviated as PFM, and some of its derivatives.

In this work, spin-coated TEM samples of PFM were characterized using in-situ and ex-situ 4D-STEM to address the structure of the polymer chains at the nanometer length scale at different annealing conditions. The polymer exhibits stronger scattering at lower q values as compared to typical crystalline materials. Using 4D-STEM, we could discern between rotationally homogeneous and oriented lobes of low-q scattering, indicating semi-crystallinity associated with π-π stacking between the polymer chains. The orientation of the polymer chain alignment (and associated π-π stacking) was then mapped to reveal the granular morphology, where in this context a grain is defined as a region of continuous single orientation of the π-π stacking, which does not change abruptly. Finally, variations in the characteristics of the polymer, undergoing a gradual microstructural transition upon annealing, were determined, and associated with enhancement in the electrochemical and mechanical properties of the polymer.

3:00 PM CH01.04.05
4D-STEM Mapping of Thermal-Induced Nanodomains in Cathode Nanoparticles and Their Role in Facilitating Ion Insertion for Zinc-Ion Batteries Zhichu Tang, Wenxiang Chen, Zhiheng Lyu, Oliver Lin, Kaijun Yin, Cheng Zhang, Hong Yang, Jian-Min Zuo and Qian Chen; University of Illinois at Urbana-Champaign, United States

Electrochemical-induced phase transformation in electrode materials during ion insertion/extraction have been widely studied, including composition and phase domain heterogeneities. However, the role of preexisting nanodomains in electrode materials on their electrochemical performance has not been fully understood yet. Here, we use single-crystalline λ-MnO_2 nanoparticles as a model system to study the effect of thermal-induced lattice distortion and nanodomain formation on Zn-ion insertion/extraction. Through in-situ four-dimensional scanning transmission electron microscopy and electron energy loss spectroscopy, we investigate the formation mechanism of nanodomains in λ-MnO_2 crystals under heat treatment. Combining with electrochemical measurements, the results show that the domain walls can accommodate the strain caused by Zn-ion insertion and thus improve Zn-ion diffusivity in λ-MnO_2 nanoparticles. Our work pinpoints the distinctive impacts of nanodomains on the ion-diffusion process, providing guidance for the structure engineering of electrode materials.

3:15 PM *CH01.04.06

***In Situ* TEM – A Critical Analysis Technique for Understanding Energy Storage Systems** Nikhilendra Singh[1], Eric A. Stach[2], Timothy Arthur[1], James Horwath[2], Daan Hein Alsem[3] and Norman J. Salmon[3]; [1]Toyota Research Institute of North America, United States; [2]University of Pennsylvania, United States; [3]Hummingbird Scientific, United States

Advances in hybrid and electric vehicle technologies combined with a demand for green initiatives have motivated necessary diversification in energy storage research. To achieve customer expectations for hybrid and electric vehicles, new battery systems with higher energy densities, power densities and cycle life than the current state-of-art Lithium (Li)-ion battery are needed. Post Li-ion battery systems, especially those focused on the utilization of Li metal have recently come to the forefront of research. The ability to directly utilize Li metal anodes in rechargeable batteries presents itself as an ideal situation via the accessibility of a maximum possible theoretical specific capacity (3860 mAh/g) in comparison to commercially used anodes (e.g., graphite – 380 mAh/g). Hence, significant efforts in recent literature have targeted the development of robust Li metal anode systems.
One such system is Li-sulfur which has attracted attention due to its high theoretical capacity (1673 mAh/g) and potential low cost. However, this system is hindered by polysulfide dissolution and electrolyte decomposition at the Li metal anode. Among the various strategies which have been employed to overcome these hinderances, the use of solid-state electrolytes (inclusive of polymers, gels and conducting ceramics) stands out since the implementation of solid-state electrolytes can also serve as a mechanical barrier towards Li dendrite formation. However, solid-state electrolytes exhibit relatively lower ionic conductivities and display poor interfacial stability towards Li metal anodes. While advances in both liquid and solid-state electrolyte materials continue, comparatively little is known about the interfacial interactions between both types of electrolytes and Li metal. Hence, studies into understanding these interactions remains essential towards realizing Li metal battery technologies.
Here, we present select studies into the interfacial interactions between various liquid and solid electrolytes being considered for metal battery systems today. The studies will cover interfacial observations, nucleation and growth of the metal anode and the chemo-mechanical transformations within electrolytes and at their interfaces with metal anode materials. Tandem analytical ex-situ and in-situ studies via transmission electron microcopy (TEM) are used to reveal the interfacial interactions and failure modes between Li metal and commonly used liquid electrolytes, lithium thiophosphate solid electrolytes, the deposition and dissolution properties of Li metal from these electrolytes, and the effects of the deposition and dissolution properties on the bulk electrolyte structure. Additional work on non-Li metal anode systems will also be presented in a similar light. The presented studies allow for comparisons of metal anode deposition and dissolution properties for each electrolyte material and stand to help clarify interfacial, morphological and failure evolution mechanisms during battery cycling from them.
Further, in this presentation an emphasis will be laid upon the methodologies created, applied and advanced to carefully study solid-state battery materials in a TEM, where both sample preparation of extremely air-sensitive materials and microscope setup to ensure damage-free characterization are equally critical towards obtaining data clarity from ex-situ and in-situ TEM characterizations for battery materials. Additionally, this presentation will support the need for bridging length scales when analyzing energy storage system materials, to facilitate the correlation of model material studies done within a TEM and phenomenon observed in larger cells which stand the ability to be scaled up for commercial applications in current and future mobility systems.

3:45 PM CH01.04.07

Illuminating polysulfide distribution in lithium sulfur batteries: Shining light on polysulfides dissolution and movement through operando optical fluorescence microscopy Kofi Coke, Paul Shearing and Thomas S. Miller; UCL, United Kingdom

Lithium sulfur batteries are a particularly exciting developing battery technology, capable of impressive theoretical gravimetric specific capacities (1672 mA h g^{-1}), and energy densities (2567 Wh kg^{-1}). However, their performance is plagued by the polysulfide shuttle effect – perhaps the most critical issue to solve to enable the wider proliferation and commercialisation of lithium sulfur batteries. This is where lithium polysulfide charge carriers generated at the cathode diffuse towards the lithium metal anode and undergo parasitic reactions, leading to active material loss, anode degradation, and rapid cell failure. Development of strategies to mitigate this effect make up a large proportion of current Li-S research, but current methods of characterising the prevalence of polysulfide shuttle either provide limited detail or are prohibitively time consuming. New methods utilising optical fluorescence microscopy and rotating-ring disc electrode study are presented, allowing facile operando characterisation of the shuttle effect.
Through the use of optical fluorescence microscopy alongside an otherwise inert polysulfide selective fluorescent dye, the intermediate polysulfides formed throughout cycling are made to fluoresce, and can thus be directly visualised. Through analysis of recordings of polysulfide movement, the kinetics of their dissolution and subsequent diffusion towards the anode, and the effectivity of mitigation strategies, are then easily quantified. Further, localised polysulfide concentration within the electrolyte can be approximated from the fluorescence intensity.
Additionally, using a rotating-ring disc electrode analogous to a Li-S cell (fitted with a sulfur/carbon disc and lithium ring), the laminar flow of redox materials produced will provide a known 'collection efficiency' of lithium polysulfides reacting with the anode, with the resultant current at the ring serving as a proxy for the extent of the shuttle reaction. This allows facile assessment of the efficacy of measures taken to protect the anode from these parasitic reactions, as well as the ability to get mass transport parameters such as diffusion coefficients, alongside kinetic parameters such as rate constants.
With these methods of rapidly characterising the occurrence of the polysulfide shuttle effect in lithium sulfur batteries, one can rapidly determine the efficacy of measures taken to mitigate the effect, such as polysulfide trapping methods in the cathode, electrolyte, or separator, and additives capable of protecting the lithium anode through SEI formation.
These methodologies serve as an ideal platform for the further development of polysulfide shuttle mitigation strategies, as they allow rapid determination of efficiency.
The work could also be of key benefit to industry. The speed and ease of the two techniques means they could easily be integrated into industrial lithium sulfur research and development, and the potential time saved in using these techniques over cycling to cell failure will be of particular interest to industry; which in turn will help to the commercialisation of lithium sulfur batteries of course of substantial benefit to consumers and to the world.

4:00 PM *CH01.04.08

Advancing Liquid-EM Techniques and Workflows for Operando Studies of Energy Materials Madeline J. Dressel Dukes, Stamp Walden, Kate Marusak, Tim Eldred, Nynke Krans, Yaofeng Guo, Alan Franks and John Damiano; Protochips, Inc., United States

The need for clean, renewable energy has driven the expansion of research focused on new materials for electrocatalysts, fuel cells, and batteries. These materials need to be plentiful, inexpensive, and have high energy capacity operating lifetimes to power a growing consumer market that is seeking alternatives to fossil-based fuel sources [1].

Operando transmission electron microscopy techniques enable dynamic, real-time imaging of a material's nanoscale processes as they occur within their functional environment [2]. A key objective in applying operando TEM to energy materials is the opportunity to observe a catalyst or battery material under its native operating conditions. Enabling researchers to simultaneously follow structural and morphological changes and correlate those to the material’s electrochemical behavior. Operando studies that utilize liquid-EM, in which a sample is encapsulated in a liquid environment between electron transparent membranes, has enabled researchers to study reactions as they occur in a liquid, electrolyte environment [1]. This technique has enabled researchers to better understand the mechanistic pathways that can result catalyst deactivation [3,4] battery capacity fading [5-7] and identify targets within these materials to improve their performance [8,9].

Successful operando liquid-EM experiments are challenging due to many factors, beginning with experiment design and workflow, and culminating complex analysis of multiple streams of large, often cumbersome, datasets. Here, we have set out to address and develop hardware and software tools which mitigate some of the most common challenges associated with operando liquid-EM electrochemical studies. Combining expertise in in-situ hardware and MEMs based sample support design, with AXON, Protochips’ recently introduced software platform, we have developed a holistic, workflow-driven approach to address key challenges and pain points associated with in-situ and operando TEM studies. New hardware and MEMs-based features integrated into the Protochips’ liquid-EM solution, Poseidon, include the ability to perform electrochemical studies beyond room temperature, and improved stabilization of electrochemical signals for correlation with bulk studies. Streamlining the operando-TEM experience, the AXON software family, utilizes machine vision and learning algorithms for improved stabilization and tracking of dynamic samples, accurate dose quantification and management, consolidation of experimental parameters and metadata, and an intuitive, free-to-use, visual data analysis tool, AXON Studio.

As operando TEM techniques continue to grow in popularity within the larger energy materials sector, there is a growing need for in-situ hardware and software solutions that permit users with minimal expertise in electron microscopy to undertake and obtain high-quality, robust, reproduceable datasets that can be shared and independently interpreted by colleagues and collaborators to further the shared goal of developing the next generation of renewable energy materials.

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4:30 PM CH01.04.09

Imaging Phase Segregation in Nanoscale Li_xCoO_2 Single Particles Elliot J. Fuller[1], David Ashby[1], Celia Polop[2], Elena Salagre[2], Bhuvsmita Bhargava[3], Yueming Song[3], Enrique Vasco[4], Joshua Sugar[1], Paul Albertus[3], Tevfik Onur Mentes[5], Andrea Locatelli[5], Pilar Segovia[2], Miguel Ángel Gonzalez-Barrio[6], Arantzazu Mascaraque[6] and A. A. Talin[1]; [1]Sandia National Laboratories, United States; [2]Universidad Autónoma de Madrid, Spain; [3]University of Maryland, United States; [4]Consejo Superior de Investigaciones, Spain; [5]Sincrotrone Trieste S.C.p.A., Italy; [6]Universidad Complutense de Madrid, Spain

Li_xCoO_2 (LCO) is a common battery cathode material that has recently emerged as a promising material for other applications including electrocatalysis(*1, 2*) and as electrochemical random access memory (ECRAM)(*3*). During charge-discharge cycling LCO exhibits phase transformations that are significantly complicated by electron correlation. While the bulk phase diagram for an ensemble of battery particles has been studied extensively, it remains unclear how these phases scale to nanometer dimensions and the effects of strain and diffusional anisotropy at the single particle scale. Understanding these effects is critical to modeling battery performance and for predicting the scalability and performance of electrocatalysts and ECRAM. Here we investigate isolated, epitaxial $LiCoO_2$ islands grown by pulsed laser deposition (PLD). After electrochemical cycling of the islands, conductive atomic force microscopy (c-AFM) is used to image the spatial distribution of conductive and insulating phases. Above 20 nm island thicknesses, we observe a kinetically arrested state in which the phase boundary is perpendicular to the Li-planes; we propose a model and present image analysis results that show smaller LCO islands have a higher conductive fraction than larger area islands, and the overall conductive fraction is consistent with lithiation state. Thinner islands (14 nm), with a larger surface to volume ratio, are found to exhibit a striping pattern which suggests surface energy can dominate below a critical dimension. When increasing force is applied through the AFM tip to strain the LCO islands, significant shifts in current flow are observed, and underlying mechanisms for this behavior are discussed. The c-AFM images are compared with photoemission electron microscopy (PEEM) images which are used to acquire statistics across hundreds of particles. The results indicate that strain and morphology become more critical to electrochemical performance as particles approach nanometer dimensions.

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4:45 PM CH01.04.10

Understanding Disparate Atomic Arrangements at Interfaces in Palladium Nanocrystals During Hydrogen Absorption and Desorption Daewon Lee[1,2], Sophia Betzler[1,2], Colin Ophus[1], Mark Asta[1,2] and Haimei Zheng[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

Solute-induced phase transformations are essential in energy material applications, including hydrogen storage and lithium-ion batteries. Solute intercalation into a host material generally leads to significant lattice expansion and lattice mismatch strain. Specific interphase boundary structures develop to compensate for the lattice mismatch strain, and dictate the phase transformations. Revealing the interfacial atomic arrangements and their formation mechanisms is pivotal to the understanding of solute-induced phase transformations. Hydrogen-induced phase transformations in palladium (Pd) is a classical study model. The palladium hydride (PdH_x) comprises a hydrogen-poor α and a hydrogen-rich β phases. The structural transformations between α and β phases are well explained at the bulk level; however, the dynamic atomic arrangements at the interphase boundaries during the hydrogen-induced phase transformations have not been achieved.

We utilize the advanced high-resolution *in-situ* liquid cell TEM (LCTEM) to directly observe hydrogen-induced phase transformations in individual Pd nanocrystals at the atomic level. We loaded the Pd nanocubes in an aqueous solution into the liquid cell. The molecular H_2 is generated inside the liquid cell *via* water radiolysis from electron beam irradiation. The hydrogen absorption in the Pd nanocrystals accompanies the propagation of a unique interfacial structure with a spatially broadened interphase boundary where both β- and α-PdH_x exist and lattice planes tilt. In contrast, the hydrogen desorption proceeds with the movement of an atomically sharp interface with edge misfit dislocations. Furthermore, we conduct a systematic study on the effects of Pd nanocubes with different sizes on the hydrogen-induced phase transformations. We observe distinctly different interfacial atomic structures and phase propagation dynamics and intermediate structures, indicating size-dependent lattice strain relaxation mechanisms. We perform theoretical calculations to understand the observed disparate interface structures during hydrogen-induced phase transitions in Pd nanocrystals. The insights from this work deepen our understanding of solute-induced phase transformations and may benefit materials/device development for renewable energy technologies.

Acknowledgment:
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SESSION CH01.05: Poster Session I
Session Chairs: Akihiro Kushima and Junjie Niu
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM CH01.05.01
GaSb for High-Performance Alkali Metal-Ion Battery Anodes Young-Han Lee, Do-Hyeon Kim, Jeong-Myeong Yoon and Cheol-Min Park; Kumoh National Institute of Technology, Korea (the Republic of)

Over the last decade, electric vehicles (EVs) that employ lithium-ion batteries (LIBs) have been successfully commercialized, and their market has rapidly expanded. However, EV batteries still require significant improvements in energy and power density, fast-charging capability, and high safety to be more competitive with combustion engine vehicles. It is challenging to fulfill all of these requirements using conventional LIBs. Therefore, new high-performance electrode materials for LIBs are highly required. Furthermore, sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs) are promising next-generation rechargeable battery systems because Na and K are abundant (deposits of Na and K are approximately three and two times larger than that of Li, respectively) and are environmentally harmless.
This study introduces a high-energy-density GaSb compound anode and optimized nanocomposite fabrication route for superior alkali metal (M)-ion batteries (M= Li, Na, K). The GaSb compound was synthesized by a simple thermal synthesis method, and its electrochemical performance for alkali M-ion battery anodes was investigated. In addition, the reaction mechanisms of GaSb with Li, Na, and K-ions were clearly investigated using state-of-the-art analytical tools. To obtain optimized GaSb anodes, two nanocomposites of the chemically modified GaSb/reduced graphene oxide (rGO) and mechanically modified GaSb/amorphous carbon (a-C) are suggested. The GaSb/a-C shows better electrochemical performance than that of GaSb/rGO nanocomposite anode. Furthermore, the GaSb/a-C nanocomposite anode exhibits higher electrochemical performance than those of conventional carbonaceous anodes. The high-performance of GaSb/a-C was attained by three-step nanoconfinement and stabilization of GaSb nanocrystallites uniformly embedded in the C matrix, which was thoroughly demonstrated. Based on the electrochemical performance, the proposed GaSb/a-C nanocomposite can be a promising alternative anode material for alkali M-ion batteries.

5:00 PM CH01.05.03
***Operando* SAXS and Synchroton Based X-Ray Analysis for Insights into Se Reaction Mechanisms Confined in Ordered Mesoporous Carbon for Li-Se Batteries** Yelim Kwon, Junwoo Yu, Won-Sub Yoon and Ji Man Kim; Sungkyunkwan University, Korea (the Republic of)

Increasing demand for advanced rechargeable batteries, especially in an electric vehicle market, requires further progress to increase energy density. Lithium-selenium (Li-Se) battery is one of the promising candidates for next-generation rechargeable batteries due to their high energy density and good kinetics. However, there is the primary problem to be commercialized, which is called shuttle effect. It is caused by the dissolution of polyselenide from Se cathode into the electrolyte in the repetitive charging and discharging, resulting in capacity fading.
Herein, we report on ordered mesoporous carbon (OMC) to confine Se (Se/OMC) to suppress the shuttle effect by providing a sufficient capability for adsorbing dissolved polyselenide.[1] It shows improved electrochemical performances, like higher capacity, better cycle retention, and lower resistance. *Operando* small-angle X-ray scattering (SAXS) is a powerful technique to analyze the structure dynamics of mesoporous materials in real-time conditions during electrochemical reations. [2,3] *Operando* SAXS, an innovative investigation on the behaviors of selenium species in the nanopores of OMC materials, combined with ex-situ analysis by synchrotron-based X-ray absorption fine structure (XAFS), X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HRTEM) allows us to understand the role of mesopores and the reaction mechanisms of selenium in OMC.

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5:00 PM CH01.05.04
Electrochemical Li Reaction Mechanism of Ge and High-Performance Ge Nanocomposite Anodes for Li-Ion Batteries Do-Hyeon Kim, Young-Han Lee, Jeong-Myeong Yoon and Cheol-Min Park; Kumoh National Institute of Technology, Korea (the Republic of)

Rechargeable Li-ion batteries (LIBs) are representative and continuously developing energy storage systems owing to their wide applicability in electric vehicles and portable electronics. Conventional rechargeable LIBs are typically composed of carbon-based graphite anodes and Li–transition metal oxide cathodes and exhibit good cyclic behavior owing to their distinctive Li intercalation reaction. However, the reversible capacity of LIBs is low owing to the low theoretical Li storage capacity of the electrodes (graphite anode: 372 mAh g^{-1} and $LiCoO_2$ cathode: ~140 mAh g^{-1}). Because the cathode materials are limited to Li–transition metal oxides, research on increasing the capacity of LIBs has focused on anode materials. Among the alternative anode materials for high-capacity LIBs, Li-alloy-based group-IV elements (Si, Ge, and Sn) have been actively studied because they can store many Li ions, thereby affording high theoretical Li storage capacities. However, these group-IV elements pose a fatal problem in that their capacity decreases during cycling due to the significant volume change during the continuous cycles. Among the group-IV elements, Ge is a highly researched anode material for LIBs owing to its high theoretical Li storage capacity and higher electrical conductivity compared to that of Si. However, Li reaction mechanism of Ge have not been

definitively established due to the formation of various and complicated Li-Ge alloy phases during lithiation/delithiation.
In this study, the electrochemical Li reaction mechanisms of nanocrystalline Ge were elucidated by applying various cutting-edge *ex situ* techniques, namely, X-ray diffraction, extended X-ray absorption fine structure, X-ray absorption near edge structure, and high-resolution transmission electron microscopy. Moreover, Ge-based nanocomposites (Ge/C and Ge/Al_2O_3/C) were synthesized using a simple one-pot mechanical solid-state method to enhance the electrochemical Li storage characteristics of Ge. The Ge/Al_2O_3/C comprising nanocrystalline Ge with Li-inactive Al_2O_3 and C matrices exhibited superior electrochemical performance compared to that of Ge/C. Thus, Ge/Al_2O_3/C is suggested as a new Ge-based nanocomposite anode material for high-performance LIB anodes. Furthermore, the roles and effects of the Li-inactive Al_2O_3 and amorphous C matrices were revealed using various analytical tools. We anticipate that the electrochemical Li reaction mechanism of Ge and the resulting high-performance nanocomposite anodes will be highly useful in investigating high-performance Ge-based anodes for LIBs.

Acknowledgements
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5:00 PM CH01.05.05
STEM-Based Techniques to Characterize Nanoscale Point Defects Formed Under Molten Salt Corrosion Sean Mills[1,2], Ryan Hayes[1], Steven Zeltmann[1], Raluca Scarlat[1] and Andrew M. Minor[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Extreme nuclear reactor environments require materials to maintain their integrity all while a range of processes act in unison to degrade their performance. Integral features of these processes are that defects produced under irradiation directly limit or accelerate the corrosion rates. Moreover, in molten-salt reactor environments, previous experimental work has shown that Cr dealloying is strongly coupled to the microstructure evolution of these alloys. Connecting corrosion attack with alloy microstructure such as grain boundaries and accumulating point defects is imperative to understanding underlying mechanisms. However, the trends associated with varying salt chemistry, temperature, and irradiation dose are not intuitive, and a mechanistic understanding of the associated thermodynamics and kinetics remains unknown. A close inspection and tracking of point defects such as vacancies and interstitials would be essential for the understanding of material behavior under complex molten salt corrosion environments. The recent developments in 4D-STEM with high-speed direct electron detectors and atomic resolution STEM allow mapping vacancy distributions at the nanoscale and their associated strains, both of which have far-reaching implications for detailed analysis of complex irradiation / corrosion damage.

This work aims to understand, through experiments and modeling, the mechanisms that govern corrosion in LiF-NaF-KF eutectic salts (FLiNaK), and how they are correlated to microstructure evolution in the metal alloy. Here, implement techniques including 4D-STEM strain mapping and high-resolution STEM-EDX/EELS elemental mapping combined with computational modeling based on density functional theory to analyze the migration of these point defects with respect to local changes in composition around corrosion pores. Using this approach, we explore the defect map surrounding boundaries and interfaces where rapid transport occurs during a series of diffusional process. At elevated temperature, formation of a passive oxide layer is suited to protecting the metal-salt interface, however, oxide layers formed in oxygenated molten salt environments are neither stable nor protective. It is understood that Cr tends to leach into the salt, in combination with the breakdown of these protective layers, and the reaction is accelerated at discrete sites such as surface pitting and further corrosion in a creviced region obtained from microscopic SEM observations of the sample surface and the cross-section. Moreover, alloying elements (Cr oxidants) are selectively removed via a redox reaction to form metal halides which may act as a mechanical barrier to continued corrosion attack. Phase field modeling has shown that these microstructural coupling trends vary for selective dissolution from a binary (e.g. Cr dissolution from NiCr). Further, we conduct simultaneous EDX-STEM and 4D-STEM mapping in situ at elevated temperatures to track time / temperature sensitive corrosion behavior within an isolated salt-filled pore. Concentrations and distributions of point defects that form by surface diffusion or by bulk lattice diffusion in response to Cr migration and leaching at the metal-salt interface are measured. This extensive study fundamentally improves the understanding of the complex corrosion and irradiation processes and provides a new pathway for engineering materials designed in future nuclear energy systems. The project is part of FUTURE Energy Frontiers Research Center (EFRC), which aims to study how the coupled extremes of irradiation and corrosion work in concert to modify the evolution of materials by coupling experiments and modeling that target fundamental mechanisms.

5:00 PM CH01.05.06
Interfaces in Lithium-Ion Batteries—Advanced Chemical and Morphological Characterization of the Solid Electrolyte Interphase Gilles Bonneux[1,2], Nicolas Cachot[1,2], Kun Feng[3] and Frank U. Renner[1,2]; [1]Hasselt University, Belgium; [2]imec, Belgium; [3]Umicore, Belgium

As the market share of electric vehicles (EVs) and mobility is expected to rise immensely over the next decades, the demand for improved energy storage technologies is currently at an all-time high. Li-ion batteries attract most attention due to their high stability alongside excellent volumetric and gravimetric energy density. One of the most important factors influencing liquid-electrolyte battery performance and lifetime is the solid-electrolyte interphase (SEI), formed at the interface between anode and electrolyte. A stable SEI is critical towards the cyclability of the cell, as its formation process leads to the (irreversible) immobilization of lithium ions inside this layer. This is especially the case for Si-based anodes, as their large volume changes during cycling will damage the integrity of the SEI layer. SEI reformation after each cycle eventually leads to undesired capacity fading. Beyond silicon-based anodes, metallic Li could be considered as the ultimate anode material due to its exceptional theoretical capacity and lowest electrochemical potential. However, many challenges surround its practical application in both liquid electrolyte and all-solid-state batteries. Due to the high reactivity of Li metal, reactions and degradation processes taking place at the interface often have a strongly negative impact on the battery stability and performance. In addition, dendrite formation issues are well known, even for solid-state electrolyte systems.

In-depth study of these interfaces often relies on advanced characterization methods for the investigation of their morphology, mechanical properties and chemical composition. However, due to the complex nature and reactivity of these interfaces, this is often challenging. Alongside real electrode samples, planar model systems with a well-structured interfacial region could provide supporting information and a better understanding of the processes taking place at the surface. By combining cross-sectional electron microscopy (FIB-SEM) with surface sensitive imaging (AFM), the morphology of the interface region can be investigated in detail. Compositional analysis of the SEI and (buried) electrode surface can be achieved with XPS/HAXPES. By combining multiple x-ray energies, the chemical environment can be probed at various depths, which allows non-destructive profiling. The ultimate goal of this study is to integrate these results, providing a deeper look into the early stages of SEI formation and reduction processes taking place at Si-based materials (Si/SiOx or Si/C composites) and metallic Li anode interfaces. This knowledge could lead to advancements of current state-of-the-art battery systems and even provide further insights towards new generation Li-ion battery technologies.

5:00 PM CH01.05.07
Raman *In Situ* Monitoring of Concentrated Solutions for Copper-Based Redox Flow Batteries Pier Carlo Ricci[1], Stefania Porcu[1], Giampaolo

Lacarbonara[2] and Catia Arbizzani[2]; [1]Univ Cagliari, Italy; [2]Alma Mater Studiorum - Università di Bologna, Italy

Nowadays the scientific community is at the forefront of the fight against climate change, exemplified by the targets set in the Paris Accord, and the goal of a zero-carbon, sustainable economy. These goals can be only achieved with a higher share of renewable energy, which being mostly of an intermittent nature, require innovative energy storage solutions deployable at large scale. A vast capacity of stationary energy storage must be created, and redox flow batteries (RFB) are one of the best technological solutions to provide it. However, multiple hurdles have to be overcome to make such deployment possible; they are of different nature, ranging from technical aspects related to performance (e.g. long cycle life or electrolyte composition optimization) to economic ones (e.g., the need to reach a competitive levelized cost of energy and to raise vast capital sums), and from environmental issues (e.g., toxicity and recyclability) to the security of supply (e.g., dependence on critical raw materials from outside of the EU or on a shallow market dependent on the production of a by-product of a non-related material).
Within the project CUBER (financed by the EU community grant number 875605) we are developing to validate in a relevant environment, a low-cost and scalable stationary energy storage technology, based on redox flow battery systems, with a proven superior environmental performance based on a non-critical and earth-abundant material (copper).
One of the main problems related to the developing of this new class of battery is the solubility problem of the high concentrated solutions.
In this regards the spectroscopic characterization and Raman measurement, in particular, can be very useful to deep understand the presence and the nature of the residues.
The stability of the solution was studied and verified with in-situ monitoring of the solution as a function of time and temperature. The measurements were acquired with BW-TEK: i-Raman® Plus, fiber-coupled Raman system with excitation at 1064 nm to avoid luminescence. The system permits to monitor of the presence of CuCl2 Raman features in the solution and helps in the definition of the temperature at which the first residues are observed. The samples were kept at 60 °C for 12 hours, then it is cooled down with different cooling rates. Remarkably, the highest temperature before the Raman feature of CuCl2 was observed depending on the cooling rate. If a slow rate is utilized, it seems that the stability is preserved for a wider temperature range, while for a faster cooling rate the precipitate was observed for higher temperatures.
The laboratory setup consists of a controlled thermal bath (40 °C) and a continuous flux obtained with a peristaltic pump at room temperature. We utilize two Raman probes, one at the beginning of the path and a second probe that monitors the effect of thermal shock.
The results confirm the possibility to verify the presence of residues and monitoring the system without the necessity to stop the flow and /or sample the solution.

5:00 PM CH01.05.11
Gallium-Based Nanocomposites for High-Performance Lithium-Ion Batteries Jeong-Myeong Yoon, Do-Hyeon Kim, Young-Han Lee and Cheol-Min Park; Kumoh National Institute of Technology, Korea (the Republic of)

With the development of various portable devices and electric vehicles, the importance of rechargeable batteries is increasing day by day. Among these rechargeable batteries, lithium-ion batteries are dominating the market due to their superior energy density and long cycle life. However, graphite, currently the most commonly used LIB anode material, has a relatively slow rate-capability and a limited theoretical capacity (LiC_6: 372 mAh g^{-1}). Li-alloy-based materials, such as Si, Sn, Ge, P, and Sb have high theoretical capacities and are therefore being researched as alternatives to graphite. However, these materials have a poor cycling behavior by the large volume changes during repeated cycling. Therefore, the search for high-capacity Li-alloy-based anode materials for LIBs that can overcome these shortcomings is highly required.
Among these materials, gallium (Ga) has unique characteristics such as low melting temperature and fluidity. It can also alloy with Li and forms Li_2Ga (762 mAh g^{-1}) phase, ensuring a high theoretical capacity. Nevertheless, Ga-based anodes are easily agglomerated during lithiation/delithiation due to its low melting temperature (29.8 ºC) and show a poor cycling behavior. In this study, various Ga-based nanocomposites were fabricated by a simple solid-state method and was applied as high-capacity anodes for LIBs. Among the various Ga-based nanocomposites, a Ga-based nanocomposite with Li-inactive metal carbide and amorphous C matrices was fabricated. The Ga-based nanocomposite with diverse matrices shows an enhanced reversibility with Li, high capacity retention of 525 mAh g^{-1} after 200 cycles, and fast rate capability of 401 mAh g^{-1} at 3C rate. Furthermore, the reaction mechanism between the Ga-based nanocomposite with Li was investigated thoroughly using various cutting-edge analytical tools.

Acknowledgements
This work was supported by the National Research Foundation of Korea grant funded by the Korea Government (MSIP) (NRF-2021R1A2B5B01002570, NRF-2018R1A6A1A03025761). This research was supported by the MSIT (Ministry of Science and ICT), Korea, under the Grand Information Technology Research Center support program (IITP-2022-2020-0-01612) supervised by the IITP (Institute for Information & Communications Technology Planning & Evaluation).

5:00 PM CH01.05.13
Fabrication of Sulfide-Based Polymer-in-Ceramic Solid Electrolytes for All Solid-State Batteries and its Distinct Ionic Conductivity Characteristics Minjae Kim, JunHyeok Seo, Jinsol Im, Jinhyeok Ahn and Kuk Young Cho; Hanyang University, Korea (the Republic of)

There is a continuous increase in the demand for safe and high energy density lithium secondary batteries to cope with exploding needs from the mid-and large-sized batteries for electric vehicles and energy storage systems (ESS). Therefore, new electrode materials, such as lithium metal, high-nickel ternary cathodes, sulfur cathodes, and silicon anodes, have been investigated for post-lithium batteries that enable high energy density. Meanwhile, replacing the conventional liquid electrolyte with a solid-state electrolyte improves the batteries' safety and it is categorized as all solid-state batteries (ASSBs).
In this work, we present stable solid-state electrolyte systems for ASSBs using the sulfide-based electrolyte that demonstrates high ionic conductivity over 1 mS/cm. We could successfully obtain thin free-standing solid-state electrolytes with the polymer-in-ceramic composite approach. We propose a model composite system that can be fabricated and investigated in the open-air atmosphere. The model composite system provides optimum fabrication conditions for the moisture-sensitive solid-state electrolyte. In addition, we, for the first time, confirmed different ionic conductivity behavior with the applied pressure for the fabrication compared to the solid-state electrolyte made only from sulfide inorganic particles. Our result shows that much unexplored in the thin, free-standing solid-state electrolyte requires detailed investigation.

5:00 PM CH01.05.14
Prevention of the Transition Metal Crossover from High-Nickel NMC Cathode Using Ceramic-Coated Separator with the Ion-Trapping Ability JunHyeok Seo, Minjae Kim, JuYeon Im and Kuk Young Cho; Hanyang University, Korea (the Republic of)

Nickel-rich lithium nickel-manganese-cobalt oxide cathodes (NMC) are gaining significant attention in both lithium-ion batteries (LIBs) and lithium metal batteries (LMBs) as high-energy cathode material due to the material's relatively high capacity. However, nickel-rich NMC cathodes suffer from capacity fade during electrochemical cycling due to the degradation resulting in transition metal dissolution from the cathode. This migrates to a lithium metal anode and forms a solid electrolyte interface (SEI). In addition, the deposited metals have been proposed to catalyze further electrolyte solvent reduction, resulting in additional trapping of lithium ions at the anode in the form of the salts that comprise the degradation products. Thus, preventing the transition

metal movement to the lithium metal anode surface is important.
In this study, we designed a new ceramic-coated separator (CCS) using an inorganic particle demonstrating ion-trapping ability. We investigated various parameters that influence ion-trapping performances. The results show that sophisticated control of the surface modification of the inorganic particle allows significant improvement in the prevention of transition metal crossover to anode surface leading to enhanced electrochemical performances of the LMB. Our research suggests that preventing the migration of transition metal ions to the lithium metal anode surface is essential to improve LMB performance.

5:00 PM CH01.05.17
***In Situ* Probing of the Interfacial Forces at Play on Catalytic Gold Surfaces** Leo Sahaya Daphne Antony[1], Loriane Monin[1], Mark Aarts[2] and Esther Alarcon-Llado[1]; [1]AMOLF, Netherlands; [2]imec, Belgium

Electrocatalysis is one of the green energy technologies which employs the use of chemical reactions to convert an unwanted feedstock into a useful energy product. The most common electrocatalysts under an investigation like Pt, Au, Cu etc. are both expensive and unpredictable due to the dynamic nature of their surface morphologies during catalysis. The recent emphasis on the surface structure of catalyst due to the electrode-electrolyte (solid-liquid) interface highlights the complexity of the surface under study and the differences that arise due to electrolyte compositions. Probing catalytic surfaces in the solid-liquid interface can provide useful information about the surface structure and composition of different ionic species (adsorbed on the catalyst surface).
In this work, we highlight the use of the in-situ Electrochemical-AFM technique to observe the local changes on gold catalyst surfaces during catalysis. In addition to local topographical information, our scanning probe also maps the local nano-mechanical properties of the catalyst under study. We measure the adhesion force between the probe and the Au catalyst under applied potentials in electrochemical conditions. These in-situ adhesion force measurements can then be exploited to learn the work of adhesion which provides useful information about the electrostatic, Vander Waals, and Electric Double Layer forces under play on the catalyst surface. To highlight the important differences in the catalytic system, we study the behavior of both polycrystalline gold film on Si substrates and single crystalline gold nano-triangles on ITO substrate in sulfate-based electrolytes. This work further highlights the nanoscopic and microscopic inhomogeneity of the solid-liquid interface structure.

5:00 PM CH01.05.18
Cobalt Coated 460FC-Based Metallic Interconnects for Solid Oxide Fuel Cell Dong-Heon Han, Seung-Ju Oh, Jae Uk Yoon, Insun Woo, Hyun-su Park, In-Seo Park, Woong Heo and Jin Woo Bae; Korea University of Technology and Education, Korea (the Republic of)

Solid oxide fuel cells (SOFCs) show excellent fuel efficiency, power reliability, lower emission, and inexpensive operating cost, as compared to other electrochemical devices. Recently, 460FC-based Fe-Cr alloy have been developed as metallic interconnect for SOFCs. However, serious problems caused by the diffusion of Cr and the growth of Cr-based oxide of 460FC-based Fe-Cr alloy during oxidation at high temperature reduce the power efficiency of SOFC. Co-based oxide layer can improve the oxidation properties of metallic interconnects at high temperature due to inhibiting the diffusion of Cr and retarding the growth of Cr-based oxide during oxidation at high temperature. Here, Co protective layer was deposited on 460FC-based Fe-Cr alloy by the electroless plating method and then oxidized at high temperature. The oxidation characteristics of Co-coated 460FC-based Fe-Cr alloy at high temperature was analyzed and compared with non-coated 460FC-based Fe-Cr alloy using X-ray photoelectron spectroscopy (XPS), focused ion beam-scanning electron microscope (FIB-SEM)/energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and area specific resistance (ASR). The Co protective layer of Co-coated 460FC-based Fe-Cr alloy was thermally oxidized to Co_3O_4 during oxidation at high temperature, which shows lower resistance than Cr-based oxide. It is confirmed that the presence of continuous Co_3O_4 layer inhibited the diffusion of Cr and retarded the growth of Cr-based oxide effectively during oxidation at high temperature. Therefore it is believed that the oxidation properties of metallic interconnects at high temperature is enough to apply to the SOFC.

5:00 PM CH01.05.19
Development of High-Resolution STEM Methods to Map Diffusional Transport of Point Defects Produced via Kirkendall Diffusion Dongye Liu[1], Sean Mills[2,1] and Andrew M. Minor[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

In nuclear reactors, irradiation damage tolerance can be increased by utilizing interfaces as vacancy sinks. Degradation mechanisms at interfaces can involve complicated defect production and evolution. Specifically, Kirkendall void formation has been attributed to the imbalance diffusion between two species of atoms, and as a result, this is counteracted by a flux of vacancies across the metal-metal interface, accumulating locally at grain boundary or dislocations to form voids. Current methods for probing accumulation and mobility of these vacancy-type point defects are largely based on bulk measurements (X-ray diffraction (XRD) and positron annihilation spectroscopy (PAS)) that do not provide the spatially resolved information necessary to track the early stage of interdiffusion at a bi-metal interface. 4D-STEM and high-resolution STEM methods have the potential to provide details on the formation of point defects by identifying changes in lattice parameters at the nanometer scale. This spatially resolved method is especially important for determining the influence of pre-existing microstructural features, such as grain boundaries or dislocations, and their role on defect kinetics. In this study, we consider a thin film bimetallic diffusion couple to track changes in vacancy concentration and Kirkendall void formation *in situ* at elevated temperatures. A Cu-Ni bimetal is utilized as an ideal specimen (both phases are miscible and no intermediate phase is expected to form) to correlate vacancy concentration fluctuation with Kirkendall void formation under designed in situ heating program. With high-resolution EDS, we track real-time motion and diffusivity/concentration of the solute atoms. 4D-STEM measurements map the local change in lattice parameter across the bimetallic interface, with custom patterned “bullseye” condenser apertures that are used to improve the accuracy of the lattice parameter mapping. DFT modeling is used to connect the divergence between solute induced lattice strain and vacancy-defect concentration. This extensive study fundamentally improves the understanding of interfaces in engineering materials (eg. Coating, welding joints, etc.) designed in future nuclear energy systems.

5:00 PM CH01.05.21
The Investigation of Well-Defined Structure and Grain Boundary on Nanocrystals Using Atomic Resolution TEM Seungkyu Kim[1,2], Jinsil Jang[1] and Myoung Hwan Oh[1]; [1]Korea Institute of Energy Technology, Korea (the Republic of); [2]UC Berkeley, United States

In past, identifying the mechanism of particle formation nearby ordered structures has been a challenge because there was no way to control the GB on nanocrystals. Recently our research group developed a process to control the grain boundary and defects on nanocrystals. Within these nanocrystals, we have succeeded in controlling the number, size, and orientation of the individual GBs, which is distinguished from disordered defects in polycrystalline materials. Therefore, observation of a responsive material to which energy is transferred and capturing the unknown variables according to the existence of defects/grain boundaries is essential to find out noble reaction pathways.

Herein, we study the grain boundary (GB) phase transition of nanocrystals with real-time monitoring atomic resolution TEM imaging. We aim to fabricate a well-defined core-shell structure sample capable of being a phase transition (ordered structure from disordered) by an external source (e.g. electron beam, heat), and enough to be confirmed atomic dynamics during TEM imaging. The formation of GB can be the matrix in which the reaction takes place. Observation of phase transformations according to external sources in GB can serve as a fundamental model for understanding nanostructure–property relationships. From this perspective, capturing unknown variables in defects/grain boundary formation enables the exploration of catalytic activity and noble reaction pathways for the electrochemical CO2 reduction reaction using TEM.

5:00 PM CH01.05.22
Preparation and Characterization of Highly Durable and Effective TiO_2-Based Pt Catalyst Support for Polymer Electrolyte Membrane Fuel Cell
Yongsug Tak, Jisu Kim, Chanmi Park, Eungjun Lee and Yonghun Yoon; Inha University, Korea (the Republic of)

Polymer electrolyte membrane fuel cells (PEMFCs) attracted attention as next-generation energy conversion devices since they use hydrogen as fuel and produce only water. PEMFC electrodes are mainly composed of a precious Pt metal and a carbon support which has large surface areas and high electrical conductivities. However, carbon materials such as carbon black, graphene, and carbon nanotubes can affect the electron transport environment and Pt catalyst stability. During the operation of PEMFC, carbon support corrosion can be caused by the high potential above 1.2 V at the cathode during start-up/shut-down and it will lead to the loss of Pt nanoparticles which results in the severe performance degradation. Metal oxide was prospectively suggested because it is stable in oxidizing atmospheres. Among them, TiO_2 has excellent chemical, electrochemical, and thermal stabilities. Furthermore, strong interaction between Pt and TiO2 can bring a higher electron density on Pt which can result in higher stability and enhanced catalytic activity for oxygen reduction reaction (ORR). However, it has two main drawbacks as a Pt catalyst support, low electron transfer and small surface area.
To overcome low electrical properties, TiO_2 was firstly doped with nitrogen. N-doped TiO_2 (TiON) produces Ti^{3+}-enriched TiO_{2-x} phases and the characterization with TEM, HR-PXRD, and XPS suggested that it affect the electrical structure and charge transport properties. Pt/ N-doped TiO_2 cathode enhanced electrochemical activity and improved durability. Secondly, Pt/Nb-doped TiO2 have a smaller Pt 4f binding energy than that of Pt/C and the H_{UPD} desorption and PtO reduction peaks in half-cell CV measurements supported higher stability. Nevertheless, modified TiO_2 with N or Nb are still lower electrically conductive than carbon materials. Hybridization of doped TiO2 with highly conductive materials can be a candidate for Pt support and pristine graphene was selected because of its high electrical conductivity, large surface area, and mechanical strength. Graphene was also doped with nitrogen. N-doped graphene (NG) exhibited higher electrical conductivity and catalytic activity and strengthened the chemical bonding between the support and catalyst, leading to the prevention of catalyst aggregation and the uniform distribution of platinum nanoparticles on the graphene support. NG-TiON hybrid support was analyzed with TEM, XRD, XPS and TG, and the investigation of electrochemical ORR activity and durability of Pt-supported with NG-TiON showed high stability and corrosion resistance with a performance degradation rate of only 9 % after 5,000 accelerated durability test cycles while the performance of Pt/C decreased 83 %. However, low surface area is an intrinsic drawback of TiO_2, compared to carbon.
In this study, the electrical conductivity of TiO_2 was controlled with Nb-doping, and SiO_2 precursor was added with a nonionic surfactant in the hydrothermal preparation of TiO_2 particles from precursors. It was expected that SiO_2 contributes to increase the surface area with the maintenance of TiO_2 structure and electrical properties by suppressing the agglomeration of TiO_2 during heat treatment. The effect of SiO_2 on the surface area of Nb-doped TiO_2-SiO_2 support was investigated by the addition of different amount of SiO_2 presursors. Pt supported Nb-doped TiO_2-SiO_2 were analyzed with X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM), and their electrochemical properties were investigated with potentiostat/galvanostat and electrochemical impedance spectroscopy (EIS). Performance of Pt/ Nb-doped TiO_2-SiO_2 catalyst as a cathode in a single-cell system will be reported.

5:00 PM CH01.05.23
Synthesis Towards TiO_2/Graphene Nanocomposites to Enhance the Energy Storage Capability and Stability of Sodium-Ion Batteries Ahmed Al-Kamal[1], Christof Schulz[1,2] and Hartmut Wiggers[1,2]; [1]Institute for Energy and Materials Processes – Reactive Fluids, Germany; [2]Center for Nano integration Duisburg-Essen, Germany

Lithium-ion batteries (LIB) are widely used for powering electric vehicles, cell phone devices, and stationary energy storage because of their long cycle life and high energy density. However, due to the limited availability and high cost of lithium and lithium-ion storage materials, the demand is raising concerning the use of other materials to store energy. Sodium-ion batteries (SIB) could be used to replace LIBs because of the low cost of sodium and its virtually unlimited availability [1]. However, the drawbacks of SIBs are Lower energy density compared to LIBs, and the larger Na^+ ion radius of (1.02 Å) compared to Li^+ (0.76Å), leading to an immediate structure change during Na^+ insertion and extraction that may cause gradual capacity fade. Suitable combinations of cathode and anode materials can provide similar energy densities of SIBs and some types of LIBs. Regarding the anode, developing long-term stable, environmentally friendly, and abundant active materials is of particular interest. Titanium dioxide (TiO_2) has been selected because it is low-cost and non-toxic and features a moderate sodium insertion/extraction voltage (~0.7 V vs. Na/Na^+), which efficiently avoids sodium plating on the anode and provides a suitable working voltage when coupled with a cathode material [2]. However, TiO_2 has poor ionic and electronic conductivity limiting its performance and practical capacity. Therefore, integrating ultrafine TiO_2 into a highly conductive and stable graphene matrix achieves exceptional rate capacity and durability [3]. Herein, we report a facile and direct self-assembly method of TiO_2/graphene nanocomposites with a controllable graphene loading to enhance the capacity and stability performance of TiO_2-based materials. The TiO_2/graphene with a graphene loading of 20 and 30 wt. % was tested as an anode in SIBs. With the outstanding conductivity enhancement and synergetic effect between TiO_2 nanoparticles and graphene sheets, the nanocomposites exhibited excellent electrochemical performance with a higher reversible capacity of 281 mAh g^{-1} at 0.1C as compared to pristine TiO_2 (155 mAh g^{-1}) at the same rate. In addition, the nanocomposites could deliver a high reversible capacity of 154 mAh g^{-1} after 500 cycles at 10 C and a high average rate capability performance of 158 mAh g^{-1} up to 20 C. Overall. The formation of TiO_2/graphene composites prevents the agglomeration of the nanoparticles and provides a high specific surface area, thus leading to an increase in the electrochemical activity of the anode materials. In addition, different in-situ and ex-situ techniques were used to study the mechanism of sodium storage in an anode structure. The synthesized route of the nanomaterials and their outstanding performance provide a new strategy to synthesize advanced nanomaterials for Na-ion batteries applications.

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SESSION CH01.06: Multi-Modal/Scale Techniques for Batteries/Fuel Cells
Session Chairs: Junjie Niu and Verena Streibel
Wednesday Morning, April 12, 2023
InterContinental, Fifth Floor, Ballroom C

8:15 AM CH01.06.01
Two Microscopes Are Better Than One – A Unique New Inspection Tool For Advanced Characterization by *In Situ* Combination of AFM and SEM Hajo Frerichs, Lukas Stuehn, Sebastian Seibert, Marion Wolff and Christian H. Schwalb; Quantum Design Microscopy GmbH, Germany

Combining different analytical methods into one instrument is of great importance for the simultaneous acquisition of complementary information. Especially the in-situ combination of two of the most powerful microscopy techniques – scanning electron microscopy (SEM) and atomic force microscopy (AFM) – enables completely new insights in the micro and nano-world. [1,2] In this work, we present a unique inspection tool that seamlessly combines SEM and AFM for inspection and process control of Micro- and Nanostructures. Due to the self-sensing piezoresistive cantilever technology used for the AFM scanner the cantilever deflection signal can be measured completely electrical and allows for simultaneous acquisition of SEM and AFM data directly at the region of interest. We will present a variety of novel case studies to highlight the advantages this new tool for interactive correlative in-situ nanoscale characterization for different materials and nanostructures.

First results will focus on semiconducting $BaTiO_3$-based ceramics with positive temperature coefficient of resistivity (PTCR) that currently gain increased attention due to their application as cabin heater in electrical vehicles. We use electrostatic force microscopy (EFM) in combination with the SEM in order to precisely analyze the grain boundary potential barriers of different $BaTiO_3$-based samples. [3] The grain boundaries were located by backscatter electron detection (BSE) and afterwards measured with in-situ EFM. The barriers were shown to be significantly thinner and more pronounced as the amount of SiO_2 was increased from 0 to 5 mol%. These results can be directly correlated with electron backscatter diffraction (EBSD) measurements to link the AFM and SEM data to the crystallographic microstructure of the different samples.

In addition, we will present first results for the in-situ characterization of nanowires that will be used for energy harvesting applications. The SEM enables the easy location of individual or multiple nanaowires, whereas the in-situ AFM allows the characterization of topography, surface roughness, mechanical, and electrical properties of the nanowires.

Based on the broad variety of applications regarding the inspection and process control of different materials and devices, we anticipate that this new inspection tool to be one of the driving characterization tools for correlative SEM and AFM analysis in the future.

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8:30 AM CH01.06.02
Operando Multi-Modal Synchrotron Study on Self-Discharge Behaviors of Li-S Batteries Pu Zhang[1,2], Molleigh Preefer[2], Johanna N. Weker[2] and Yi Cui[1]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States

Lithium-sulfur batteries (LSBs) are the next-generation energy storage alternative to traditional Li-ion batteries (LiBs). An LSB can pack twice the energy (550 Wh/kg for LSB vs. 260 Wh/kg for LiB), costs ~1000x less (sulfur: $46/ton vs. cobalt used in LiB: $50,097/ton), and has fewer harmful environmental impacts. If commercialized, LSBs could power long-lasting mobile devices EVs and replace LiBs for grid energy storage. However, during battery charging and discharging, intermediate-state chemicals, known as polysulfides, form and dissolve into the electrolyte, freely move inside an LSB and form by-products, shortening the LSB lifetime. Moreover, while the battery is not being used, these polysulfides continue to cause energy loss that amounts to over 50% of energy loss per month. This energy loss during resting, also known as self-discharge, is more prominent in LSBs than in LiBs.

Much of the attention has been focused on novel electrolytes and coatings to minimize polysulfide diffusion during cycling. However, the polysulfide diffusion kinetics during resting has not been thoroughly explored. Previous studies on minimizing self-discharge used electrochemistry before and after resting to estimate the polysulfide diffusion rate during resting. While electrochemistry is the gauge of the battery bulk performance, the behaviors of the particles locally could serve as direct evidence for fundamental properties in LSBs, such as polysulfide diffusion kinetics. The morphological, structural, and chemical changes required to understand the sulfur species' behavior during cycling could be applied to study the batteries during resting. I will discuss the operando findings conducted via Transmission X-ray Microscopy, X-ray Diffraction, and X-ray Absorption Spectroscopy. This multi-modal operando synchrotron study will guide the better design of Li-S batteries for longer cycle life and calendar life.

8:45 AM CH01.06.03
Tightly Coupled Experiment-Theory X-Ray Absorption Spectroscopy Characterization of Carbon Electrode in Vanadium Redox Flow Batteries Wenyu Sun[1], Namhoon Kim[1], Liwen Wan[1], Aaron Hollas[2], Qian Huang[2], Vijayakumar Murugesan[2], David Reed[2], Edwin Thomsen[2], Tony Van Buuren[1] and Jonathan Lee[1]; [1]Lawrence Livermore National Laboratory, United States; [2]Pacific Northwest National Laboratory, United States

Vanadium redox flow batteries (VRFBs) are promising solutions to stationary grid energy storage given their advantages towards high efficiency, scalability, safety, near room temperature operation, and the ability for independent sizing of power and energy. Because VRFBs operate on redox couple reactions of V^{2+}/V^{3+} and VO_2+/VO^+ on the carbon electrodes, thorough understanding of the surface functionality of the carbon electrodes and their propensity to degradation during electrochemical cycles is prerequisite for the design of future VRFBs with extended lifespans. In this talk, we will present a tightly coupled experiment-theory approach based on X-ray absorption spectroscopy (XAS), to characterize the carbon electrodes prepared under different conditions and identify relevant functional groups that may give rise to unique spectroscopy features. A series of atomic models were created for different functional groups, including hydroxyl, carbonyl, methyl and carboxyl on representative carbons with either sp2 or sp3 bonding environment. The interactions between functionalized carbon and various solvated V complexes were explicated modeled using density functional theory. A library of carbon K-edge XAS were collected for all distinct carbons with different functional groups before and after interacting with solvated V complexes. Here we will demonstrate how these simulated spectra can be used to deconvolute the ex-situ measured experimental spectrum of carbon electrodes immersed in different solutions and cycled at different stages, and to determine the active species appeared on the carbon electrons that may dictate their performance.
Acknowledgements: This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract number DEAC52-07NA27344. Authors acknowledge financial support from the U.S. Department of Energy′s Office of Electricity, and the use of Stanford Synchrotron Radiation Light source, SLAC National Accelerator Laboratory, supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515 and the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.

9:00 AM CH01.06.04
Simultaneous Mapping of Hydration and Temperature in Proton Exchange Membrane of Fuel Cells Using Magnetic Resonance Imaging Darshan

Chalise and David Cahill; University of Illinois at Urbana-Champaign, United States

The efficiency of a proton exchange membrane (PEM) fuel cell is partly determined by the mobility of protons in the PEM, which depends on the hydration and temperature of the membrane. Due to the ability to provide non-invasive 3D images, spin-lattice relaxation time (T1) and spin-spin relaxation time (T2) contrast magnetic resonance imaging (MRI) of protons in PEMs has been suggested as methods to map hydration in the fuel cells. In this work, we show that while T1 and T2 imaging may be used to map hydration in PEMs under isothermal conditions, proton T1 and T2 are also functions of temperature. Different levels of hydration can have identical T1 and T2 values for different temperatures. Therefore, for PEM fuel cells, where current densities are large and thermal gradients are expected, T1 and T2 relaxation times cannot be used for mapping hydration. The chemical shift of the mobile proton is, however, a strong function of hydration but not temperature. Therefore, chemical shift imaging (CSI) can be used to map hydration. We further show, T1 and T2 imaging cannot be used for temperature mapping even when CSI has decoupled the information on hydration as same T1 or T2 can correspond to different temperatures for the same hydration. The diffusion coefficient, on the other, increases with both temperature and hydration. Therefore, CSI followed by direct imaging of diffusion via pulsed field gradients can be used for individual mapping of hydration and temperature in PEMs.

9:15 AM CH01.06.05

DFT Modeling of Solid State NMR—From Electronic Structure to Measurement of Acidity and Basicity of Oxide Materials Farahnaz Maleki and Gianfranco Pacchioni; University of Milano-Bicocca, Italy

Today one of the most powerful spectroscopic techniques available for the structural characterization and detailed investigations of solid materials is solid-state nuclear magnetic resonance (NMR). Density functional theory (DFT) calculations of NMR properties, in combination with experimental measurements, can provide reliable results for spectral assignments. Recently, we have studied DFT calculations of ^{17}O NMR chemical shift in zirconia surfaces and nanostructures. Our results showed that the ^{17}O NMR chemical shift is a sensitive probe of the coordination and electronic nature of zirconia surfaces or nanostructures.

On the other hand, solid state NMR spectroscopy is in principle a useful tool for probing the acidity and basicity of solid catalysts. We have studied the surface basicity in a series of alkaline earth metal oxides, by means of DFT calculations of the ^{17}O NMR chemical shift. The changes in the ^{17}O NMR chemical shift of the anions on the surface after adsorption of BF_3 and $B(OCH_3)_3$ exhibit a linear correlation with several other properties of the adsorbed molecules.

The ^{31}P NMR chemical shift of adsorbed trimethylphosphine, $P(CH_3)_3$, has been used to identify the presence of different facets in oxide nanocrystals and to study the acid–base properties of the adsorption sites. The NMR signal of adsorbed $P(CH_3)_3$ molecules has been studied for various oxide surfaces, facets, different coverages, and for both stoichiometric and reduced surfaces to titrate Lewis acid sites with ^{31}P NMR. The order of Lewis acid strength for oxides where cations have the same +IV oxidation state is $SnO_2 > TiO_2 > ZrO_2 > CeO_2$.

9:30 AM CH01.06.06

Impact of Aging Inverse Vulcanized Copolymeric Cathodes on Li-S Cell Performance Lisa Djuandhi and Neeraj Sharma; University of New South Wales, Australia

Lithium-sulfur(Li-S) cells possess a high theoretical capacity (1672 mAh g^{-1}) however they suffer from poor capacity retention over electrochemical cycling due to the dissolution and precipitation of redox active lithium polysulfides.[1] To minimize Li-S cell capacity loss, adsorptive cathode matrices such as porous carbons that physically confine redox species are typically used to impede detrimental effects from polysulfide migration.[2-5]

Besides physical confinement, strategies to improve Li-S cell capacity retention have also been reported by using copolymeric sulfur cathodes such poly(S-*r*-DIB).[6, 7] The copolymeric hydrocarbon moiety is a central part of cathode rational design despite ambiguity on the role of covalent carbon-sulfur crosslinks and factors governing degradation during cell operation. As such, despite promising effects, it is unclear whether copolymeric cathodes have reached their limits to improve the Li-S cell system and whether there is any scope in further optimization.

This work provides comprehensive analysis of the effects to Li-S cell capacity through aging poly(S-*r*-DIB) cathodes. The aged cathodes resulted in significant improvements in capacity retention (ca. 99%, 20th cycle @0.1C) compared to without aging (ca. 70%, 20th cycle @0.1C). This implies evolution of the cathode material upon aging and that different mechanistic effects are in play. Most pertinently, ^{7}Li NMR on aged cathodes revealed a stronger Li affinity to copolymeric hydrocarbons over non-hydrocarbon components, similarly observed in low molecular weight poly(S-*r*-limonene), which has also been demonstrated to produce superior benefits to cell capacity retention.[8] The developed NMR approach provides an unprecedented level of spatial and dynamic insight not only for copolymers but possibly for any organic electrode material, setting a new standard in the analysis of organic electrodes.

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9:45 AM CH01.06.07

Understanding Interfacial Phenomena in Battery Systems—Addressing the Measurement Challenges Sofia Marchesini[1], Benjamen Reed[1], Helen Jones[1], Lidija Matjacic[1], Timothy E. Rosser[1], Yundong Zhou[1], Barry Brennan[1], Mariavitalia Tiddia[1], Rhodri Jervis[2,3], Melanie Loveridge[3,4], Scott A. Brown[5], Stuart D. Robertson[5], Rinaldo Raccichini[1], Juyeon Park[1], Andrew J. Wain[1], Gareth Hinds[1], Ian S. Gilmore[1], Alexander G. Shard[1] and Andrew J Pollard[1]; [1]National Physical Laboratory, United Kingdom; [2]University College of London, United Kingdom; [3]Harwell Science and Innovation Campus, United Kingdom; [4]University of Warwick, United Kingdom; [5]University of Strathclyde, United Kingdom

In the quest to reach Net Zero targets, the development of improved energy storage systems plays a key a role. However, Lithium-ion batteries suffer from stability issues that lead to capacity loss with time and use. Huge research efforts are being dedicated to improving the performance of existing lithium-ion systems, as well as pursuing new battery chemistries as viable alternatives. This challenge requires improved understanding of how battery systems work, as well as why their performance degrades with use, from the macroscale down to the nanoscale.

With most reactions occurring at surfaces and interfaces during battery operation, techniques that allow these surfaces to be characterised for both in operando and post-mortem settings are critical. However, the measurement of such complex and heterogeneous systems is not trivial and still lacks standards and guidelines for data collection and interpretation, which can lead to a lack of trust in the data. Without reliable materials characterisation data, accurate conclusions cannot be made and therefore the research and development of improved batteries will be hindered.

In this talk, I will demonstrate the measurement challenges for key post-mortem surface analysis techniques, namely focused ion beam scanning electron microscopy (FIB-SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and time-of-flight secondary ion mass spectrometry (ToF-SIMS). I will describe the current best practice for these techniques and, specifically, I will provide key recommendations to improve the reproducibility of measurements, to enable both academia and industry to better understand the degradation mechanisms for these electrodes and aid in the development of better lithium-ion batteries.

Furthermore, I will show examples of typically used spectroscopy techniques (Fourier transform infrared and Raman spectroscopy) when applied to studying new electrolytes for use in magnesium battery applications in operando, during electrochemical cycling. The development and validation of “minimally-invasive” test protocols for in operando testing allows direct measurement of the material changes under realistic operating conditions, rather than ex-situ after battery teardown. To this end, the changes in the electrolyte during electrochemical cycling can be studied, which we have demonstrated can be used to study the mechanisms of plating and stripping.

Addressing the metrology challenges in the analysis of battery electrodes both in operando and ex-situ is key for the battery community and will ultimately lead to the improvement of existing battery systems and enable the transition to post lithium-ion technologies.

10:00 AM BREAK

10:30 AM *CH01.06.08
Multilength Scale *In Situ* Analysis of Nanomaterials at Johnson Matthey/Diamond Light Source Manfred Erwin Schuster; Johnson Matthey, United Kingdom

Studying nanostructured materials with atomic resolution by (scanning) transmission electron microscopy (S)TEM is nowadays routinely carried out to reveal their structural and electronic properties. These are considered key to understanding reactivity. A much deeper and more robust level of understanding of reaction mechanisms can be achieved by imaging catalyst dynamics in their catalytic active state usually at elevated temperatures and pressures in a liquid or gas environment. This approach is at the heart of the research at Johnson Matthey to design improved catalytic materials.
In this contribution I will showcase experiments carried out with a DENSsolution Climate gas flow system used in JMs aberration corrected ARM200F electron microscope located within the electron Physical Sciences Image Center (ePSIC) at the UK synchrotron facility Diamond Light Source. I will discuss a recent development which enables us to utilize our TEM in-situ gas cell at the nanoprobe beamline I14 of the DLS [1]. This capability allows us to carry out multilength scale in-situ experiments by combined TEM and nanoprobe XANES, thereby linking dynamics observed on a nm- scale with those at the um scale.
I will show examples of advanced characterisation developed and applied to materials relevant in Power to gas technologies.

[1] J.E. Parker et al, .J. Synchrotron Rad. 2022, 29, 431-438.

11:00 AM CH01.06.09
Atomic Scale Imaging of Li Vacancies in a Li-Ion Battery Cathode Material via Multislice Electron Ptychography Dasol Yoon, Yao Yang, Dong Ren, Hector Abruna and David A. Muller; Cornell University, United States

Understanding Li diffusion remains challenging for the development of battery materials, especially due to the difficulties associated with simultaneous imaging of both light and heavy elements at the atomic scale. In this talk, we demonstrate the power of multislice electron ptychography on four-dimensional scanning electron transmission microscopy (4D-STEM) dataset, which allows atomic-scale imaging and depth sectioning of light and heavy elements at the same time. The depth sectioning reveals Li vacancies within a lithium nickel manganese cobalt oxide (NMC-111) cathode material and opens up possibilities of better understanding the Li diffusion mechanism.

Multislice electron ptychography solves the multiple scattering problem by retrieving phase information using a 4D-STEM dataset. This technique is enabled by a fast high-dynamic-range electron microscope pixel array detector, which records a full distribution of momentum transfer at every probe position—unlike conventional detectors such as annular detectors [1]. This allows us to image both light and heavy elements at a resolution of < 20 pm in a dose-efficient manner [2, 3]. In some cases, the lateral resolution is no longer limited by instrumental errors, such as lens aberrations, but by fundamental thermal fluctuations of atoms [3]. Another major advantage of using multislice ptychography is that it retrieves a three-dimensional atomic structure. By iteratively solving the electrostatic potential of the sample at each slice along the depth direction, we are able to discover Li vacancies embedded in the cathode material.

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11:15 AM CH01.06.10
***Operando* Visualization of Perovskite Structural Transformation Using Transmission Electron Microscopy for Light Emitting Diode Application**
Lan L. Nguyen, Martial Duchamp and Yeng Ming Lam; Nanyang Technological University, Singapore

Halide perovskite light-emitting diode (LED) has gained significant interest due to its cheap fabrication process, color tunability, and color purity [1]. Despite considerable achievements in the field, perovskite LEDs commercialization is still met with considerable challenges such as short-term stability, high driving voltage and intensity inhomogeneity [1-3]. Among these factors, high driving voltage is challenging to tackle as it is needed to inject and confine carriers for radiative recombination and can thus not be reduced [1]. As a result, perovskite LEDs often operate at a voltage above the perovskite bandgap, thereby, inducing electrochemical degradation and ionic migration that shorten the device lifetime [1]. Therefore, understanding degradation mechanisms of perovskite LEDs is imperative to design effective solutions to lower the driving voltage and impede degradation.
To facilitate our comprehension of perovskite degradation in LED, transmission electron microscopy (TEM) provides an invaluable tool for showing direct

observations of degradation pathways. A few *operando* TEM studies of perovskite devices were performed and showed interesting mechanisms. Jeangros et al. demonstrated the nanoparticle formation at the perovskite–hole TL interface at forward bias and void formation at perovskite–electron TL interface at reverse bias [4]. Amorphization of perovskite was also observed and was reversible under low heating [5]. Commonly, devices for *operando* TEM were prepared using focused ion beam which may introduce unwanted degradation from air exposure during sample transferring process and ion beam damage [4]. To solve these challenges, we devise a novel design of horizontal arrangement of different layers of perovskite LED that is fabricated directly on MEMS chips using electron beam lithography. Together with a hermetic set-up, the MEMs chips are transferred directly into TEM for *operando* measurements to preserve perovskite structural integrity. Non-exposure to air is shown to improve perovskite stability under electron beam, allowing for observation of degradation with minimal beam damage. Low-dose bright field images are recorded, denoised and reconstructed to follow perovskite structural alteration during LED operation.

This new perovskite LED design also creates new possibilities for tuning transport layers using sputtering and atomic layer deposition. The use of such techniques is previously minimized as ionic bombardment from sputtering and high temperature in ALD may damage perovskite [6, 7]. Additionally, our design allows for easy removal and redeposition of perovskite, eliminating the need to fabricate a new lamella-on-chip device for each *operando* measurement. All in all, the new LED configuration promises to ease preparation process for *operando* TEM measurement and provide opportunities for new material exploration.

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11:30 AM CH01.06.11
Operando Investigation of Energy Storage Material Across Multiple Length Scale by Electron Microscopy Yuzi Liu[1], Xinwei Zhou[1], Likun Zhu[2], Wenquan Lu[1] and Zonghai Chen[1]; [1]Argonne National Laboratory, United States; [2]Indiana University Purdue University Indianapolis, United States

Lithium-ion battery is one of the most needed energy storage technologies and being used from portable electronics to electric vehicles. However, the capacity and energy density of current battery materials cannot meet the requirement for long lasting applications or long-range driving. In order to impove the performence and understand the fading mechanism of energy storage materials, various charicterizations were employed to study the working mechanism of the energy storage materials in real time. *In situ* characterization methods such as X-ray diffraction, X-ray absorption spectroscopy, coherent X-ray diffraction imaging and analytical scanning/transmission electron microscopy (S/TEM) were used to monitor materials evolution during electrochemical cycling. In the assembled battery device, the dimensions of the materials ranges from nanometers (single primary particles) to micrometers (secondary particles and some single crystal Si, Ge and ternary cathode material). The investigation at each length scale provides valuable insights about the battery materials. Electron microscopy is a versatile tool to study materials in wide range of length from atomic scale (S/TEM) to mesoscale (Scanning Electron Microscopy). We employed TEM and FIB-SEM to study structure and composition evolution of single particle Li-ion battery during electrochemical cycling. The all-solid state single particle battery was built in FIB-SEM. The morphology changes of micrometer-sized single particles during lithiation and delithiation was directly observed. The crystal structure transformation was investigated by S/TEM for fundamental understanding of how the materials fail from atomic level. The lithium dendrite evolution on electrolyte, electrodes and the mechanical contact between the electrolyte and electrodes along with electrochemical testing were studied to provide constructive solution for building battery with better performance.

This work was performed at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, and supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.

11:45 AM CH01.06.12
***Operando* Electrochemical Atomic Force Microscopy of Model Electrocatalysts** Andrew Akbashev; Paul Scherrer Institute, Switzerland

Operando studies of model electrocatalysts can provide precise potential-dependent quantities that are vital for accurate assessment of theoretical models and predictions. The structural evolution of materials under highly oxidizing conditions represents a particular challenge for *operando*experiments. To gain the necessary insight into the surface behavior, one should combine advanced *in situ* characterization techniques with well-defined materials that can be directly compared to computational models.

In this talk, I will discuss how epitaxial oxide films can be used as model systems for real-time tracking of materials' evolution during electrocatalytic water splitting (OER). Specifically, I will show how *operando* electrochemical atomic force microscopy (EC-AFM) can be used to record tiny changes in the surface morphology during anodic corrosion of the perovskite $SrIrO_3$ surface. In the experiments, we employ epitaxial films of $SrIrO_3$ with a sharp step between the film and substrate, which allows us to precisely track the dissolution rates. The degradation of $SrIrO_3$ electrocatalyst was found to follow different potential-dependent leaching and dissolution profiles in acidic and basic electrolytes.

Ultimately, our work shows that (1) Sr leaching precedes perovskite dissolution by up to 0.8 V, leading to a wide voltage window of stability where water oxidation occurs on a Sr-depleted surface without significant corrosion; (2) the overall stability of perovskite oxides during electrocatalysis can be substantially improved by suppressing A-site leaching.

SESSION CH01.07: Advanced Characterization for Electrocatalyst I
Session Chairs: Rosa Arrigo and Manfred Erwin Schuster
Wednesday Afternoon, April 12, 2023
InterContinental, Fifth Floor, Ballroom C

1:30 PM *CH01.07.01

Ambient-Pressure X-Ray Photoelectron and Absorption Spectroscopy to Study Electrode Materials Under Working Conditions Verena Streibel; Technische Universität München, Germany

The combination of ambient-pressure X-ray photoelectron spectroscopy (APXPS) and X-ray absorption spectroscopy (XAS) has revolutionized our understanding of working functional interfaces by providing access to both the composition and chemical state of electrode materials under reaction conditions. This line of research has been enabled by technological advances on the analytical side and the development of tailored electrochemical cells compatible with spectroscopic requirements.[1] In the present contribution, we will discuss the development of XPS from a purely ultra-high vacuum (UHV)-based technique towards being able to collect spectra while catalytic reactions proceed at surfaces under (close-to) atmospheric conditions. The focus will be on electrochemical studies of electrode materials, especially those materials that are catalyzing the oxygen evolution (OER) and CO$_2$ reduction (CO2RR) reactions.[2–5] We will highlight the capabilities, advantages, and challenges of the developed electrochemical cell types and discuss the insights that have been generated using these approaches. Importantly, we will describe how a detailed understanding is commonly obtained by tightly integrating operando experimental observations with computational spectroscopy, i.e. by comparing measured spectroscopic fingerprints with first-principles simulated spectra.[6] While these experiments have so far mainly been performed at synchrotron end stations, multi-colored APXPS systems are starting to become available as lab systems with the advantage of providing flexible daily access for rapid feedback during material development processes. Within the German excellence cluster *e*-conversion, we have recently ordered a powerful and versatile lab-based APXPS system, available for user operation from summer 2023. Our APXPS features a vertically mounted electron analyzer, operable in gas phase or vapor environments of up to 100 mbar, while also being perfect for probing samples in contact with 'open' liquids. Three monochromatized X-ray sources (1.5 - 5.4 keV) allow us to probe surfaces as well as buried solid|solid, solid|liquid, and hybrid interfaces. A dedicated gas-phase manipulator enables *operando* experiments of heterogeneous (photo)catalysts in different gas atmospheres at a wide range of temperatures. A second, electrochemical manipulator features an 'open-liquid' three-electrode electrochemical cell, continuous electrolyte flow capabilities, and versatile connections for custom-made cells. In addition, surfaces and interfaces can be illuminated to investigate photo(electro)catalytic processes and modified photoelectrode properties or degradation processes. In this respect, we will discuss the possibilities and challenges of such lab-based systems. We will conclude with an outlook on future developments within the field of APXPS to study energy materials.

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2:00 PM CH01.07.02
***In Situ* X-Ray Absorption Study of Electrocatalytic Carbon Dioxide Conversion to Multicarbon Organic Liquids at High Single-Product Faradaic Efficiency and Low Over-Potentials** Tao Xu; Northern Illinois University, United States

The conversion of carbon dioxide (CO2) to storable multi-carbon (with two or more than two C-C bonds) organic liquids by electrocatalytic reduction of CO2 provides a promising and value-added route to mitigate the greenhouse gas emission. Here, we present a family of carbon-supported transition and non-transition metals-based electrocatalysts with varing sizes that can electrochemically reduce CO2 to C2 and C3 liquid organic compounds with high single-product selectivity at relatively low potentials. The reaction mechanism is extensively studied by in-situ synchrotron X-ray absorption techniques that identify the dynamic evolution of the catalytic center. (Nature Energy, 2020, *5*, 623-632)

2:15 PM CH01.07.03
Probing Lattice Oxygen Oxidation in Electrocatalysts by Resonant Inelastic X-Ray Scattering Jan Bosse[1,2] and Andrew Akbashev[1]; [1]Paul Scherrer Institute, Switzerland; [2]ETH Zürich, Switzerland

Oxygen evolution reaction (OER) is the main bottleneck in water electrolysis. Under OER conditions, oxide electrocatalysts undergo structural degradation and can become amorphous. Lattice oxygen oxidation was proposed as a possible cause for the observed amorphization. However, because lattice oxygen oxidation is notoriously challenging to probe, its unambiguous detection in oxide electrocatalysts has been elusive so far.

I will show how oxygen oxidation can be detected in single-crystalline (model) oxide electrocatalysts using high-resolution resonant inelastic X-ray scattering (RIXS). For this, I will present the case study of perovskite materials where the emergence of oxidized oxygen depends on the transition metal and extent of oxygen intercalation. Finally, I will discuss how lattice oxygen oxidation is related to the degradation of oxide electrocatalysts during OER.

2:30 PM CH01.07.04
Unraveling Charge Carrier Dynamics in Cu3N Photocathodes Using In-Operando Transient Absorption Measurements During Photoelectrochemical CO2 Reduction Finn Babbe[1,1], Mohammed Ebaid[1,1], Noah Bussel[1,2], Jason K. Cooper[1,1], Shaul Aloni[1,1] and Adam Schwartzberg[1,1]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

A crucial challenge for the next century will be the generation and storage of renewable energies at relevant scales. A stepping stone for this is the generation of artificial fuels by electrochemical CO2 reduction into more useful products by utilizing solar energy as a source. An emerging semiconductor system for this is Cu3N, which has a 1.8 eV direct bandgap, high optical absorption coefficient, p-type doping, and high carrier mobility. Within this study, high-quality thin films are grown by direct nitridation of copper films sputtered on FTO covered glass substrates. Prepared thin films exhibit grains of up to a few micrometers and are phase pure as shown by X-ray diffraction (XRD) and Raman. Tested in a potassium bicarbonate solution (KHCO3) with potassium persulfate (K2S2O8) as an electron scavenger, simulating the charge transfer into a CO2 molecule, the electrodes initially show a low photocurrent. However over the course of a few hours of continued chronoamperometry measurements under 1 sun illumination the photo-current increases up to 3 mA/cm^2. Scanning electron images after the photo-electrochemical (PEC) testing show a restructured surface with voids and pits. In operando-Raman and in-operando Incoming Photon Conversion Efficiency measurements as well as ex-situ XRD and X-ray photoemission measurements show that no secondary phases or metallic copper forms. This indicates that the improved performance is inherent to the Cu3N electrodes. To investigate this behavior in more detail, we combined photo-electrochemical testing with ultra-fast pump-probe spectroscopy in the visible range. The transient absorption (TA) spectra exhibit four peaks related to two direct bandgap transitions from an unstrained Cu3N phase and a strained Cu3N phase shifted towards higher energies. Within the first hour of the prolonged PEC testing, the carrier lifetime increases from 70 ps to 150 ps indicating a reduction of non-radiative recombination. After this, the lifetimes continuously drop over 6 hours concurrently with an increased TA signal and measured photocurrent. The higher TA signal shows a higher carrier concentration within the semiconductor after excitation, while shorter lifetimes and increased current show an increased carrier injection efficiency into the electrolyte. TA measurements further indicate that carriers generated in the strained phase only contribute to the generated photocurrent indirectly by carrier diffusion into the lower bandgap unstrained materials within the first 5 ps. In summary, the combination of photo-electrochemical and transient absorption measurements allows direct insights into the charge carrier dynamics under operational conditions showing the charge carrier generation, transport, recombination, and injection into the electrolyte. Thus paving the way for the rational design of efficient and selective PEC systems.

2:45 PM *CH01.07.05
The Structure of the Electrical Double Layer on Suspended Graphene in Contact with Salt Solutions Miquel B. Salmeron[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

The structure of interfacial water near suspended graphene in contact with aqueous solutions of Na_2SO_4, NH_4Cl and $(NH_4)_2SO_4$ was studied using confocal Raman spectroscopy, sum frequency vibrational spectroscopy (SFVS) and Kelvin probe force microscopy (KPFM). SO_4^{2-} anions were found to preferentially accumulate near the interface at open circuit potential (OCP), creating an electrical field that orients water molecules below the interface, as revealed by the increased intensity of the O-H stretching peak of fully H-bonded water. No such increase is observed with NH_4Cl at OCP. The degree of orientation of the water molecules as well as the electrical double layer strength increased further when positive voltages are applied. We show that preferential anion-accumulation at the interface at OPC is driven by segregation from the solution bulk, and is not driven by electrostatic effects nor by formation of specific chemical bonds, which is impeded by the large energy required to desolvate sulfate anions. The first water layer in contact with graphene has dangling O-H bonds that point to the graphene with an intensity that remains unchanged in both with salt concentration and with increasing positive potentials. However the first water layer undergoes a chemical interaction with graphene at negative values that decreases the intensity of the dangling bond peak and redshifts its frequency, pointing to orbital hybridization between dangling H and graphene.

3:15 PM BREAK

3:45 PM CH01.07.06
Many-Body Contributions to X-Ray Spectroscopy and Relevance to Interfacial Characterization David Prendergast, Subhayan Roychoudhury and Ana Sanz-Matias; Lawrence Berkeley National Lab, United States

X-ray spectroscopy is an invaluable tool for the analysis of materials, their surfaces and interfaces. However, studies of functional materials, especially in interfacial contexts, are likely to explore atomic and electronic structure that does not have a pre-existing set of standard spectra, due to the limited, nanoscale dimensions of the interfacial zone or due to the transient nature of its state under operando conditions. Therefore, first-principles simulations can be a vital component in the design of such experiment, either for predicting possible spectral outcomes or interpreting existing measurements. We report on recent advances in the use of a Slater determinant many-electron representation for X-ray transition amplitudes to provide more accurate estimates and more facile interpretation of X-ray absorption, emission and resonant inelastic scattering spectroscopies. The same approach can also provide atom-by-atom interpretation of Electron Energy Loss Spectra (EELS). Applications will be presented in various materials contexts of relevance to energy conversion processes.

4:00 PM CH01.07.07
Real-Time Probing of Interfacial Processes in Oxygen-Evolving Oxide Catalysts Tzu-Hsien Shen and Vasililki Tileli; EPFL, Switzerland

Operando characterization techniques are indispensable for understanding the catalysts evolution during operation. Electrochemical liquid-phase transmission electron microscopy (ec-LPTEM) grants the capability of real-time imaging of electrochemically-induced processes in liquid media. Herein, we describe the advancements of ec-LPTEM towards studying the solid-liquid-gas interfacial processes occurring on Co-based oxide oxygen evolving catalysts [1]. By performing real-time measurements, we can associate the potential-dependent variation of the local contrast to the effects that precede the electrocatalytic reaction such as electrowetting and redox-induced reactions. Further, through optimization of the microcell, we report on the direct probing of the evolution of molecular oxygen by *operando* electron energy loss spectroscopy (EELS). Similar experiments on IrO_2 particles indicate the capability to separate the contribution of different components in the EEL spectra, providing qualitative maps of O_2 and liquid electrolyte, and demonstrating that ec-LPTEM is a promising technique for probing interface phenomena in a range of electrocatalytic processes [2].
[1] T.-H. Shen, L. Spillane, J. Peng, Y. Shao-Horn, and V. Tileli, Nature Catalysis **5**, 30 (2022)
[2] T.-H. Shen, R. Girod, J. Vavra, and V. Tileli, under review

4:15 PM CH01.07.08
Operando pH Imaging to Investigate the Influence of the Micrometer-Scale Morphology on CO_2 Gas Diffusion Electrode Performance Annette Boehme[1], Aidan Fenwick[1], Rohit Bhide[2], Cassidy Feltenberger[2], Shane Ardo[2] and Harry A. Atwater[1]; [1]California Institute of Technology, United States; [2]University of California, Irvine, United States

We developed an experimental technique to map the local in situ pH value around operating CO_2 reduction gas diffusion electrodes with confocal laser scanning microscopy and two fluorescent ratiometric dyes. This allowed us to demonstrate that microcavities on the order of 5 µm on the surface of copper CO_2 reduction gas diffusion electrodes serve as local hotspots with enhanced activity for CO2 reduction, including multicarbon products.
Fluorescent confocal laser scanning microscopy is a very powerful tool because it allows to map an entire macroscopic sample in three spatial dimensions with sub-micrometer resolution. In combination with pH-sensitive fluorescent dyes, it offers the unique opportunity to probe the pH value within microstructures on the surface of a sample of interest such as an active gas diffusion electrode. As pH probes, we use two different commercially available ratiometric fluorescent photoacids with different sensing mechanisms. The first dye we use is 6,8-dihydroxypyrene-1,3-disulfonic acid disodium salt (DHPDS). Its pH sensing capacity is connected to proton-transfer reactions in its electronic ground state to perturb its absorption spectrum. We excite it with lasers at 458 nm and at 488 nm and collect the signal separately for both excitations between 405 nm and 754 nm. The ratio between the two signals is a measure for the local pH value and is independent of the local dye concentration. It is sensitive to pH values between 6 and 10. To extend the accessible pH range, we implemented a measuring protocol for a second novel pH probe, 8-aminopyrene-1,3,6-trisulfonic acid trisodium salt (APTS). Its sensing mechanism relies on quenching of its thermally equilibrated electronic excited state by direct proton transfer to aqueous OH^{-}. We excite this probe at 458 nm and collect the emission signal separately in the range 480-550 nm and 551-754 nm. The ratio between the two signals is sensitive to pH values between 11.2 and 14. This work presents the demonstration of APTS as a probe for the local pH value for the first time. By combining both probes DHPDS and APTS, we can cover pH values between 6 and 14 with a gap between 10 and 11.2.
We developed an experimental setup that uses these two dyes to probe the local pH value around an operating CO_2 reduction gas diffusion electrode made of carbon paper with a 300 nm copper catalyst layer. The pH-sensitive dyes are diluted in 100 mM KHCO3 electrolyte which is pumped through an electrochemical cell optimized for use with confocal microscopy. The pH is monitored under operation of the CO_2 reduction gas diffusion electrode with current densities as high in magnitude as 200 mA/cm^2. We can create three-dimensional maps of the pH value by collecting of the fluorescent emission from the focal point of the laser and scanning the laser beam over the sample. Using this technique, we could gain valuable insight into the influence of microstructures on the CO_2 reduction performance of a gas diffusion electrode. We demonstrated that narrow trenches in the electrode surface are local hotpots with enhanced CO_2 reduction activity and selectivity.

We expect that these insights will help inform the design of advanced gas diffusion electrodes for CO_2 reduction with enhanced efficiency and multicarbon product selectivity. Furthermore, the developed technique can potentially be used in other electrochemical applications where the pOH value plays an important role and could be extended to additional fluorescent dyes.

SESSION CH01.08: Poster Session II
Session Chairs: Daan Hein Alsem and Akihiro Kushima
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM CH01.08.01
Mechanism Exploration of Hydrogen Evolution Reaction on Platinum Single Atom Catalyst Using Electrodeposition Technique Sohui Kim[1], Mansu Kim[2] and Dongmok Whang[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Northwestern University, United States

Due to global climate change and the energy crisis, the demand for low-cost, high-efficiency catalysts for hydrogen generation reaction (HER) is increasing. Platinum is the most suitable metal as the HER catalyst and has excellent catalytic activity compared with other transition metals. However, it is essential to reduce the amount of use in the catalyst due to its high cost and scarcity. The synthesis of Pt single atom catalyst is promising strategy to maximize atomic utilization efficiency and decrease the Pt content. In recent years, the research on Pt single atom catalyst has been actively conducted because of low platinum content and excellent catalytic activity per unit mass. However, it is tricky to synthesize highly uniform Pt single atom catalysts and interpret the distinguished catalytic activity of Pt single atom because Pt clusters or small nanoparticles could be unavoidably formed, and it led to remain obscure in interpreting the mechanism of Pt single atom catalyst. In this study, we developed a fast and facile method to synthesize single Pt atoms on carbon support (Pt SA/C) using electrodeposition technique. Pt particle formation was concisely controlled from Pt single atom to Pt nanoclusters (~2 nm) to Pt nanoparticles (3-5 nm). The very uniform Pt SA/C was identified through HR-TEM and XPS analysis, which is distinguished from the existing Pt single catalyst in which some platinum nanoclusters are coexist. The Pt SA/C displays excellent HER activity with a mass current density of 81.11 Amg_{Pt}^{-1} which is overwhelmingly superior catalytic activity compared to the recent research works. the HER mechanism on Pt SA/C was interpreted using DFT calculation and CO stripping analysis. In this study, the finely dispersed Pt SA/C was synthesized using the electrodeposition technique and the unique catalytic activity and HER mechanism were identified.

5:00 PM CH01.08.02
Synthesis of Highly Monodispersed Iron Oxide Nanocrystals in Various Well-Defined Sizes and Morphologies and Elucidation of the Reaction Mechanism Agnes Weimer[1,2], Artur Feld[1,2], Andreas Kornowski[1], Naomi Winckelmans[3], Jan-Philip Merkl[1], Hauke Kloust[1], Robert Zierold[1], Christian Schmidtke[1], Theo Schotten[4], Maria Riedner[1], Sara Bals[3] and Horst Weller[1,4,1]; [1]University of Hamburg, Germany; [2]Hamburg University, Germany; [3]Electron Microscopy for Materials Science, Belgium; [4]Fraunhofer-CAN, Germany

Magnetic nanoparticles are of significant interest and immense importance for research as well as technological application. These nanoparticles exhibit fascinating magnetic properties, including blocking temperature, coercivity, saturation magnetization, magnetic domain size, and exchange coupling effects, which are affected by size, shape, and crystal structure. [1–3]
For these outcomes, a new synthetic route was developed[4], based on the thermal decomposition of iron oleate. The oleate was synthesized by use of a novel precursor system - Fe(II)CO_3 and Fe_2(III)$(CO_3)_3$. The method allows the synthesis of highly monodisperse nanocrystals (NC) in various well-defined sizes and morphologies on a gram scale. Furthermore, the elaborated synthetic route accomplished a strict kinetic separation of the formation of iron oleate from the generation of reactive pyrolysis products and the subsequent nucleation during the synthesis.
Size and shape control was achieved by varying the concentration of the ligand oleic acid and the non-coordinating solvent 1-octadecene, the temperature and reaction time, so that octapod-shaped NC in a size range of 20-80 nm and cubic NC with sizes from 20-60 nm could be synthesized. With dilution, the size of the nanoparticles decreases significantly, while at higher concentrations, they become larger.
The octapod star-shaped morphology, formed shortly after nucleation as a kinetically favored product, could be characterized by a comprehensive structure analysis using transmission electron microscopy (TEM) and electron energy loss spectroscopy tomography (EELS-tomography). As a result of thermodynamic control they transformed into cube-shaped structures due to metamorphosis in 4 phases.
Furthermore, the hydrophobic NCs were transferred into water and encapsulated with a polystyrene shell, based on the seeded emulsion polymerization technique[5], providing biocompatibility and water solubility. This enables the way for a broad spectrum of applications.
Especially iron oxide nanocrystals can be used to effectively remove micro polystyrene particles via adsorption from water showing potential advantages of this particles for removing environmental pollutants by an environmental-friendly procedure.[6]
Finally, the goal is to optimize this synthetic approach so that it is biobased and sustainable. One way to do this would be to use bacteria[7] to produce particles via biomechanisms. However, such production methods using bacteria allow poor control of shape and size, so in the future, it would be purposeful to adapt the method presented here to a biologically synthesized strategy.

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5:00 PM CH01.08.03
Advanced Electrocatalyst for Efficient Water Splitting Tao Jiang, wenjing zhang and Poul Norby; Denmark Technical University, Denmark

Transition metal sulfides for electrocatalysis have been a hot topic in recent years, because of their high intrinsic activity and excellent electrical conductivity, they have become one of the candidates for basic OER industrial catalysts. Herein, We have successfully synthesized iron-sulfur-doped nickel foam by organic solvent thermal method. We optimize the adsorption behavior of active intermediates at the interface, by inducing interfacial electron rearrangement of Ni and Fe_3O_4,Notably, The obtained catalyst exhibits remarkable OER catalytic activity, requiring only an overpotential of 297 mV to stably drive the OER reaction to a current density of 10 mA cm^{-2}. When applied for the total water splitting reaction, it exhibits excellent catalytic activity and excellent stability, and a current density of 10 mA cm^{-2} can be obtained at 1.57 V.

5:00 PM CH01.08.04
Additive-Driven Alternative Redox of Iron Oxides for High-Capacity and Reversible Aqueous Batteries Sathya Narayanan Jagadeesan; Worcester Polytechnic Institute, United States

Aqueous alkaline iron (Fe) batteries (AIBs) are promising energy storage systems because of the distinctive merits of Fe materials, including high abundance, low cost, nontoxicity, and multiple valent states. Conventional AIBs relying on a conversion storage mechanism at the Fe anode have limited faradaic efficiency and storage capacity due to the formation of electrochemically inert Fe_3O_4 upon discharging $Fe(OH)_2$ in the alkaline solution. Herein, we report the study of the redox behavior of iron (II, III) oxide materials containing α-FeOOH and Fe_3O_4 in NaOH solution with a low concentration silicate introduced to enable the one-charge transfer $Fe(OH)_2$/FeOOH reaction in the AIB anode and mitigate Fe_3O_4 formation. The system with silicate added exhibits an enhanced storage capacity and cycling life. Supported by experimental evidence, molecular dynamics simulations reveal that silicate additives strongly interacted with $Fe(OH)_2$ surface, inhibiting the water transport and favoring $Fe(OH)_2$/FeOOH over $Fe(OH)_2/Fe_3O_4$ conversion. This study paves a path to realizing green battery systems for efficient energy storage.

5:00 PM CH01.08.05
Lithium Phosphate Covered Reduced Graphene Oxide as Anode Material for Lithium-Ion Batteries Wei-Yi Huang, Wen Sun and Che-Ning Yeh; National Tsing Hua University, Taiwan

The solid electrolyte interface (SEI) formed between anode materials and the electrolyte is important for the cycling performance of the lithium-ion batteries, which promotes much research effort on studying the effect of SEI on the performance of the batteries. However, the complicated structures and chemical compositions of the SEI layer make it a complex component to understand. Therefore, investigating a specific component in the SEI can provide helpful guidelines to the design of electrolytes and artificial SEI. In this work, we chose lithium phosphate (Li_3PO_4), one of the attractive solid electrolytes, as an artificial SEI and studied the electrochemical performance of Li_3PO_4 covered reduced graphene oxide (r-GO) as anode materials for lithium-ion batteries. R-GO was produced by reducing graphene oxide using a hydrothermal process. Rather than typical coating methods such as sputtering or chemical vapor deposition, the process we chose for coating lithium phosphate layer on r-GO is through wet chemical synthesis. Since the formation of SEI occurs at all the interface between anode materials and the electrolyte instead of only the surface of the anode materials, wet chemical synthesis ensures high surface coverage of lithium phosphate on r-GO. The role of lithium phosphate on the electrochemical properties of SEI was investigated by studying the cycling performance and electrochemical impedance spectroscopy (EIS) of lithium phosphate covered r-GO as anode materials. This work provides insights for the design of artificial SEI which could effectively passivate the electrode, thereby improving the safety and cycle life of the lithium-ion batteries.

5:00 PM CH01.08.06
Investigating *In Situ* Corrosion Dynamics During CO_2 Reduction Using Inductively-Coupled Plasma Mass Spectrometry Katherine Yan, Kyra Yap, Gaurav A. Kamat, Adam C. Nielander, Michaela Burkes Stevens and Thomas Jaramillo; Stanford, United States

There is a critical need to develop new technologies for the sustainable production of carbon-based fuels and chemicals. The electrochemical CO_2 reduction reaction (CO_2RR) provides a path to meet this need, offering opportunities to use renewable electricity to drive the conversion of CO_2 into products such as ethylene, ethanol, and methane. A challenge limiting the implementation of CO_2RR is catalyst stability during reduction. Greater fundamental understanding is needed to uncover the governing physical and chemical factors as well as mechanisms of degradation in CO_2RR operating conditions. Catalysts of interest for CO_2RR include Ag and Au, but one particularly interesting catalyst is Cu, as it can form C_{2+} products. Changes to the Cu surface morphology can favor the formation of certain products.

The goal of this research is to quantify dynamic corrosion of Cu CO_2RR electrocatalysts. Specifically, we aim to probe the relationship between degradation rate and catalyst morphology changes and applied potential. Cu electrocatalyst degradation in CO_2RR conditions was examined in varying electrolyte pH, gas environments to isolate the effects of hydrogen evolution and CO_2RR, and potentiostatic conditions in Faradaic and non-Faradaic regions to determine the effect of catalysis. Atomic force microscopy (AFM) was used to characterize the electrode surface pre- and post- electrolysis by distinguishing nanostructures on the electrode surface and calculating surface roughness, which was found to be dependent on applied potential. While AFM allows for examination of the resulting morphology of electrode surfaces due to various experimental conditions, the use of inductively coupled plasma mass spectrometry (ICP-MS) enables on-line studies for quantifying catalyst degradation. Using a flow cell allows for simultaneous application of a potential and/or current density while sending electrolyte effluent to the ICP-MS to detect corroded catalyst species in trace amounts (low ppb level), coupling the examination of reaction and corrosion kinetics. On-line ICP-MS data indicates that during CO_2 reduction in potassium bicarbonate electrolyte, Cu degrades at negative applied potentials. Greater fundamental understanding of Cu morphology changes and degradation during CO_2RR conditions can help to steer selectivity towards desired products and improve catalyst performance. The use of on-line ICP-MS studies accelerates corrosion studies by enabling real-time measurements during reaction conditions. Elucidating the factors that drive catalyst degradation enables the assessment of the lifetime and long-term stability of electrocatalytic devices.

5:00 PM CH01.08.08
Asynchronous-to-Synchronous Transition of Li Reactions in Solid-Solution Cathodes Nikhil Sharma, Luize S. Vasconcelos and Kejie Zhao; Purdue University, United States

The composition dynamics regulate the accessible capacity and rate performance of rechargeable batteries. Heterogeneous Li reactions can lead to nonuniform electrochemical activities and amplify mechanical damage in the cell. Here, we employ *operando* optical microscopy as a laboratory tool to map the spatial composition heterogeneity in a solid-solution cathode for Li-ion batteries. The experiments are conducted at slow charging conditions to investigate the thermodynamic origins. We observe that the active particles charge asynchronously with reaction fronts propagating on the particle surfaces during the first charge, while subsequent (dis)charge cycles transition to a synchronous behavior for the same group of particles. Such transition is understood by computational modeling, which incorporates the dependence of Li diffusivity and interfacial reaction rate on the state of charge. The optical experiments and theoretical modeling provide insight into the reaction heterogeneity of porous electrodes and electrochemical conditioning for layered oxide cathodes.

5:00 PM CH01.08.09
Anisotropic Mechanical Properties of Single Crystalline NMC Cathode Materials for Li-Ion Batteries Nikhil Sharma and Kejie Zhao; Purdue University, United States

Nickel manganese cobalt oxides (NMC) are state-of-the-art cathode materials for Li-ion batteries. The layered lattice structure of NMC exhibits highly anisotropic strains upon Li intercalation, leading to particle fracture and interfacial delamination of the active particles from the conductive matrix. Such mechanical degradation becomes a crucial issue in pursuing high Ni-content and Co-free cathodes. Notably, the experimental information regarding the anisotropic mechanical properties of NMC cathodes is missing in the literature. In this study, we measure the stiffness constants of single crystalline NMC cathodes using environmental nanoindentation. The correlative measurements of the elastic stiffness and the lattice orientations allow us to fully determine the stiffness matrix. Furthermore, we compare the effective elastic indentation modulus, hardness, and fracture toughness of different NMC compositions. The complete information on the mechanical properties of NMC cathodes will enable accurate computational modeling and assist in designing and manufacturing durable rechargeable batteries.

5:00 PM CH01.08.10
Machine Learning for High Throughput Characterization of Oxide Nanoparticles Min Gee Cho[1,2], Mary Scott[2,1], Katherine Sytwu[1,2], Catherine Groschner[2] and Luis E. Rangel DaCosta[2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

Nanomaterials exhibit new properties that do not exist in the bulk state and have infinite potentials to be applied to key industrial technologies in the future, such as nanocatalysts, sensors/optical devices, and energy storage/conversion devices. A recent research trend is to control the size and shape of nanoparticles to increase the activity of catalysts of noble metals such as platinum and palladium, so that specific active sites are exposed on the surface a lot. As mentioned above, the catalytic activity is different depending on the surface facet. However, despite the development of nanoparticle synthesis, the individual particles cannot be perfectly identical. Each individual has a slightly different size and shapes even if the nanoparticles are synthesized under the same synthesis conditions. For this reason, there is a limitation in directly correlating the surface structure of nanoparticles with catalytic activity.
In this study, we focused on this point and imaged hundreds of thousands of individual nanoparticles with a high-resolution transmission electron microscope (HRTEM), and put these images into a trained neural network to extract key features of nanocrystals and obtain statistical distributions. Achieving the goal of developing a pipeline for the characterization of nanocrystals with high-throughput microscopic data requires machine learning analysis. We used a convolutional neural network (CNN), a machine learning technique that analyzes data on a pixel-by-pixel basis. It was possible to more consistently measure the gradient of the surface facet of nanoparticles and the atomic-scale patterns, which were difficult to distinguish by the human eye. In previous studies, materials with large atomic numbers, such as platinum or gold, have been frequently studied. Here, we study Co3O4 nanocrystals for their great potential as cost-effective energy-related materials. The key challenge is that we are analyzing high-resolution TEM images with lower contrast. In this study, we started by developing a method for synthesizing cobalt oxide with sizes and shapes. We prepared the cubic-shaped Co3O4 nanoparticles with different sizes and with different degrees of truncation of the corner and the convexity of the face. After synthesizing several different samples of cobalt oxide nanoparticles, tens of thousands of sizes and shapes of each nanoparticle sample were imaged and analyzed using transfer learning to obtain a statistical distribution from the TEM images. In this process, we are able to compare the data preparation process with and without human intervention and compare how it affects the prediction performance of machine learning.
In this study, we trained a neural network and used the trained neural network to find an optimized labeling strategy to segment particles and backgrounds in TEM images. After achieving accurate detection of particles, we classified the segmented particles to obtain a population of nanocrystals using a Random Forest classifier or K-means clustering algorithm. Through machine learning, we were able to uncover not only nanocrystal shapes consistent with existing knowledge about nanocrystal systems but also microscopic properties of nanocrystal surfaces that are difficult to recognize with the human eye. This will become a pipeline that can be used for the development of new materials in the future.

5:00 PM CH01.08.12
Developing Redox Booster Materials to Increase the Capacity of Non-aqueous Redox Flow Batteries Sara Amin; National Science Foundation, United States

Redox flow batteries are a promising energy storage system for renewable energy-powered grids. However, relatively low energy density has been achieved by these systems thus far, due to a combination of low active-material solubility and high-viscosity of concentrated electrolytes. These challenges can be mitigated by using solid active materials as boosters in a redox-targeting flow battery (RTFB) system. Cobalt hexacyanoferrate (CoHCF), a Prussian blue analog (PBA), is a promising candidate for this application, however, its redox-intercalation chemistry in non-aqueous flow battery systems is not well established. Understanding the mechanism behind these electrochemical processes of PBA in the non-aqueous solvent is crucial to developing better-performing high-capacity redox flow batteries.

Here, we report PBA-modified electrodes using various substrates including glassy carbon, ITO glass, and, FTO glass, prepared by the dispersion drop-cast method. Voltammetry of the PBA-modified electrodes was performed under various conditions that are analogous to those of an operating, nonaqueous RTFB. We will describe the custom electrochemical cell that is used as a platform to investigate RTFB electrolyte/booster interactions, along with results from the investigation of CoHCF and its interaction with the NFRB active-material, vanadium bis-hydroxyaminodiacetate (VBH).

5:00 PM CH01.08.14
Design Novel Polymer Materials for Advanced Redox Flow Battery Technology Hyung-Seok Lim, Sujong Chae, Litao Yan, Guosheng Li, Ruozhu Feng, Yongsoon Shin, Zimin Nie, Bhuvaneswari Sivakumar, Xin Zhang, Yangang Liang, David Bazak, Vaithiyalingam Shutthanandan, Vijayakumar Murugesan, Soowhan Kim and Wei Wang; Pacific Northwest National Laboratory, United States

Redox flow batteries are considered a promising technology for grid energy storage. However, capacity decay caused by crossover of active materials is a universal challenge for many flow battery systems, which are based on various chemistries. In this work, we demonstrate a new gel polymer interface (GPI) consisting of crosslinked polyethyleneimine with a large amount of amino and carboxylic acid groups introduced between the positive electrode and the membrane. The GPI functions as a key component to prevent vanadium ions from crossing the membrane, thus supporting stable long-term cycling. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted to investigate the effect of GPI on the electrochemical properties of graphitic carbon electrodes (GCFs) and redox reaction of catholyte. Results from inductively coupled plasma mass spectrometry (ICP-MS), Fourier-transform infrared (FTIR) spectroscopy, and energy-dispersive X-ray (EDX) spectroscopy proved that the GPI is effective in maintaining the concentration of vanadium species in their respective half-cells, resulting in improved cycling stability because of it prevents active species from crossing the membrane and stabilizes the oxidation states of active species. X-ray photoelectron spectroscopy (XPS) and ^{1}H nuclear magnetic resonance (NMR) spectra demonstrated that the cross-linked GPI is chemically stable for 100 cycles without dissolution of polymers and swelling in the strong acidic electrolytes.

5:00 PM CH01.08.15
Unraveling Metal-to-Metal Hydride Phase Transformation at the Atomic Level Using *In Situ* Tem Techniques Gopi Krishnan and Joerg Jinschek; Technical University of Denmark, Denmark

In our quest for a solution to drive the decarbonization of our society and economy, hydrogen shows unique properties as a zero-emission fuel, energy storage solution, and chemical feedstock. However, compact storage remains a scientific and technological challenge.

Safely storing hydrogen e.g. in the solid form of metal hydrides, has many advantages, but further improving its storage properties requires a thorough understanding of the metal-to-metal hydride phase transformation at the atomic level. Although many techniques have been applied to understand these phase transformations, in-situ visualization of the transformation process with the high spatial resolution is essential for a quantitative understanding. For example, stress/strain, defects, and intermediate phase evolution during metal-to-metal hydride phase transformation are crucial to interpret the hydrogen sorption properties.

In this study, we use MgTi thin film as a model system to test, understand, identify and resolve metal-to-metal hydride phase transformation via in situ transmission electron microscopy (TEM). MgTi thin films were prepared via magnetron sputtering, and a focused ion beam (FIB) was used for TEM sample preparation. We observed the Mg to MgH_2 phase transformation by following the bulk plasmon resonance shift in electron energy loss spectroscopy (EELS) and the transition from hexagonal to the tetragonal structure by selected area electron diffraction (SAED). The local strain was measured using HRSTEM, and hydrogen atoms in the MgH_2 matrix were identified using integrated differential phase contrast imaging (iDPC). To confirm experimental findings, the accuracy of strain measurement is validated by geometric phase analysis, and the interpretation of iDPC contrast is supported by image simulation.

5:00 PM CH01.08.16

Microscale Evaluation of the Lithium Content in Lithium-Ion Battery Cathode Materials in the Scanning Electron Microscope Jonathan D. Lee[1] and Shangshang Mu[2]; [1]Gatan, Inc., United States; [2]EDAX, United States

Lithium (Li) ion-based electrochemical cells have been widely adopted due to their capacity for energy storage and low mass. However, due to a lack of characterization techniques that allow microscale analysis of the Li content, understanding of lithium plating and dendrite growth, and solid electrolyte interphase formation remain a major obstacle in the development of improved Li-based cells.

Commonly, microanalysis by energy dispersive X-ray spectroscopy (EDS) in the scanning electron microscope (SEM) is used for detection and mapping of elemental distribution, however, this remains unfeasible in commercially important materials consisting of elements with low atomic number ($Z < 4$), including Li [1, 2]. However, recently the composition-by-difference method (CDM) was shown to be a viable method for determining the Li content quantitatively at the microscale, with an accuracy of ~1 wt. % and was demonstrated in lightweight structural alloys [3] and metal oxides [4]. CDM uses quantitative analysis of the EDS and backscatter electron (BSE) signals to calculate the lithium content indirectly. In this study, we extend the CDM approach to Li-ion battery cathode materials including lithium nickel manganese cobalt oxide particles (NMC).

High-grade NMC 811 particles of nominal composition $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ were analyzed (MSE Supplies). A sample of the NMC 811 was prepared by embedding the powder in epoxy before a cross-section was prepared by broad-beam argon milling (PECS™ II system, Gatan, Inc.). The sample was held at a temperature of 0 °C during the milling process and, subsequently, a 2.0 nm carbon coating was deposited (PECS™ II system, Gatan, Inc.). The sample was transferred under vacuum conditions to a conventional field emission SEM and compositional analysis was performed using the Cipher™ system (Gatan, Inc.). Quantitative BSE analysis was performed and evaluated according to the modified electron approach [5] with a screening factor of 0.7. Quantitative EDS analysis at select locations within NMC particles was performed revealing O, Ni, Mn, and Co with little-to-no variation within or between particles that were analyzed; no other elements were found to be present above the minimum detection level. The Ni:Mn:Co ratio was determined experimentally to be 8.07:1.00:1.01, consistent with the nominal 8:1:1 ratio of this NMC. The lithium content from 6 different NMC particles was determined using Cipher and the mean lithium concentration was determined to be 22.5 at. % (5.7 wt. %) within ~1.5 wt. % of the nominal composition value of 7.3 ± 0.3 wt. %.

This is a significant step forward in the analysis of battery materials as, for the first time, the charge state of a cathode material is determined in a conventional SEM—where 25 at. % Li corresponds to an uncharged battery state with NMC 811 cathode.

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5:00 PM CH01.08.17

Direct Observation of Rutile-TiO_2 Recrystallization Under Electron-Beam Irradiation Silu Guo, Hwanhui Yun, Sreejith Nair, Bharat Jalan and K. A. Mkhoyan; University of Minnesota, United States

Radiolytic damage of materials under electron beam irradiation has been a significant problem in transmission electron microscopy over the years with particular severity in beam-sensitive materials such as zeolites and MOFs [1]. Despite the prevalent theory of bond breakage mechanisms in materials due to electron beam irradiation [2], there has not been a solid study showing how a material undergoes radiolytic damage. In particular, the detailed stages in which a material experiences crystalline-to-amorphous phase transition have not been explored at atomic level. Here, we present a scanning transmission electron microscopy (STEM)-based study on the electron-beam-induced structural modification of rutile-TiO_2. We reveal that rutile-TiO_2 undergoes degradation and recrystallization through radiolytic reactions, including a motion of the TiO_6 octahedra building blocks upon 200 keV electron beam irradiation exposure. Through atomic-resolution imaging, for the first time, we were able to directly visualize the bond breakage and reconstruction processes during the radiolysis. By combining atomic-resolution STEM imaging with energy dispersive X-ray spectroscopy and electron energy loss spectroscopy, we have explored both chemical and electronic structures of TiO_x during the reactions. This enables us to unveil a detailed radiolytic mechanism for the structural modifications of the material. Elucidating the degradation and recrystallization process of rutile-TiO_2 under electron-beam irradiation allows us to develop potential solutions for characterizing beam-sensitive materials and design novel synthesis techniques guided by electron beam.

Acknowledgement:
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5:00 PM CH01.08.18

Transition Metal Ion Doping on ZIF-8 for Enhanced the Electrochemical CO_2 Reduction Reaction Jin Hyuk Cho and Sooyoung Kim; Korea University, Korea (the Republic of)

The electrochemical reduction of CO_2 to diverse value-added chemicals is a unique, environmentally friendly approach for curbing greenhouse gas emissions while addressing sluggish catalytic activity and low Faradaic efficiency (FE) of electrocatalysts. Here, zeolite-imidazolate-frameworks-8 (ZIF-8) containing various transition metal ions—Ni, Fe, and Cu—at varying concentrations upon doping were fabricated for the electrocatalytic CO_2 reduction reaction (CO_2RR) to CO without further processing. Atom coordination environments and theoretical electrocatalytic performance were scrutinized *via* X-ray absorption spectroscopy and density functional theory calculations. Upon optimized Cu doping on ZIF-8, $Cu_{0.5}Zn_{0.5}$/ZIF-8 achieved a high partial current density of 11.57 mA cm^{-2} and maximum FE for CO of 88.5% at –1.0 V (vs. RHE) with a stable catalytic activity over 6 h. Furthermore, the electron-rich sp^2 C atom facilitated COOH* promotion after Cu doping of ZIF-8, leading to a local effect between the Zn–N_4 and Cu–N_4 moieties. Additionally, the advanced CO_2RR pathway was illustrated from various perspectives, including the pre-H-covered state under the CO_2RR. Our findings expand the pool of efficient MOF-based CO_2RR catalysts, deeming them viable alternatives to conventional catalysts.

5:00 PM CH01.08.20
Experimental and Theoretical Studies on the Effect of Microstructure and Mechanical Properties of LLZO Md Zakariya Mohayman[1,2], Akihiro Kushima[1], Nan Li[2] and Tongjun Niu[2]; [1]University of Central Florida, United States; [2]Los Alamos National Laboratory, United States

All-solid-state lithium batteries are considered an ultimate choice for energy storage systems due to their high energy density and safety. Unlike conventional lithium-ion batteries, solid-state batteries do not rely on the flammable organic electrolyte and are expected to prevent lithium dendrite penetrations, which lead to the use of lithium metal anode further enhancing the energy density. However, the practical implications of solid-state batteries are limited due to poor mechanical stability and complex electro-chemo-mechanical reactions at the interface between solid electrolyte and metal anode. Garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) is one of the promising solid electrolytes for all-solid-state lithium batteries due to its low activation energy, high ionic conductivity, and high chemical stability against metal lithium enabling safe cycling of Li anodes. Although LLZO has a much higher modulus than lithium metal, penetrations of lithium are still observed in LLZO electrolytes leading to premature failures of the batteries. This is particularly evident at the grain boundaries involving nano-scale events of grain-boundary fracture, lithium deposition/penetration, and crack nucleation/propagation. Therefore, it is important to understand the fundamental mechanical properties of LLZO at the nanoscale and the influence of microstructures and loading conditions. In this work, nano-indentation and micro-pillar compression tests were performed to evaluate the mechanical properties of LLZO and clarify the effect of microstructures. In addition, *ab initio* simulations were conducted to evaluate the change in the mechanical strength of LLZO at different lithium concentrations which may occur during the charge/discharge process and at or near the grain boundaries. The insights obtained in this work provide a fundamental understanding of the mechanical properties and nano-mechanics of LLZO solid electrolytes, contributing to the development of all-solid-state lithium battery technology.

5:00 PM CH01.08.21
Development of Metal Sulfide/Oxide Decorated N, S-Doped Carbon Prepared by the Coordinated Polymer Obtained Using a New Synthetic Method Kyubin Shim, Sungwoo Park, Hyun Woo Kim and Hae Jin Kim; Korea Basic Science Institute, Korea (the Republic of)

Recently, hybrid organic-inorganic materials have received much attention in both industry and academia. [1,2] In particular, three-dimensional (3D) porous coordination polymers as a carbon precursor gives many advantages, such as rich active sites, high porosity, etc. [3] Among them, the metal-ion coordination polymers composed of metal center linked to each other through organic chains are useful to prepare the catalytic materials.
Here, we synthesized a Mn^{2+} coordinated polymer bonded by a sulfur atom with acetate counter ions (Mn-DTOGA) by an imine formation reaction. Then, from calcination of the Mn ion-coordinated polymer (700, 800, and 900 ^oC), MnS/MnO decorated N, S-doped carbon nanoparticles (MnS/O-SNC) are then prepared for the practical applications of catalytic reactions.
The prepared Mn-DTOGA and MnS/O-SNC structures are characterized using various physical, chemical, and electrochemical analyses such as FT-IR, MALDI-TOF, XRD, SEM, TEM, etc. The electrochemical measurements were conducted with a 0.070 cm^2 glassy carbon electrode with an Ag/AgCl reference electrode and a Pt wire as a counter electrode. The as-prepared electrode using the materials was tested for the electrochemical oxidation of hydrogen peroxide (H_2O_2) in a 1.0 mM H_2O_2 solution.
The Mn-DTOGA reveals a homogeneous sphere shape having a diameter with an average size, estimated to be ~500 nm. The MnS/O-SNC is also a spherical shape with a particle size of around 350 nm. Among catalysts prepared at different calcination temperatures the MnS/O-SNC (900 ^oC) shows the best performance in H_2O_2 catalytic oxidation. The XPS analysis demonstrates that the MnO decorated outward N, S-doped carbon nanoparticles mainly function for H_2O_2 oxidation. The decomposition potentials of H_2O_2 (1.0 mM) on the catalyst modified electrode are observed to be +0.40 V. The sensor prepared catalytic materials displays two dynamic ranges with a detection limit of 0.08 (± 0.02) μM.
Conclusively, we designed a new synthesis way to synthesize a coordination polymer as a precursor for carbon catalysts. From calcination of the coordinated polymer, MnS/MnO decorated S, N-doped carbon (MnS/O-SNC) nanoparticles were successfully obtained and examined for catalytic oxidation of H_2O_2. We confirmed that the catalytic performance of the oxidation reaction was mainly related to MnO decorated outside the SNC particles. The results show that it can provide a new direction for further study on catalyst design for the practical applications of catalytic reactions.

5:00 PM CH01.08.24
Orange Peel Biomass-derived Carbon Supported Cu-Electrocatalysts Active in the CO_2-Reduction to Formic Acid Izuchika Nduka[1], Tanvir Miah[1], Palmarita Demoro[2], Federica Deluca[2], Salvatore Abate[2] and Rosa Arrigo[1]; [1]University of Salford, United Kingdom; [2]University of Messina, Italy

Introduction: The use of carbonaceous materials in sustainable energy applications such as catalysis and electrocatalysis is deemed important (1). The production of these carbon materials from biomass waste is being thought to increase the economic value of the waste especially in emerging markets. Of the biomass wastes that have been explored, citrus waste is of utmost interest because of all the numerous useful chemical compounds it possesses, ascorbic acid is currently being used as both a capping agent and a reducing agent in the synthesis of Cu nanoparticles active in CO_2 electroreduction (2). In our study, we have explored a green approach towards the production of C-supported Cu electrocatalysts active in CO_2 reduction to formic acid. Using orange and lemon peels as a C-support precursor and as a source of reducing agent for Cu, we synthesized some Cu nanoparticles (Cu-O and Cu-L) by means of microwave irradiation and studied their performances in the electrochemical reduction of CO_2. The performances were correlated to the structural characteristics of these systems determined by means of scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS) at the $Cu2p_{3/2}$, C1s, and O1s core levels.
Results: The Cu2p3/2 XPS spectra showed the presence of Cu(I) and Cu(II) species and two satellite peaks which we think are related to sulphate Cu species derived from the precursor used, and they remained partially unreduced under the synthesis conditions for the Cu-L; for the C1s XPS spectra, the peaks seen suggests that for Cu-L, some of the original peel remained unaltered after the hydrothermal synthesis; and for the O1s spectra, peaks belonging to both Cu(I)-O particles and O species on the C support were present. In contrast, Cu-O presents Cu(I) species together with a more graphitized C matrix. On evaluating the electrocatalytic performance of both Cu-O and Cu-L on CO_2 reduction, we find that the Cu-O-derived electrodes outperformed Cu-L-derived electrodes in terms of activity as well as selectivity towards CO_2 reduction products (with a maximum Faraday efficiency to formic acid of 30%) and stability, thus providing a more favourable structure for application in electrocatalysis. Taken together, these findings show that the chemical composition of the peels play an important role in determining the chemical speciation in the samples of both the Cu nanostructures and the C support.
Conclusion: In conclusion, not only have we demonstrated the viability of directly utilizing citrus waste to produce useful material in a green fashion, but we have also provided a rational strategy for tailored synthesis of Cu electrocatalyst from biomass derived precursors active in the electroreduction of CO_2. Whilst our work focused on CO2 reduction, our findings can generally be applied to the preparation of orange peel derived c-supported metal

electrocatalysts for other electrocatalytic reactions of relevance in energy conversion and storage.

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SESSION CH01.09: Advanced Characterization for Electrocatalyst II

Session Chairs: Rosa Arrigo and Avetik Harutyunyan
Thursday Morning, April 13, 2023
InterContinental, Fifth Floor, Ballroom C

8:30 AM CH01.09.02

Electrochemical Impedance Spectroscopy Combined ETEM Study of Solid Oxide Material Gadolinium Doped Ceria (GDC) Zhongtao Ma, Waynah L. Dacayan, Christodoulos Chatzichristodoulou, Kristian S. Mølhave and Søren B. Simonsen; Technical University of Denmark, Denmark

In response to climate change it is necessary to develop sustainable fuel production and storage technologies. Solid oxide electrolysis/fuel cell has recently become a research hotspot due to their high energy conversion efficiency [1]. However, its degradation mechanisms at high working temperatures are still unclear, advanced characterization methods are necessary to be further developed, especially *operando* techniques.

Electrochemical impedance spectroscopy (EIS) is a classic technique in electrochemistry, and one of its advantages allows *operando* characterization on a running system without causing damage to the research object [2].

In this work we are combining an Environmental TEM [3], and a heating and biasing TEM holder connected to a potentiostat for performing EIS in the TEM. This combination allows us to mimic the operation conditions of a solid oxide electrolysis/fuel cell. In addition, combining simultaneous EIS signal, one can investigate the structural/compositional evolutions and their effect on the electrochemical performance.

We have investigated the feasibility of performing EIS in ETEM. An electrolyte-electrode barrier layer material, mixed ionic and electronic conductor $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ (GDC), which is widely used in the composite electrodes of the SOEC and SOFC cells [4], was chosen as a test sample. Our preliminary results are consistent with the documented data in terms of ionic conductivity, electronic conductivity, activity of surface-gas exchange reactions, and chemical capacities, which verified the reliability of the EIS-TEM test.

We believe the correlative EIS-TEM method will be crucial for understanding the electrochemical processes at nanoscale such as degradation in electrolysis cells, fuel cells and batteries.

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8:45 AM CH01.09.04

Dynamics of an Oxide Fuel Cell Catalyst Revealed by Operando X-Ray Scattering Jason J. Huang[1], Yao Yang[1,2], Jacob Ruff[1], Hector Abruna[1] and Andrej Singer[1]; [1]Cornell University, United States; [2]University of California, Berkeley, United States

Furthering understanding of the catalytic mechanism in the oxygen reduction reaction (ORR) is critical to advancing and enabling fuel cell technology. In this work, we use operando synchrotron diffraction and resonant elastic X-ray scattering (REXS) to investigate the interplay between the structure and oxidation state of a Co-Mn oxide catalyst, which shows an impressive ORR activity in alkaline fuel cells. REXS was used to simultaneously observe the dynamic changes in the structure and valence state of both Co and Mn under steady state (constant applied potential) and non-steady state (cyclic voltammetry). Under steady-state conditions, an irreversible structural phase change is observed at low potentials, along with an accompanying reduction in both Co and Mn valence. With fast diffraction data collection enabled by a synchrotron source, we resolved periodic changes in the lattice parameter aligned with the cyclically applied potential. When cycled through low potentials, the catalyst exhibited a reversible rapid increase in strain. Through this work, we gained a greater understanding of the ORR mechanism in Co-Mn oxide catalysts and demonstrated the unique capabilities of combining structural and chemical characterization in REXS.

9:00 AM CH01.09.05

Combining *In Situ* Mass Spectroscopy and Active Learning for Rapid Development of Pre-Treatment Protocol for Electrocatalysts Aniket Sandip Mule[1,2], Kevin Tran[3], Ashton Aleman[1,2], Gaurav A. Kamat[1,2], Weike Ye[3], Shijing Sun[3], Michaela Burkes Stevens[2] and Thomas Jaramillo[1,2]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States; [3]Toyota Research Institute, United States

Electrocatalysts are materials that speed up an electrochemical reaction. In the last few decades, researchers have observed that activation or "pre-treatment" protocols, such as electrochemical cycling, can significantly modify the structure and the performance of electrocatalysts. However, the mechanistic details of such a structure modification remain poorly understood. Consequently, a pre-treatment protocol is often chosen arbitrarily. To gather insight into the underlying mechanism and accelerate the optimization of the pre-treatment protocol, we employ a two-fold strategy: 1) systematic design of experiments (DoE) and 2) in-situ characterization of electrocatalysts to obtain time-resolved data. Commercially available Pt/C electrocatalysts for oxygen reduction reaction (ORR) were chosen as a model system. First, a central composite design based on multiple parameters (> 6) was applied to generate different pre-treatment protocols. The protocols were then investigated using a custom-made experimental setup that provided simultaneous and real-time information about the electrochemical performance and the stability of the catalyst. Specifically, an electrolyte saturated with O_2 or N_2 was guided through a flow cell to perform electrochemical experiments (pre-treatment or ORR). The flow cell outlet led to an inductively-coupled plasma mass spectrometer (ICP-MS) that monitored the in-situ dissolution of the electrocatalyst. Modifying parameters in the pre-treatment protocol showed a sizeable impact on charge transfer and dissolution during ORR. For example, increasing the upper potential from 1.5 V to 2.5 V decreased the charge transferred and increased dissolution during ORR by a factor > 2. Additionally, during pre-treatment and ORR, the dissolution occurred primarily when the potential was swept from oxidizing currents to reducing currents. Furthermore, our DoE-based approach unraveled the interaction between different parameters. Thus, the data obtained from in-situ ICP-MS by applying a DoE-based approach provided mechanistic insight and enabled efficient training of the active learning algorithms. We then exploited such machine learning models to identify characteristics of an ideal pre-treatment protocol that lead to maximum activation of an electrocatalyst. Finally, we also provide strategies to rapidly extend our parametric space to evaluate the effect of additional parameters (*e. g.*, electrolyte flow rate) and transfer our knowledge to different systems (*e. g.*, compositions of catalysts). Therefore, besides advancing the fundamental knowledge of electrocatalyst behavior, our study provides a framework for the accelerated development of pre-treatment protocols for new electrocatalysts.

9:15 AM CH01.09.06
***Operando* Correlative Studies of Evolving Cu Nanocatalysts for CO_2 Electroreduction** Yao Yang[1], Sheena Louisia[1], Sunmoon Yu[1], Hector Abruna[2] and Peidong Yang[1]; [1]University of California, Berkeley, United States; [2]Cornell University, United States

In an era of shifting the energy paradigm from fossil fuels to renewable energy, CO_2 reduction reaction (CO_2RR) emerges as a promising approach to covert greenhouse gas into valuable chemical fuels and close the carbon cycle for a sustainable energy supply. Since Cu remains the sole element for CO_2RR to multicarbon products (C_{2+}), significant efforts have been devoted to developing Cu electrocatalysts with higher selectivity and activity. However, the complex nature of active sites and the intrinsic structures under reaction conditions have remained largely elusive due to the lack of *operando*/*in situ* methods.[1-3]
In our previous studies, we reported that small Cu nanoparticles (sub-10 nm NPs) showed superior C_{2+} superior C_{2+} selectivity, relative to the larger sized Cu NPs, especially at low overpotentials.[4,5] In this work, we present a comprehensive *operando* correlative study of dynamic evolution of a family of monodisperse Cu NP ensemble electrocatalysts under CO_2RR.[1] *Operando* electrochemical liquid-cell scanning transmission electron microscopy (EC-STEM) and 4D-STEM resolves microscopic dynamic morphological and structural evolution at the nm scale. Correlated *operando* high-energy-resolution fluorescence detected (HERFD) X-ray absorption spectroscopy (XAS) reveals dynamic macroscopic changes in valence states and coordination environment. Statistical analysis of interparticle dynamics was probed by *operando* resonant soft X-ray-based resonant soft X-ray scattering (RSoXS).[2] The *operando* correlative strategies, described herein, elucidates the longstanding enigmatic nature of Cu active sites for selective CO_2 electroreduction. The strategy described herein can serve as a general platform to resolve the electrocatalytic interface of nanoparticle catalysts under real-time operating conditions across multiple time and length scales, thus serving the fundamental understanding necessary to development of many other electrochemical reactions for renewable energy technologies.

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9:30 AM BREAK

10:00 AM CH01.09.07
Gas-Phase Reactions of Metal-tmhd Compounds—New Insights from Microreactor Studies Using Synchrotron Radiation Sebastian Grimm[1,2], Patrick Hemberger[3] and Burak Atakan[1,2]; [1]University of Duisburg-Essen, Germany; [2]Center for Nanointegration (CENIDE), Germany; [3]Paul Scherrer Institute, Switzerland

Metal-β-diketonate complexes are widely used as precursors for thin film deposition in the fields of catalysis, microelectronics and functional materials for energetic applications.[1] This is mainly because of their superior physical and chemical properties such as the volatility and inertness, which can be customized by changing the β-diketonate group attached to the respective metal center.[2]
When used in deposition processes, often gas-phase reactions are the initial decomposition step, but gaseous intermediates can lead to unwanted film morphology and unsatisfactory purity or a depletion of the precursor by side reactions, and consequently a reduction in growth rate. A precise understanding of the decomposition mechanism, especially the sequence of bond dissociation steps, is important for improving and modelling such a processes.
Consequently, the analysis of the initial stages of growth is important and requires sensitive analytical techniques with sufficiently low detection limits for elusive gas-phase species. Because of limitations in experimental techniques, it was until recently not possible to detect most of the postulated intermediate species; their temperature-dependent kinetics often remained unknown.[3]
We have overcome some of these challenges and demonstrated for various metal-organic precursors, that by using a microreactor coupled to a very mild ionization source, aided by numerical simulation, we are capable to detect and characterize elusive species, especially metal-containing intermediates with short lifetimes below 50 µs.[4]
Building up on previous work on acetylacetonate complexes, we present insights into the reactions of 2,2,6,6-tetramethyl-3,5-heptanedionate (tmhd) compounds. The vacuum pyrolysis of aluminium and zirconium 2,2,6,6-tetramethyl-3,5-heptanedionate, $Al(tmhd)_3$ and $Zr(tmhd)_4$ is investigated here. In brief, the precursor is sublimed, subsequently transported by helium carrier gas, and expanded through a pinhole into a resistively heated 1 mm inner diameter SiC-microreactor of 10 mm length. Species leaving the reactor are ionized by tuneable vacuum ultraviolet (VUV) synchrotron radiation, and characterized by imaging photoelectron photoion coincidence spectroscopy (i^2PEPICO) and mass spectrometry at the Swiss Light Source. We recorded photoionization efficiency curves (PIE) and threshold photoelectron spectra (TPES) at photon energies of 6.3-11.5 eV, which give us direct evidence for the characterization of reactive intermediates and products.
In the experiments, hydrocarbons, oxygenated and metal-containing species were detected and characterized unambiguously in the gas-phase at temperatures from 450-950 K, which provides insights in the underlying decomposition mechanisms. Most importantly, we detected and characterized metal-bis(diketo)acetylacetonate-H, $M(C_{11}H_{19}O_2)(C_{11}H_{18}O_2)$ as major initial decomposition product in the gas-phase at temperatures above 650 K, which subsequently forms $M(C_{11}H_{19}O_2)(C_{10}H_{15}O_2)$ by a methyl loss. Additionally, several hydrocarbons and oxygenated species were detected and assigned as decomposition species for the first time, i.e. H-tmhd ($C_{11}H_{20}O_2$), $C_7H_{11}O_2$, pinacolone ($C_6H_{12}O$), the tert-butyl radical (C_4H_9), which afford the formation of metal-containing intermediates. The temperature-dependent formation mechanisms of the assigned species will be discussed and compared to previous results on M(acac) precursors.

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10:15 AM CH01.09.08

Nanoscale Characterization for Understanding Performance Limitations in Water Splitting Photoelectrodes Lukas Wolz[1], Harishankar Balakrishnan[2], Guanda Zhou[1], Ian D. Sharp[1], Achim Hartschuh[2] and Johanna Eichhorn[1]; [1]Technische Universität München, Germany; [2]Ludwig-Maximilians-Universität München, Germany

Photoelectrochemical water splitting is a promising route for efficient conversion of solar energy into chemical fuels. In this context, economically viable photosystems are often based of semiconductor thin films which are polycrystalline or nanostructured with highly complex architectures e.g. with boundaries between differently orientated grains, different crystal facet orientations, as well as locally varying composition or phase. These nano- to micrometer properties often control critical processes, such as efficiency and stability, of the macroscale system. To understand the impact of nanoscale properties on the macroscopic performance, we aim at resolving local structural, chemical, and optoelectronic heterogeneities and at elucidating their effect on light-driven processes.

In this work, we use a correlative approach to elucidate the nanoscale properties of polycrystalline BiVO$_4$ thin film photoelectrodes. Mapping of the local charge transport properties by photoconductive atomic force microscopy reveals the tolerance to grain boundaries.[1] Interestingly, scanning nearfield infrared microscopy shows strongly varying absorption from VO$_4$ stretching modes between grains and at grain boundaries which correlate with the heterogeneities in the local photoconductivity across the polycrystalline thin films. Furthermore, local temperature-dependent current-voltage spectroscopy show that the low intrinsic bulk conductivity of BiVO$_4$ limits the electron transport through the film, and that the transport mechanism can be attributed to space charge limited current in the presence of trap states.[1] Performing the same measurements in-situ in controlled gas-phase environment reveals the influence of chemical interactions of adsorbed oxygen and water on charge transport and interfacial charge transfer.[2] For BiVO$_4$, we demonstrate that adsorbed oxygen acts as a surface trap state for electrons, which enhances the built-in potential and depletes the BiVO$_4$ layer. Overall, combining insights from different nanoscale techniques generates a comprehensive picture of charge separation, transport, and transfer at the nanoscale. The gained nanoscale understanding of energy materials enables the rational design of durable and efficient solar fuel devices.

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10:30 AM *CH01.09.09
A Multitechnique Approach for The Investigation of Reaction Mechanisms in Cu-Zeolite Catalysts Gloria Berlier; University of Turin, Department of Chemistry, Italy

Heterogeneous catalysis is involved in the vast majority of industrial chemical processes, with a growing attention to sustainability, energetic and environmental aspects. To develop a sustainable and cleaner technology, based on new or optimized solid catalysts, a comprehension of the working principles of heterogeneous catalysis is a prime requirement. Spectroscopies play a pivotal role in this complex subject, addressing some of the main challenges: i) determine the nature and distribution of the catalytically active sites; ii) unveil the underlying catalytic mechanisms; iii) define structure/properties relationship (activity, selectivity and stability); discriminate between active sites and spectators in reaction conditions [1].
This contribution focuses on the use of *in situ* and *operando* vibrational and electronic spectroscopies (infrared, Raman, UV-Vis, X-ray absorption and emission) for the characterization of heterogeneous catalysts for selective redox reactions, *i.e.* the Selective Catalytic Reduction of NO$_x$ with NH$_3$ (NH$_3$-SCR) and the direct conversion of methane to methanol (DMTM) [2,3]. Cu-exchanged zeolites are among the most studied catalysts for both reaction, in relation to the reversible Cu^{2+}/Cu^{+} redox cycle and to the ability of Cu^{+} ions to active O$_2$ in specific conditions. In particular Cu exchanged chabazite (Cu-CHA) is the catalyst of choice for NH$_3$-SCR, due to high activity and good hydrothermal stability. The high symmetry of the CHA framework coupled to the intrinsic structural definition of Cu counterions implies that this system is also an ideal playground for spectroscopy and computational studies [3,4,5]. Some of the most recent and relevant results obtained on the Cu-CHA catalysts by applying advanced spectroscopic techniques together with complementary computational studies will be discussed, with particular focus on the fundamental knowledge related to the different techniques and the importance of a holistic multitechnique approach. This will include advanced data analysis, such as the wavelet transform (WT) analysis and machine learning (ML)-assisted fitting of the extended X-ray absorption fine structure (EXAFS) spectra [4,6], and experimental methodologies such as Modulation Excitation (ME) spectroscopies [7].

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11:00 AM *CH01.09.10
Understanding Catalyst Deactivation via Electron Microscopy Qian He; National University of Singaproe, Singapore

In textbooks, a catalyst is often defined as: "a substance that makes a chemical reaction happen faster without being changed itself". However, in practice, all catalysts deactivate for one reason or another [1]. As a powerful tool to probe local structural and chemical information about practical catalysts at atomic resolution, Electron Microscopy (EM) can be used to follow the evolution of catalysts under reaction conditions to provide insights into the deactivation mechanisms. This not only can help us to develop catalysts with better stability but also can shine a light on the nature of the active sites. This is often a challenging task due to the structural complexity of practical catalysts, which can make it difficult to correlate the observed results with catalytic performance. Although many in situ/operando EM techniques [2] have been developed, it can still be challenging to reproduce the reaction environment for many industrially important reactions.

In this presentation, we will give a few examples of using identical location electron microscopy to understand the deactivation of catalysts used for gas-phase and electrochemical reactions, that are still difficult to reproduce with the current in situ techniques. The first example is the study of Au catalysts used for the low-temperature water gas shift (LT-WGS) reaction, which can be used for the PEMFC applications. Both the nature of the active sites and the deactivation mechanism have been under debate. Flytzani-Stephanopoulos *et al.* [3] suggested that the cationic Au was the active site, and hence the deactivation was due to sintering. Hardacre et al.[4] suggested that the interface between the metallic nanoparticle and the support are the active sites and the deactivation was due to the loss of the interfaces via "dewetting". Our identical location EM studies [5] showed that the loss of cationic Au happens at the early stages of the reaction and can only be partially responsible for deactivation, while the deactivation at a later stage of the reaction was likely due to dewetting.

Another story is about CO2 reduction reactions (CO2RR) via Cu catalysts, which are the best catalysts to produce C2+ products but are also known to show morphological instability. Understanding the mechanisms of these morphology changes can help us to further optimize the catalysts. Current views as to why this occurs include copper redox reaction or intermediates adsorption inducing the morphological restructuring and leading to the fac

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SESSION CH01.10: Advanced Material Development and Analytical Technique I
Session Chairs: Rosa Arrigo and Akihiro Kushima
Thursday Afternoon, April 13, 2023
InterContinental, Fifth Floor, Ballroom C

1:30 PM *CH01.10.01
Status, Challenges and Advanced Characterization Needs of Automotive Solid State Batteries Alvaro Masias; Ford Motor Company, United States

Lithium ion battery technology has improved continuously since its introduction in 1991. In the last decade, the automotive sector has experienced a huge revival of interest in electrification as the continuously growing energy density of the lithium ion battery has enabled more and more practical vehicle designs. However, the rate of improvement of lithium ion battery technology maybe slowing down and to support the mass adoption of electrification, superior battery technologies are being pursued the world over.

Lithium solid state batteries hold great promise as a next generation battery chemistry for automotive electrification. Through the enablement of advanced anodes such as majority silicon or lithium and the replacement of flammable liquid solvents, solid state batteries are believed to offer opportunities for improvements in energy and safety. However this chemistry family has a wide range of maturity and scale challenges when compared to conventional liquid lithium ion.

This presentation will describe how the current status of solid state batteries compares to liquid lithium ion for the automotive market. We will also highlight the most pressing materials and characterizations challenges of the solid state battery class from the perspective of an automotive manufacturer and discuss some advanced characterization techniques of active study such as the usage of fluorophores and neutron reflectometry.

2:00 PM CH01.10.02
Using Correlations to Reveal Fine Details on Structural Disorder in Solid-State Electrocatalysts Rodney Smith; University of Waterloo, Canada

Transition metal ions in undercoordinated sites, such as edge-sites in layered double hydroxides or adjacent to oxygen vacancies in perovskites, have long been envisioned as catalytically relevant sites for electrochemical reactions such as the oxygen evolution reaction. Direct analysis of such defect chemistry in solid state electrocatalysts is impeded by the low concentrations of defects relative to bulk sites, multitude of viable defects in any given material, potential for dynamic changes during catalysis, and fundamental limitations inherent in every characterization technique. We pursue experimental evidence for strained, distorted, or defective coordination environments in common electrocatalysts such that we can systematically identify and rule out specific features as catalytically relevant sites to guide efforts to design improved catalysts. Our strategy is to combine systematic variations in synthesis with comprehensive characterization. Synthetic strategies are developed to prepare series of samples that, ideally, are dominated by changes in a single type of structural disorder. The structure, properties, and electrochemical parameters extracted from diverse techniques are then comprehensively compared to each other to identify useful structure-property and structure-structure correlations. These correlations can provide chemical insights that cannot otherwise be attained. This talk will demonstrate how this strategy enabled identification of distortions and unreported coordination environments in iron-nickel hydroxide,[1,2] and defects such as interstitial protons and associated iron vacancies in hematite photoanodes.[3,4]

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2:15 PM BREAK

3:15 PM *CH01.10.05
Imaging Characterization Challenges and Solutions for Advanced Battery Development Zhao Liu; Thermo Fisher Scientific, United States

Lithium battery is an energy storage system with highly complex microstructures covering multiple length scales, namely from millimeters to nanometers. The performance of the battery is dependent on the battery microstructures. Therefore, accurately characterizing the battery microstructure at different length scales is critical for interpreting battery performance, which ultimately advances battery technology.

Imaging characterization via electron microscopy, including SEM, FIB-SEM, and TEM, has been recognized as an effective approach to studying battery microstructure. However, it is challenging to capture the materials at the full-length scale and also correlate each data set. In addition, some materials are beam-sensitive and air sensitive, making it challenging to observe the structure at its native state.

In this talk, I will discuss a comprehensive approach to studying the battery structure at multiple length scales in 2D and 3D. In addition, solutions such as cryogenic FIB and TEM, inert gas sample transfer, and dose management approach to observe the battery materials are their native state will also be discussed.

3:45 PM CH01.10.06
Lithium Excess-Driven Redox Imbalance Between Cationic and Anionic Redox Causes Electro-Chemo-Mechanical Failure in High-Energy Layered Cathode Materials Hoyoung Jang, Donggun Eum and Kisuk Kang; Seoul National University, Korea, Korea (the Republic of)

Despite the high-energy density of lithium- and manganese-rich layered oxides (LRLOs) provided through the high-voltage anionic redox chemistry, critical issues such as capacity fading, voltage decay, and hysteresis have limited their real-world applications. As an elegant solution, O2-type LRLOs were recently reported to mitigate these voltage issues via reversible transition-metal (TM) migration during the successive charging and discharging; however, these materials still suffer from capacity degradation during long-term cycling. Repetitive mechanical stress and failure, one of the prevailing degradation factors for other layered oxide electrodes, has also been proposed as the origin of the capacity fading even in LRLOs. Nevertheless, in-depth studies on the mechanical behavior in LRLOs, particularly with respect to the extent of high-voltage oxygen redox, remain elusive. Herein, a series of O2-type LRLOs were designed and synthesized to investigate the evolution of the bulk structures as a function of varying oxygen-redox capabilities and to examine their effects on persistent electrochemical degradation. We demonstrate that the generation of bulk microcracks in the particles is strongly coupled with repeated lattice evolution and structural distortions during the high-voltage oxygen redox. These internal cracks lead to the formation of an electrochemically inactive phase near the cracks, which is followed by capacity fading as extended cycling occurs. Based on these results, we propose redox engineering strategy via Ni redox buffer to increase the ratio of cationic to anionic redox activity and thereby mitigate severe lattice disruption, achieving improved capacity retention during long-term cycling. These findings clarify how the oxygen redox in LRLOs is highly correlated to the mechanical degradation (and consequently capacity fading) and provide a general design principle towards genuine high-energy cathode materials.

4:00 PM CH01.10.07
Fundamental Studies on Enhanced Redox Performance of Alkaline Iron Batteries by Silicate Additives Sathya Narayanan Jagadeesan; Worcester Polytechnic Institute, United States

Iron oxides or hydroxides are highly desirable "green" battery electrodes owing to their abundance, multiple oxidation states, low cost, and environmental beneficence. However, their low storage capacity and poor cycling life have been lingering concerns due to the substantial hydrogen evolution on charging and the formation of inactive spinel phase on discharging. Herein, we report a fundamental physicochemical study of the redox behavior of iron (II, III) oxide materials containing goethite (α-FeOOH) and magnetite (Fe_3O_4) in an alkaline solution. Also, an unprecedented discovery of how the low concentration of sodium silicate (Na_2SiO_3) electrolyte additive improves the conversion of $Fe(OH)_2$ into FeOOH through a one-electron-transfer reaction by mitigating the formation of Fe_3O_4.
The phase information is provided by *in operando* synchrotron X-ray diffraction (XRD) during the redox cycling. X-ray photoelectron spectroscopy (XPS) and electrochemical measurements revealed the iron-oxide/silicate interaction that introduces diffusion limitation of oxygen species on the surface of the electrode, thus favoring the FeOOH formation. As per the classical molecular dynamics (CMD) simulations, the addition of Na_2SiO_3 results in increased Na ions in the solvation shell. Theoretical calculations (DFT) also supported that the $(SiO_3)^*$ adsorption is more energetically favored than the $(OH)^*$ on the $Fe(OH)_2$ surface. Moreover, this new battery chemistry enables the high capacity and reversibility of the iron electrode, which could contribute to developing new alkaline battery systems built on non-critical materials for sustainable energy storage.

SESSION CH01.11: Poster Session III
Session Chairs: Junjie Niu and Chongmin Wang
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM CH01.11.01
Variable-Temperature Hall Study in High Performance Perovskite and Kesterite Films Using High Sensitivity Parallel-Dipole-Line Hall System
Chaeyoun Kim[1], Oki Gunawan[2] and Byungha Shin[1]; [1]KAIST, Korea (the Republic of); [2]IBM Research, United States

High sensitivity Hall effect system capable of measuring wide range of sample resistance, carrier density, mobility and temperature is critically needed for development of many advanced electronics material. We recently developed a high-sensitivity variable temperature Hall measurement system based on rotating parallel dipole line (PDL) magnet. The PDL system is an emerging AC field Hall system that has played a key role in the recent discovery of carrier-resolved-photo Hall effect [1]. This variable temperature Hall system allows us to study the mobility scattering mechanism and extracting the donor or acceptor level of the material. We demonstrated these applications in several high-interest materials such as high performance kesterite (CZTS) and perovskite solar absorber films. For example, we extracted the CZTS acceptor level of 210 meV, very close to the theoretical prediction of 217 meV level associated with Cu_{Zn} antisite acceptor level. [1] O. Gunawan et. al., Nature 575, 151 (2019).

5:00 PM CH01.11.02
Synthesis, Characterization and Electrochemical Analysis of Porous Carbon/Tungsten Oxide Composites Bishnu Bastakoti and John Bentley; North Carolina A&T State University, United States

Over the years, the development of sustainable and renewable energy storage systems has accelerated because of the need to preserve natural resources and control energy consumption. Non-conventional energy devices, such as batteries, supercapacitors, and fuel cells, have been utilized in hybrid vehicles and portable electronic devices where chemical energy is converted to electrical energy via electrochemical reactions. Here, we synthesized mesoporous WO_3-mesoporous carbon composites using a micelle assembly approach with a poly(styrene-*b*-vinyl pyridine-*b*-ethylene oxide) block copolymer and studied the electrochemical properties focusing on its application in supercapacitor. The uniformly distributed WO_3 nanoparticles through the carbon mesostructured are effectively utilized to enhance capacitive performances. Through a combination of both faradaic and non-faradaic processes, WO_3-mesoporous carbon exhibited a high specific supercapacitance of 381 $F.g^{-1}$ in 1 M H_2SO_4.

5:00 PM CH01.11.04
Regulating Surface Redox Activity in Li-Rich Layered Oxides via Band-Aligned Vanadium Phosphate Coatings Tristram Jenkins[1], Jose A. Alarco[1], Bruce C. Cowie[2] and Ian D. Mackinnon[1]; [1]Queensland University of Technology, Australia; [2]Australian Nuclear Science and Technology Organisation, Australia

With a specific energy density >250$mAhg^{-1}$ and average voltage of ~3.6V, Li-rich layered transition metal oxides (LLOs) are a commercially interesting high energy cathode material for the next generation of Li-ion batteries. However, LLOs critically suffer from accelerated capacity and voltage decay caused by a layered-to-spinel phase transition triggered by the involvement of O 2p states and formation of electron holes, causing lattice destabilization during redox[1]. This structural transformation is recognized as a surface-propagating phenomenon, so surface modification to improve chemical bonding stability with oxygen has become a primary approach to restrain structural transformation and its associated side effects (i.e., O_2 evolution, electrolyte side reaction, transition metal dissolution etc.) [2] . However, the behavior of the electronic structure at the interface between surface-modifier and bulk of LLOs is generally less investigated but is potentially an important aspect for oxygen redox charge transfer as well as general structural stability during cycling.

In this work, we systematically investigate the influence of redox-active vanadium phosphate (VP) coatings, $Li_3V_2(PO_4)_3$ (LVP) and $Na_3V_2(PO_4)_3$ (NVP) on the electronic structure, surface redox activity and electrochemical performance of a typical LLO ($Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$) using both experimental investigation and *ab initio* DFT calculations. Experimentally, XPS, UPS, UV-Vis-NIR and ex-situ O K- and Ni, Mn, Co L-edge soft X-ray absorption spectroscopy (sXAS) were used study the redox reactions of the pristine and VP-LLOs and to map their intrinsic surface and interfacial electronic structures. Ex-situ sXAS comparison of pristine and VP coatings during both initial and long-term cycling shows significant reduction in O 2p-TM 3d hole formation at the surface (PEY, TEY) and better redox reversibility during cycling of VP-coated samples. Electronic structure investigation via DFT and spectroscopic techniques indicate evidence of electronic band alignment and a reduced surface polarization for VP-LLOs compared to pristine sample surfaces. Practically, we find VP-coated LLOs offer improved charge transfer kinetics and exhibit far better capacity and voltage retention than pristine samples with up to 90% capacity retention and -0.18eV median voltage fade after over 100 cycles. These results point to the practical utility of considering the electronic compatibility of surface modification agents at the interface in addition to current ionic transport, phase compatibility and chemical stability considerations for aiding charge transfer and alleviating structural deterioration in high energy Li-rich layered oxide battery cathodes.

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[2]S. Zhao, Z. Guo, K. Yan, S. Wan, F. He, B. Sun, et al., Towards high-energy-density lithium-ion batteries: Strategies for developing high-capacity lithium-rich cathode materials, Energy Storage Materials, vol. 34, pp. 716-734, 2021.

5:00 PM CH01.11.07
Cu_2WO_4 Semiconductor Electrode—A Promising Photocathode for CO_2 Reduction Jessica C. Alvim[1], Nadia G. Macedo[1], Leonardo C. Soares[1], Márcio Sangali[1], Miguel T. Galante[1], Flavia Cassiola[2], Dwayne Carranza[2], Rubens Caram Jr[1] and Claudia Longo[1]; [1]Unicamp, Brazil; [2]Shell Technology Center, United States

The search for suitable materials to promote the conversion of CO_2 to value-added chemicals has been motivating researchers over the last decade. In the photoelectrochemical (PEC) approach, the CO_2 reduction reaction (CO_2RR) can be achieved under low overpotential and higher Faradaic Efficiency (FE) using a sunlight irradiated p-type semiconductor electrode as a photocathode. This work describes the investigation of photoelectrodes based on copper (I) tungstate (Cu_2WO_4) for PEC-CO_2RR. Cu_2WO_4 was synthesized by arc melting, using Cu_2O and WO_3 as precursors. After ground, the resulting reddish particles exhibited the X-ray diffraction (XRD) pattern of Cu_2WO_4; also, UV-Vis diffuse reflectance spectroscopy (DRS) revealed a broad absorption in the visible range and the band gap energy was estimated as 2.0 eV. The electrochemical properties in aqueous media were initially investigated for electrodes consisted of a porous film of Cu_2WO_4 particles deposited by drop-casting on glass-FTO. The FTO|Cu_2WO_4 behaved as a p-type semiconductor electrode, exhibiting positive photopotential and cathodic photocurrent under solar-simulated irradiation, and notable activity for PEC-CO_2RR. Also, Incident Photon-to-Current conversion Efficiency (IPCE) curve was coherent with the DRS measurements. Moreover, gas diffusion electrodes were prepared by depositing Cu_2WO_4 particles on carbon paper, that was placed between two titanium mesh (to improve the mechanical stability). The GDE|Cu_2WO_4|Ti-mesh photocathode, under CO_2 flow, was associated with a photoanode consisted of a titanium foil covered with a thin film of $BiVO_4$ modified with Ni-Fe oxyhydroxides (Ti|$BiVO_4$/FeOOH/NiOOH), in a PEC H-cell (separated compartments) containing aqueous $NaHCO_3$. Under irradiation, this PEC reactor exhibited an open circuit potential of +0.4 V;also, with no external bias, a short-circuit photocurrent of ca. 0.7 mA was observed, continuously sustained by CO_2RR and oxygen evolution reaction. After 2h-phtoelectrolysis, the main registered liquid product in this system was ethanol, with FE of (13 ± 3)%. Therefore, the p-type semiconductor Cu_2WO_4 exhibits efficient sunlight harvesting and activity for ethanol production from CO_2 reduction.

5:00 PM CH01.11.08
On The Fly Rietveld Analysis of Synchrotron Powder X-Ray Diffraction Monty R. Cosby[1,2], Adam A. Corrao[2], Gerard S. Mattei[2], Kevin Stone[1] and Peter G. Khalifah[2,3]; [1]Stanford Synchrotron Radiation Lightsource, United States; [2]Stony Brook University, The State University of New York, United States; [3]Brookhaven National Laboratory, United States

Modern synchrotrons can acquire high-resolution 1D XRD patterns containing a system's crystallographic information within seconds. With an appropriate setup, *in situ* or *operando* experiments can be performed on one or many experiments with a temporal resolution of thousands of scans per day. Unfortunately, analysis of X-ray diffraction is a tedious process that can often exceed weeks for adequate structural determination of a single pattern. This has been sped up substantially with previous software developments (such as TOPAS and GSAS-II) that have enabled refinement of many patterns sequentially. For this work, a code was developed to both perform Rietveld analysis and analyze the resulting structural information X-ray diffraction seconds after the data has been acquired enabling users to follow experiments as they develop in real-time. *In situ* and *operando* experiments have been followed with this code at SSRL, NSLS-II, and APS both on-site and with remote operations. Using on-the-fly analysis not only allows for real-time monitoring of experimental progress, but also permits experiments to be more data driven with users and can potentially enable AI making informed decisions based on the structural evolutions that occur during *in situ* synchrotron experiments.

5:00 PM CH01.11.09
Altering Solvation at the Electrolyte/Electrode Interface in a Precisely Defined Manner Feipeng Yang[1], Yang Ha[1], Kun Qian[1,2], Scott A. McClary[3], Nathan Hahn[3], Kevin R. Zavadil[3] and Jinghua Guo[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]The University of Akron, United States; [3]Sandia National Laboratories, United States

Calcium is a promising candidate in multivalent battery technologies because of its safe, economical, and nontoxic nature. It offers the promise of a more than two-fold increase in the volumetric capacity compared to monovalent lithium-ion batteries. The understanding of the solvation and charge transfer mechanism at the electrolyte/electrode interface and how different types of cations and anions will affect the calcium solvation at this interface is the key to developing novel calcium batteries since the solvation of an electrolyte near the interphase dictates the charge transfer efficiency and therefore affects the performance of a battery. However, current understanding regarding this interphase was limited due to the lack of direct interphase probing approaches under in-situ/operando conditions. In this talk, using synchrotron-based X-ray absorption spectroscopy and resonant soft X-ray scattering through a patterned e-chip, the solvation of a calcium organic electrolyte was investigated under operando conditions. The disruption of the solvation structure by a secondary anion or cation was evaluated using the methodologies developed, which will guide the designing of electrolytes for future energy storage. The strategy of these new methodologies developed will also benefit the investigation of catalysis at interphases and electrochemical microenvironments in general.

5:00 PM CH01.11.10
Visualizing Stacking Fault Formation in Shocked Diamond by Femtosecond X-Ray Radiography Kento Katagiri[1], Leora E. Dresselhaus-Marais[1], Tatiana Pikuz[2], Genki Kamimura[2], Hirotaka Nakamura[2], Gooru Masaoka[2], Ryosuke Kodama[2], Masato Ota[2], Shunsuke Egashira[2], Youichi Sakawa[2], Takayoshi Sano[2], Frank Schoofs[3], Michel Koenig[4], Bruno Albertazzi[4], Gabriel Rigon[5], Lichao Fang[1], Zoe Smith[1], Yuichi Inubushi[6], Kohei Miyanishi[7], Keiichi Sueda[7], Tadashi Togashi[6], Makina Yabashi[6], Toshinori Yabuuchi[6] and Norimasa Ozaki[2]; [1]Stanford University, United States; [2]Osaka University, Japan; [3]UK Atomic Energy, United Kingdom; [4]LULI, CNRS, CEA, Ecole Polytechnique, France; [5]Nagoya University, Japan; [6]JASRI, Japan; [7]RIKEN, Japan

Since plastic deformation of crystals is primarily driven by the motion of dislocations (line defects), it is necessary to understand how fast they can propagate in order to describe the deformation dynamics of solids compressed at highest strain rates. Although many models predict the upper bound of dislocation velocities to lie between the longitudinal and transverse acoustic velocities, experimentally capturing the ultrafast dislocation motion under high strain-rate deformation remains elusive. We present our recent experimental results of *in-situ* X-ray radiography of laser-shocked single crystal diamonds. By using the ultra-bright femtosecond-duration pulses available at the SACLA X-ray Free Electron Laser facility, we imaged inelastic shock waves in diamond that propagated with a velocity comparable to the bulk sound velocity of diamond (≥ 11 µm/ns). For these waves, we observed shock-induced stacking faults form along diamond's {111} slip planes via imaging, at velocities that indicate that the dislocations leading the stacking fault formation propagate transonically (*i.e.*, with a speed between the transverse and longitudinal wave velocities of the crystal). Our advanced characterization of transonic dislocation motion gives new insights into the fundamental behavior of the dislocation propagation in crystals.

5:00 PM CH01.11.11
Advancing Titration Mass Spectrometry to Decouple Oxygen-Redox and Manganese-Redox Voltage Hysteresis in a Li-Excess Cation-Disordered Rock Salt Cathode Tzu-Yang Huang[1,2] and Bryan McCloskey[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Voltage hysteresis can significantly drag down the round-trip energy efficiency of a Li-ion battery cathode. For Li-excess cathode materials, coexisting transition-metal and oxygen redox makes it challenging to evaluate how each redox mechanism impacts voltage hysteresis. In this work, we re-designed conventional aqueous redox titration with the aid of mass spectrometry (MS) gas analyzer to quantify two coexisting solid-phase analytes, namely oxidized oxygen and $Mn^{3+/4+}$, in a representative Li-excess cation-disordered rock salt — $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$(LMTO). Two MS-countable gas molecules evolve from two separate titrant-analyte reactions, which allows decoupling Mn and O redox capacities. As incremental redox capacities are quantitatively decoupled, each redox voltage hysteresis can be further evaluated through deconvoluted energy efficiency and overvoltage distribution, which unambiguously inform how different each redox mechanism contributes to the overall voltage hysteresis. Our results show promise of designing new analytical workflow to experimentally measure intermixed redox capacities and their round-trip energy efficiencies, even in a disordered material having complex local coordination environments.

5:00 PM CH01.11.12
Characterization of Annealing-Induced Phase Segregation in Composite Silicon Anodes for Li-ion Batteries Zoey Huey[1,2], Gerard M. Carroll[1], Patrick Walker[1], Steven C. DeCaluwe[2] and Chun-sheng Jiang[1]; [1]National Renewable Energy Laboratory, United States; [2]Colorado School of Mines, United States

Silicon (Si) anodes present a promising alternative to graphite anodes for lithium ion batteries (LIBs), as Si has a greater specific capacity, but issues arise as Si expands during lithiation which results in an unstable solid-electrolyte interphase (SEI).[1] One solution for this issue is the use of Si nanoparticles (NPs) that maximize the surface area to volume ratio. Here, we discuss electrodes made with Si NPs treated with polyethylene oxide (PEO) (for improving dispersion during processing), conductive carbon NPs, and P84 polyimide binder. These electrodes show significant improvements in active material utilization, first cycle efficiency, and capacity retention with extensive cycling after an annealing treatment.

We used air-free argon ion polishing to create electrode cross sections and imaged through the electrode thickness using atomic force microscopy (AFM)-based nano-electrical characterization of scanning spreading resistance microscopy (SSRM), nano-mechanical characterizations of contact resonance and force volume (CR-FV), and scanning electron microscopy-based energy dispersive x-ray spectroscopy (SEM-EDS). Results comparing unannealed and annealed electrodes show that the Si and conductive carbon segregate into phases, with the carbon-rich phase forming a distinctive banded morphology that surrounds the Si-rich phase after annealing. In pristine electrodes, the carbon- and SEI-rich bands exhibit a higher electronic conductivity and a lower elastic modulus than the Si active material phase. These banded structures, as well as distinct electronic and mechanical properties, remain after cycling. This phase separation may be a major contributor to the improvement seen in electrochemical performance after annealing, as it may provide an improvement of electrical conduction pathways and a mechanical strain buffer for active Si material expansion during cycling. Our nm-scale and multi-mode characterizations provide a novel route for understanding and improving energy storage devices, which is advantageous for imaging the highly inhomogeneous structure of composite electrodes on the nano and micro scales.

1. W.-J. Zhang, *Journal of Power Sources,* **196** (1), 13-24 (2011).

5:00 PM CH01.11.13
Intrinsic Variability in the Electrochemical Properties of Individual Battery Particles Yiyang Li; University of Michigan, United States

Advanced characterization methods including in situ microscopy have often shown substantial heterogeneity and variability upon electrochemical charge and discharge. However, while such methods can uncover qualitative differences in electrochemistry, they do not directly quantify current and voltage. In this work, we utilize the microelectrode array which enables direct measurements of electrochemical current and voltage of individual micron-sized battery particles. After cycling >20 individual NMC-532 particles, we found that, while the specific volumetric capacity of the particles has <2% variability, the exchange current density has >3x variability between the "best" and the "worst" particles. This intrinsic variability is presently not considered in electrochemical models, and can provide opportunities for uncovering structure-property relationships and engineering improved battery particles.

5:00 PM CH01.11.14
Nanocrystal Orientation Analysis of PbSe Quantum Dot 3D Superlattices Enabled By Atomic Lattice Resolved Electron Tomography Ethan M. Field[1], Xiaolei Chu[1], Alex Abelson[2], Caroline Qian[2], Oleg Igouchkine[1], Kwan Liu Ma[1], Matt Law[2,2,2] and Adam J. Moule[1]; [1]University of California, Davis, United States; [2]University of California, Irvine, United States

Colloidal quantum dot superlattices with semiconductor properties promise many exciting properties for opto-electronic devices including the delocalization of electronic bands with tunable energies. We have applied novel data analysis techniques to HAADF STEM tomographic reconstructions to measure the nanoparticle atomic lattice orientation of each of the 633 quantum dots within a 3D superlattice. Inhomogeneity in position and orientation reveal how surface layers remain more ordered after synthesis and effect interior layering. Current characterization methods like 4D-STEM and GISAXS do not probe the exact the structure of the superlattice in three dimensions. This presentation will highlight the data used and its applications in improving the superlattice structure to achieve next-generation opto-electronic properties.

5:00 PM CH01.11.15
Non-Invasive Monitoring of Lithium-Solid State Electrolyte Interface Morphology From *In Situ* Thermal Resistance Measurement Divya Chalise[1,2], Robert Jonson[2], Pallab Barai[3], Sumanjeet Kaur[2], Sean Lubner[2,4], Venkat Srinivasan[3], Michael Tucker[2] and Ravi Prasher[2,1]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Argonne National Laboratory, United States; [4]Boston University, United States

Void-formation and interface morphology change at the lithium metal solid-state electrolyte interface has been identified as a significant challenge in the development of solid-state batteries. However, operando monitoring of the buried interface morphology is challenging. Several techniques that require isolating/exposing the interface for characterization inadvertently modify the interface and cannot be used for monitoring. While non-destructive methods such as Electrochemical Impedance Spectroscopy (EIS) and X-ray Tomography (XRT) have been employed to study the interface, XRT is not easy to use, whereas EIS cannot resolve other interface effects with the change in the morphology. In this work, we introduce thermal interface resistance measured using modified 3-omega sensors as a reliable method to monitor the interface morphology evolution in lithium metal-solid state cells. We first relate the thermal interface resistance at the lithium-LLZO interface with the physical morphology of the interface and then use the measured thermal interface resistance to extract morphological parameters such as the average contact radius and the number density of contacts. In this work, we study the evolution of the morphology as a function of stack pressure and the number of cell cycles in symmetric lithium-LLZO cells and verify our observations through ex-situ optical characterization.

5:00 PM CH01.11.16
***In Situ* Atomic-Scale Observation of $(Cr,Mn,Fe,Co,Ni)_3O_4$ High-Entropy Spinel Oxide Formation During Calcination Process** Yu-Tzu Yeh and Wen Wei Wu; National Yang Ming Chiao Tung University, Taiwan

High-Entropy Oxide (HEO) is a new-type of anode materials for lithium ion batteries (LIBs), owing to their stable crystal structure, superionic conductivity and high capacity. In recent years, High-Entropy Oxide (HEO) nanoparticles were synthesized via surfactant-assisted hydrothermal method [1], which exist problems of complicated synthesis procedure. In this work, we prepared the $(Cr,Mn,Fe,Co,Ni)_3O_4$ HEO by high-temperature solid state reaction [2]. In order to improve the synthesis efficiency, the formation mechanism is necessary. However, the study on the microstructure changing during calcination is still lacking. Therefore, we recorded detailed information of calcination with the temperature increasing by high-resolution transmission electron microscopy (HRTEM), and the $(Cr,Mn,Fe,Co,Ni)_3O_4$ HEO was obtained at 900°C. The entire forming process includes the aggregation of precursors at 500°C; when annealing at 600°C, MnO_2 and NiO diffused into Co_3O_4 , and the spinel-structured $(Mn,Co,Ni)_3O_4$ was formed. With the temperature increasing constantly, Fe_2O_3 and Cr_2O_3 combined with $(Mn,Co,Ni)_3O_4$ sequentially and formed $(Cr,Mn,Fe,Co,Ni)_3O_4$ spinel-structured HEO at 900°C. Furthermore, from the *in-situ* TEM observation, the particle growth direction and the structure of intermediate products were identified through the corresponding FFTs. We also unravel the valence change mechanisms and ion arrangements of $(Cr,Mn,Fe,Co,Ni)_3O_4$ via electron energy loss spectroscopy (EELS), and X-ray absorption near edge spectroscopy (XANES).
This study successfully revealed the formation and growth process of HEO at atomic scale for the first time. The results provide the roadmap on improving the manufacturing process of $(Cr,Mn,Fe,Co,Ni)_3O_4$ HEO, which are expected to play a vital part in the development of anode materials for next generation LIBs.

Keywords: High entropy oxides, TEM, Calcination, Spinel-structured
Reference:
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Spinel-structured high entropy oxide (FeCoNiCrMn)3O4 as anode towards superior lithium storage performance, J. Alloy. Compd. 844 (2020) 156158

5:00 PM CH01.11.19
Selective Oxygen Reduction to Hydrogen Peroxide on Organic Mixed Ionic-Electronic Conducting Polymers Ana De La Fuente Duran, Allen Liang, Ilaria Denti, Alexander Giovannitti, William C. Chueh, Alberto Salleo and Tyler Mefford; Stanford University, United States

The oxygen reduction reaction (ORR) can involve the transfer of four electrons, resulting in the formation of H_2O, or two electrons, yielding hydrogen peroxide (H_2O_2). For either product, several reaction schemes with different intermediates are possible, complicating the identification of a detailed mechanism for a given material. Nevertheless, mechanistic studies of ORR-active materials are critical for optimizing of the use-cases for the ORR, whether it be fuel cells or electrochemical H_2O_2 synthesis. Developing a rigorous framework for the study of oxygen reduction is crucial to understanding whether the reaction proceeds via an electrocatalytic mechanism.
Using a multi-faceted approach to study oxygen reduction, our work sets out to identify the operating mechanism of hydro(gen)peroxide production on organic mixed ionic-electronic conducting polymers (OMIECs). As a model system, we primarily study p(NDI-T2 P75)—a random copolymer comprised of naphthalene diimidie (NDI) and bithiophene (T2) units, where 75% of the NDI units have polar sidechains. Through the use of rotating ring disk electrode measurements, we find that this OMIEC is capable of reducing oxygen and that it is highly selective for the two-electron reaction. Further, using operando UV-Vis and Raman spectroscopy measurements, we find the mechanisms through which this OMIEC becomes active. To gain further insights about the reaction path, we construct and test a microkinetic model. Through this model, we show that this material, as well as a number of other OMIECs, reduces oxygen through a non-electrocatalytic, outer-sphere electron transfer mechanism.

5:00 PM CH01.11.20
Selenium Nanowire Cathodes Coated with Conductive Polymers for Fast Electron Transfer and Suppression of Shuttle Effect of Conversion Cathodes Seokgyu Ryu, Jeeyoung Yoo, Juyeon Han, Harim Seo, Eunbin Jang, Wonwoo Choi, Jaeyoung Oh and Seungjin Park; Kyungpook National University, Korea (the Republic of)

For a few decades, rechargeable batteries have been widely applied in a wide range of applications, from portable electronics to electric vehicles(EVs), and the energy market in developing and continues to grow. Especially, EVs are increasingly in demand, require higher energy density than conventional lithium-ion batteries. This generation of LIBs is limited to a specific energy of around 225 Wh kg–1. To expand the use of LIBs into heavy equipment and heavy vehicle and other long-range automotive applications, there is a strong motivation to develop batteries with energies over 400 Wh kg–1. For this demand, many researchers are looking for cathode electrode with improved electrochemical properties to satisfies the requirements of high-energy lithium-ion batteries (LIBs).Therefore, it is urgently needed to pursue other new battery systems with high energy density. Of the explored candidates, conversion cathode, respresentative, Lithium-sulfur (Li-S) batteries have been widely studied as one of the most promising next-generation energy storage systems due to their high theoretical capacity (1675 mAh g-1) and fairly good energy density (2600 Wh kg-1). Furthermore, abundant reserves in nature, Nickel and Cobalt free, which are unstable in supply and demand, and low cost are the competitive advantages of Li-S battery.
Selenium is an element in group 16 of the periodic table like sulfur, and the Li-Se battery also exhibits a redox mechanism similar to Li-S battery. Li-Se batteries have a lower specific capacity than Li-S batteries, but the volumetric energy density is not significantly different from that of Li-S batteries. On the other hand, the conductivity, which is an important property of the cathode material, is Se , which is much higher than that of S .
Based on these advantages, Li-Se batteries have been researched a lot to improve their performance. Especially, carbon base materials such as CMK-3 and activated carbon are widely used for selenium anodes. Its wide porosity makes it suitable for stored large amounts of selenium, and its high conductivity can improve the poor conductivity of selenium. Additionally, many studies have been conducted to suppress the shuttle effect through surface treatment by adding functional groups to carbon. However, many processes using carbon have the disadvantage of having to manufacture the electrode through high temperature & high pressure at the high melting temperature of selenium.
To clarify these issues, We synthesized selenium nanowire through selenium dioxide(SeO2) rather than melting process to compensate for these shortcomings, to facilitate electrode manufacturing. Selenium nanowire with 1d structure has superior conductivity compared to conventional selenium, and by compounding with carbon nanotube, which was the same 1d material, selenium-carbon electrode can be manufactured without melting process. Moreover, we processd of synthesizing selenium nanowire, PEDOT:PSS coating improved the conductivity of selenium nanowire and wettability with SWCNT.
Our research team increased wettability with SWCNT through PEDOT:PSS coating on self-developed 1d wire Selenium nanowire, which is proved by numerous electrochemical data. After 100 cycles, the PEDOT:PSS coated SeNW capacity was down to under 20% to 410 mAhg-1, while the Pristine SeNW cathode was 162 mAhg-1, under half. Moreover, it appeared to have higher capacity at higher rates as well. This improved electrochemical stability is because the PEDOT:PSS coating layer not only plays an excellent electron transfer role to SeNW, but also improves the binding energy with lithium polyselenide, causing a faster conversion reaction.In order to further prove this phenomenon, DFT was applied to the VASP simulation to calculate the binding energy of the electrode surface and polyselenide according to the presence or absence of the PEDOT:PSS coating layer.

5:00 PM CH01.11.21
Effects of Ionic Liquids Confined in Carbon Nanopores with Different Geometries and Surface Charges Vladimir Pavlenko; Al-Farabi Kazakh National University, Kazakhstan

During the presentation an important role of nanopores having different geometries and various surface charges on the nanoconfinement of ionic liquids utilized to assembly the electric double-layer capacitors (EDLCs) operating at sub-zero temperatures will be discussed. Home-made carbons were prepared via different methods of templated synthesis, while a pristine imidazolium-based fluorinated ionic liquids and their binary mixture were used as a solvent-free electrolyte. It will be shown that short-range graphene layers produced with 8-nm silica nanoparticles lead to the creation of transport channels which better accommodate ions. We explain these findings per coulombic interactions among the ions and between the pore wall and the ionic species under confinement and electrochemical polarization conditions. Further, it will be shown that a microporous carbon performs better than hierarchical carbons at room temperature; however, owing to the large fraction of mesopores, the latter exhibit far higher capacitance down to −40 °C. While the ordering of ions in confinement is more critical at room temperature and dictated by the micropores, low temperature performance of supercapacitors is determined by the mesopores that provide channels for facile ion movement and keep the bulk ionic liquid–like properties.

5:00 PM CH01.11.22
Enabling High Performance Potassium Storage in Ceramic Structures by Dual Salt Electrolyte Shakir Bin Mujib and Gurpreet Singh; Kansas State University, United States

A dual-salt electrolyte of KPF_6/KFSI in carbonate ester solvents have been developed for long-life and high-capacity SiOC ceramic anodes in K-ion batteries. The KPF_6/KFSI in ethylene carbonate (EC)/diethyl carbonate (DEC) exhibits higher ionic conductivity than single-salt KPF_6 solution. Here, it is shown that the capacity retention and Coulombic efficiency of polymer-derived SiOC ceramics can be remarkably improved by simply using KPF_6/KFSI dual salt dissolved in EC/DEC as the electrolyte over the KPF_6 salt dissolved in EC/DEC electrolyte. By investigating different SiOC electrode structures (powder and fiber), it is discovered that the degradation of SiOC half-cells in KPF_6-containing electrolyte originates from the failure of the electrode. The SEI layer formed on SiOC during cycling was systematically investigated by using a series of characterizations.

SESSION CH01.12: Advanced Material Development and Analytical Technique II
Session Chairs: Rosa Arrigo and Junjie Niu
Friday Morning, April 14, 2023
InterContinental, Fifth Floor, Ballroom C

8:00 AM CH01.12.01
Nanostructure and Defects Tailoring of Fe Oxide Catalysts for Nitrogen Reduction Reaction Stefania M. Privitera[1], Giuseppe Tranchida[1,2], Rachela G. Milazzo[1], Marco Leonardi[1,2], Silvia Scalese[1], Luca Pulvirenti[2], Guglielmo Guido Condorelli[2], Corrado Bongiorno[1] and Salvatore A. Lombardo[1]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]Università degli Studi di Catania, Italy

Electrochemical ammonia synthesis under mild conditions is considered a promising strategy to produce green ammonia for renewable energy storage, taking advantage of its high hydrogen content and easy liquefaction. However, the use of electrochemical processes for ammonia synthesis has been so far challenging due to the absence of efficient catalysts, able to break the N_2 triple bond, and to the competition with the more favorable hydrogen evolution reaction in aqueous solution, preventing the nitrogen reduction to ammonia. In this work we adopt several advanced characterization techniques to optimize the efficiency of Fe oxide nanoparticles as a sustainable, earth-abundant catalyst for nitrogen reduction. SEM, XPS and TEM analyses with electron energy loss spectroscopy (EELS) have been employed to compare different deposition conditions and to optimize the morphology and composition of the nanoparticles, allowing higher catalytic activity toward electrochemical ammonia synthesis. The produced ammonia has been determined through the indophenol blue method, adopting a rigorous experimental protocol to avoid environmental contaminations. The structural characterization of the catalyst has been coupled to an electrochemical activation process, which is effective in increasing the electrochemical active area. XPS analyses performed after the electrochemical activation have shown that the increase of available active sites corresponds to an increase of oxygen vacancies and of the Fe^{+2}/Fe^{+3} ratio. After the activation process, the faradic efficiency for nitrogen reduction increases from 3.8 % to 20.4 %, giving insight on the physical mechanisms which determine the performance of FeOx catalysts for ammonia synthesis.

8:15 AM *CH01.12.02
High Energy Density and Ecofriendly Lithium-Ion Battery with Operando Health Evaluation Avetik Harutyunyan and Oleg A. Kuznetsov; Honda Research Institute USA Inc, United States

The resolution of the energy-environment dilemma demands protection the vulnerable and limited resources of Nature while meeting the growing energy demand of the world. This makes the sustainable development of renewable energy a mission of central importance. The success of this mission depends on the advances in storage technologies such as rechargeable batteries. Therefore, the rapidly growing battery market should provide both high energy density and waste-management solutions for the anticipated global annual battery waste of about two million metric tons.
To address this dilemma, we developed self-standing composite electrodes for Li-ion batteries without electrochemically inactive metal current collectors, additives, and binders, increasing energy density by up to 40%. The resulted flexible electrodes were prepared via in situ mixing of as-grown single-wall carbon nanotubes (SWNTs) with aerosolized electrode active materials. Apparently, well dispersed pristine SWNT scaffold exhibits a piezoresistive effect. This intrinsic piezoresistance of SWNT network enables operando self-monitoring of battery structural health without implanting any new components into the battery architecture. Proposed new solution-free battery electrode fabrication technology and architecture eliminates environmentally harmful chemical compounds from the production line and enables recycling and recovery of active materials by only mechanical separation, aiming at safety and circular economy.

8:45 AM CH01.12.03
Listening to Batteries—Using Acoustic Techniques for Advanced Characterisation to Improve Battery Performance and Safety Arthur Fordham[1,2], Rhodri Owen[1,2] and Rhodri Jervis[1,2]; [1]The Faraday Institution, United Kingdom; [2]University College London, United Kingdom

The growing electrified transport and stationary storage sector continues to drive demand for more powerful and energy dense lithium-ion batteries. Therefore, it is crucial that battery monitoring systems advance at the same rate with improved diagnostics to maximise performance and safety. Acoustic methods are one of the most promising diagnostic techniques for batteries. The technique, in addition to being low-cost, non-invasive, and non-destructive, offers the potential for a real-time *operando* prediction of the State of Health (SoH), State of Charge (SoC) and State of Safety (SoS). Acoustics can complement electrochemical and crystallographic methods to better understand the phase transitions and defects occurring within cells.

The acoustic techniques can be divided into Acoustic Emission (AE) and Ultrasonic Testing (UT) methods; each slightly differs in terms of purpose and experimental setup. Both techniques can detect the physical and electrochemical changes within the cell during usage such as gas formation and cracking. Recent papers focus on SoH estimation based off the ability of acoustics to monitor these changes(1-3). However, there remain outstanding gaps in the literature which necessitate continued investigation into these techniques.
This work, based on research undertaken at UCL as part of the Faraday Institution (FI) SafeBatt project, covers three aspects of the use of acoustics in battery characterisation. The first uses a combination of AE and UT in a novel dual-sensor approach to detect how well the solid electrolyte interface (SEI) grows during the cell's formation cycle, and how this SEI layer effects long-term cell performance and degradation. This technique can characterise how successfully a cell has formed based on the acoustic signals released, offering the opportunity for optimisation of the formation process of cells, which is a critical bottleneck in industry.
The second aspect focuses on the use of acoustics to predict thermal runaway (TR). It is now required that an EV's Battery Management System provides a 5-minute advance warning to the passenger before a hazard stemming from TR occurs(4). Experiments simulated real world abuse conditions for cells to initiate TR whilst monitoring the internal structure of the cell with AE. It was found that AE can detect the damage occurring in the cell before failure by using the types of signals generated demonstrating that AE can be implemented within an EV and supply improved warning systems.
The third aspect of the work focuses on acoustics complemented with other non-destructive diagnostic techniques including X-ray computed tomography and X-ray diffraction. This work demonstrates how acoustics can be used for diagnosing aging for cells at their end of life. UT offers a rapid and non-destructive alternative to measure the degradation in each individual cell. This maximises the use of the battery and minimises the waste of raw materials.

Based on the three experimental applications outlined above, machine learning (ML) classification models are being developed to automate the signal diagnosis. ML can characterise the types of signals being produced and can be used to determine when problems are occurring within the cell. Automation is vital to reduce costs whilst simultaneously increasing accuracy of the signal classification *operando* during electrochemical cycling. The overarching aim of these investigations is to demonstrate how acoustics can be used as an advanced characteristion technique for batteries and its future use across different electrochemical technologies.

(1) Wang, K. *et al.* Cyclic aging monitoring of Li-ion battery based on acoustic emission. (2022)
(2) Wang, Z. *et al.* Rapid SoH Estimation of Li-ion Batteries based on An Active Acoustic Emission Sensing Method. (2022)
(3) Robinson, J. B. *et al.* Identifying Defects in Li-Ion Cells Using Ultrasound Acoustic Measurements. (2020)
(4) Stephan Rindfleish. Making EV's Safer (2022)

9:00 AM CH01.12.04
Discovery of Stable Sodium-Ion Battery Cathodes with Machine Learning Minseon Kim and Kyoungmin Min; Soongsil University, Korea (the Republic of)

Despite their success in commercialization, lithium-ion batteries(LIBs) have a problem of cost increase due to limited Li resources. In this respect, sodium-ion batteries(SIBs) have similar chemical properties to analogous Li-based structures and high price competitiveness, making them a strong candidate to replace LIBs. The cathode mainly determines the stability and the performance of SIBs; hence, it is important to perform research on finding the next-generation materials to develop SIBs cathode materials with high voltage, capacity, and life cycle.
Among the cathode candidates of SIBs, layered oxides, which have a high capacity and a simple structure, are mainly classified into O3 and P3, and especially, O3 has capable of improving electrochemical performance. However, an irreversible phase transition occurs from O3 to P3 during the

(de)intercalation process. Since this phenomenon causes structural and performance degradation, it is imperative to develop a thermodynamically stable material for the commercialization of SIBs. The stability can be determined by obtaining the energy difference(ED) of the O3-P3 phase. In the process of developing new materials, selecting appropriate compounds is required, but testing all materials takes excessive time and cost. Density functional theory(DFT) calculations and machine learning(ML) are efficient for the initial new material screening. Therefore, in this study, we employed DFT and ML to explore cathode candidates which potentially resist irreversible O3-P3 phase changes during electrochemical cycling.
In this study, two classification prediction models have been constructed for two states: pristine and desodiated. In the layered structure of $Na_xTM_aTM'_bO_{24}(6\leq x\leq 12)$, 27 transition metals(TM) were combined at a ratio of a:b=5:1 and 3:3 to generate a total of 2,916 candidates. A total of 392 input features were generated using chemical descriptions(CDs), atomic features, and raw chemical information used in CDs calculations. The total energy of O3-P3 materials was calculated in each state using DFT calculation. ED is a value obtained by subtracting the energy of the P3 phase from the O3 phase in each of the predefined states. If pristine and desodiated ED is negative, it is classified as stable material, and this means that the phase would not be easily transformed.
As a result of comparing several models using the Pycaret, the ExtraTrees Classifier showed the best performance and it was used as the base model. In the pristine state, unstable(194) and stable(1,257) structures were found, which is a serious data imbalance problem. However, in the desodiated state, it has a uniform distribution of unstable(697) and stable(754). To overcome such issues, data sampling algorithms(SMOTE, SMOTE+Tomek, SMOTE+ENN) and stratified sampling were conducted. As a result, in a pristine state, the model applying SMOTE+ENN to the base model performed the best, with significant performance improvement from an accuracy value of 0.878 to 0.976 and an F1 score of 0.404 to 0.979. In addition, the desodiated model also showed the highest performance with the SMOTE+ENN model and demonstrated that the accuracy and an F1 score increased from 0.650 to 0.945 and from 0.631 to 0.947, respectively.
As a result of analyzing the calculated ED of the O3-P3 phase, 1,257 stable materials in the pristine state and 754 stable materials in the desodiated state were identified. The number of intersection data in the two states was 637, and a material with high stability that did not change the phase was found. Among them, 155 materials with a voltage of more than 3V and a theoretical capacity of more than 200mAh/g were selected. New cathode candidates were presented, showing values far beyond the performance of the existing Na cathode materials. We believe that the current study provides meaningful insights into the SIB research society by providing the database of O3-P3 phase stability and the potential cathode materials.

9:15 AM BREAK

9:45 AM *CH01.12.05
Gas-Phase Composition as a Predictive Metric for Calendar Life Behavior of Next-Generation Silicon Anodes Kae Fink, Mel Soto, Maxwell Schulze, Gerard M. Carroll, Peter J. Weddle, Ankit Verma, Nathan R. Neale, Andrew Colclasure and Bertrand Tremolet de Villers; National Renewable Energy Laboratory, United States

The expansion of renewable technologies and electrification of the transportation sector is driving increased demand for next-generation battery materials that provide higher power and energy density with superior cycling and calendar life stability. Silicon (Si) has a theoretical capacity nearly 10x that of graphite, and is therefore a promising anode material candidate to meet these rigorous performance demands. While leading Si anode battery demonstrations are approaching target metrics for cycle life, a series of complex and interrelated modes of reactivity lead to reduced calendar life and therefore challenge practical adoption of these materials. Deconvoluting the degradation processes that impact Si calendar life is critical to informing the rational and accelerated design of improved Si materials. In the present work, we employ novel sampling techniques and GC-MS-FID characterization to measure gas-phase composition during initial Si cycling, which we tie to selective mechanisms of Si passivation. We utilize a tiered analysis approach to identify and quantify the gas-phase reaction products associated with three advanced Si material candidates under practical operating conditions. *Ex situ* analysis of Si powders (pure chemical reactivity) is coupled with nondestructive *in situ* sampling of Si electrodes in a practical pouch-cell format (coupled chemical and electrochemical reactivity). We link the observed gas-phase species evolution to electrochemical behavior and measured calendar life of the three Si materials. Further, we evaluate the voltage-resolved evolution of gas-phase species for one such Si nanomaterial, where nonmonotonic gas generation implies competition between passivating reaction pathways. The measured gas-phase compositional data serves as a critical input for our advanced electrochemical SEI models to identify favorable vs unfavorable reaction pathways to stabilize Si. In addition to bolstering a fundamental understanding of Si reactivity, the present approach informs specific and quantifiable gas-phase metrics tied to calendar life improvements in Si, which can streamline and accelerate the process of next-generation material development.

10:15 AM CH01.12.06
Evaluation of Lithium-Ion Batteries Following a Single Thermal Insult Gordon Waller, Corey T. Love and Rachel Carter; Naval Research Laboratory, United States

Lithium-ion batteries (LIB) typically have a manufacturer recommended temperature range of 0 °C to 60 °C depending on operation. Heating cells well above the recommended upper temperature limit is a common method to evaluate the safety of lithium-ion batteries. Above some critical temperature, LIB undergo a series of exothermic reactions leading to rapid self-heating, referred to as thermal runaway (1). Exothermic reactions in LIB begin with decomposition of the solid electrolyte interphase (SEI) layer on the anode at temperatures in the range of 60-80 °C, or just above the manufacturer recommended upper limit (1) (2). However, temperatures above 120 °C are typically needed before self-heating can no longer be mitigated through passive heat rejection and cell failure occurs. Observed LIB failures depend on chemistry, cell design, and state-of-charge but can range from relatively benign such as the activation of an internal safety device or venting electrolyte vapors to incredibly energetic ejections of flaming debris (3). Aging effects by cycling or storing cells near the manufacturer recommended upper temperature limit have been evaluated and generally result in a higher observed onset temperatures for thermal runaway due to growth of the SEI, however reported results vary with cathode chemistry (4)(5). Impacts of LIB exposed to temperatures in the range of 60 °C to 120 °C, or above the manufacturer recommended limits but below the onset of self-sustaining thermal runaway, have not been broadly studied. An important scenario to consider are large LIB containing many cells in which one or more cells have undergone thermal runaway. Propagating thermal runaway can occur due to the failure of a single cell, however brief exposures of adjacent cells to temperatures well above the manufacturer recommended limit without propagating failure is also a possibility. The impacts of these "thermal insults" on of cell performance and safety will be the subject of this presentation. High energy (3.4 Ah) 18650 LIB were subjected to thermal insult conditions including temperatures of 100 °C at 100% state-of-charge. After the thermal insult, galvanostatic cycling and electrochemical impedance spectroscopy were used to determine impacts on the cell capacity and impedance. Isothermal Battery Calorimetry (IBC) was used to observe changes in heat generation during cycling, while Accelerating Rate Calorimetry (ARC) was used to evaluate the thermal runaway behavior of the cells.

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10:30 AM CH01.12.07

High Throughput Characterization Methods at the Wafer Scale for Sputtered Films Used in Micro-Supercapacitors and Li-Ion Micro-Batteries

Aiman Jrondi[1,2], Khac Huy Dinh[2,1], Bukola Jolayemi[2], Maxime Hallot[2], Clément Leviel[1,2], Christophe Lethien[2,3] and Pascal Roussel[1]; [1]UCCS - CNRS UMR8181, France; [2]IEMN - CNRS UMR 8520, France; [3]Institut Universitaire de France, France

The emergence of new miniaturized and autonomous electronic technologies leads to a request of efficient microdevices for energy storage. The development of thin film Li-ion micro-batteries or micro-supercapacitors is an interesting way to power connected sensors, as their manufacturing method is compatible with the techniques used in the microelectronics industry[1–4]. These miniaturized electrochemical energy storage devices can thus be easily integrated into embedded electronics. Most of the time, for the development of such energy microsources at the laboratory scale (and more specifically at the electrode level), studies are conducted on small pieces of substrates where the area of tested electrode material is restricted. It is however important to study the homogeneity of thin film electrodes, not only on small pieces of substrates, but at the wafer scale, in the case of an industrial transfer of more fundamental researches led at the laboratory scale (i.e the upscaling of the technology, needed for the collective fabrication of hundreds/thousands of microdevices on a single wafer). We have developed a complete mapping strategy of thin film electrodes characterization at the wafer level on different techniques, such as X-ray diffraction, X-ray fluorescence, scanning electron microscopy, Raman spectroscopy, electrical conductivity and more especially for this project, an electrochemical mapping[5,6]. By combining the information given by all these complimentary techniques, we can correlate the differences of properties observed for different zones of the wafer. For instance, in some vanadium nitrides for micro-supercapacitors applications, a strong variation of the preferred orientation (as measured by an XRD mapping of the full wafer) is evidenced, depending on the scanning area of the wafer, without any change of the chemical composition and of the electrochemical performance. It is not the case for some spinel-type compounds (i.e. sputtered $LiNi_{0.5}Mn_{1.5}O_4$ films) used as the positive electrode for Li-ion micro-batteries, that behave differently depending on the preferred orientation (i.e compounds with privileged conduction path in the structure)[7–10].

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10:45 AM CH01.12.08

Ni-Rich Layered $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ with Dual Gradients on Both Primary and Secondary Particles in Lithium-Ion Batteries

Mingwei Shang, Xi Chen and Junjie Niu; University of Wisconsin--Milwaukee, United States

Abstract

As an important component in lithium-ion batteries (LIBs), cathode material is regarded as the major limiting factor for the energy density of LIBs. To meet the requirement of high energy density of LIBs, it is important to improve the capacity retention and long cycling performance. Currently the Ni-rich layered cathode materials such as NMC811 are regarded as a class of promising cathode material and attracting considerable attention due to the high capacity and the high discharge potential. However, some challenges related to the poor cycling stability and rate capability of Ni-rich oxide cathode materials still need to be addressed. The performance fading is mainly originated from the Li^+/Ni^{2+} cation mixing, Li residues, overcharging, crystal orientation of the secondary particles, etc.
Due to high surface area, controllable porous structure and periodic arrangement of metal atoms, the highly ordered 3D MOFs have been demonstrated as new pyrolytic precursors in obtaining non-precious metal oxides with homogeneous particle distribution. Here we present a novel layered NMC811 with dual Ni-gradients on both primary and secondary particles that was synthesized by applying Ni-MOF-74 during the coprecipitation (Shang, Chen, Niu. ***Cell Reports Physical Science***, 3 (2022), 100767). The introduced self-healing phase by forming a cation mixing layer on the surface of particles effectively improved the structural stability by suppressing the phase transition and internal cracks upon cycling. The battery performance with the designed D-NMC811 as cathode electrode was greatly improved. An initial specific capacity of 203.5 mAh/g at 0.1 C and a capacity retention of 88.5% after 300 cycles at 1/3 C were obtained. At the elevated temperature of 55 degree, the battery still showed a CE of 99.47% at 1/3 C after 300 cycles. Compared to the conventional NMC811, the full-cell battery with D-NMC811 exhibited an increased capacity retention of >86.7% with a CE of >99.86% at 1/3 C after 300 cycles. Moreover, the large-scale pouch cell using the D-NMC811 as cathode delivered an initial capacity of 297.62 mAh and a CE of 99.48% after activation, which contributed to an energy density of 216.41 Wh/kg. After long 500 cycles at 1.0 C, the capacity retention was still as high as 84.1%, which was much higher than the battery made by conventional NMC811. The compatible manufacturing process by incorporating with MOFs provides a new route to produce Ni-rich transition metal cathode materials at large scales with high-capacity retention and long cycling capability in next-generation batteries.

Keywords: Li-ion batteries; Ni-rich cathode materials; MOF; Concentration gradient

11:00 AM CH01.12.09

Revealing Dynamic Electrochemical Interface of $LiNi_{0.5}Mn_{1.5}O_4$ Spinel Cathode for Realizing Simultaneous Mn and Ni Redox for Cost-Effect High-Energy Rechargeable Lithium Batteries

Jihyun Hong; Korea Institute of Science and Technology, Korea (the Republic of)

The exploding electric-vehicle market requires cost-effective high-energy materials for rechargeable lithium batteries (RLBs), including Li-ion and Li-metal systems. For a decade, substituting cobalt with nickel in cathodes has been an effective strategy to reduce the materials cost for RLB production while increasing the energy density. However, the rapid spread of EVs has consumed a tremendous amount of metal resources, eventually triggering a price surge of nickel and lithium. In contrast, the price of manganese has remained incomparably low. Consequently, the use of Mn-rich chemistry has attracted

attention from researchers as a promising option to realize cathode materials with high economic sustainability and reasonable energy density.
Among the Mn-rich cathode materials, spinel-type $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is an attractive alternative to the Ni-rich layered oxides. LNMO is renowned for the high potential of the Ni^{2+}/Ni^{4+} redox couple, 4.7 V (vs. Li), offering a theoretical energy density of 690 Wh kg^{-1}, within a conventional voltage range of 3.5–4.9 V. A more exciting feature of LNMO is its capability to store more energy using an additional Mn^{3+}/Mn^{4+} redox reaction at 2.7 V, exhibiting a capacity greater than 200 mAh g^{-1}. The simultaneous use of Ni and Mn multi-cation redox reactions in LNMO enables an energy density exceeding 860 Wh kg^{-1}. Combining the high energy density with low materials cost, LNMO exhibits a high energy-to-cost ratio of 89.7 Wh USD^{-1}, corresponding to 547% and 279% of that of $LiCoO_2$ and $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$, respectively, when cycled over a wide voltage range.
Despite this benefit, a long-established hypothesis has restricted the use of multi-cation redox reactions in LNMO: the reduction of Mn^{4+} to Mn^{3+} inevitably results in poor capacity retention.[1] The Jahn-Teller distortion of the Mn^{3+} octahedral sites causes the phase transition from cubic (*Fdm*) to tetragonal ($I4_1/amd$) phases, inducing an extra anisotropic lattice strain. Furthermore, trivalent Mn is considered labile to the disproportionation into Mn^{4+} and Mn^{2+}, which has a high solubility in organic electrolytes. The reversible use of the Mn redox reaction, however, has been successfully demonstrated in many other cathode materials, such as Li-rich Mn-rich layered oxides and disordered Li-rich rocksalt oxides. The extended cycle life of Mn-based cathodes confirms that the formation of divalent and trivalent manganese cations does not necessarily deteriorate the battery performance. Such inconsistency requires a precise understanding of the degradation mechanism to facilitate the stable use of Mn redox chemistry in LNMO in addition to the conventional Ni redox.
Herein, for the first time, we demonstrate the excellent reversibility of Mn^{3+}/Mn^{4+} redox within 2.3–4.3 V, leading us to revisit the conventional theory of LNMO degradation. LNMO loses capacity only when cycled within a wide voltage range of 2.3–4.9 V, simultaneously employing Mn^{3+}/Mn^{4+} and Ni^{2+}/Ni^{4+} redox. Using surface-sensitive structural and chemical probes, we reveal that a dynamic evolution of the electrochemical interface, e.g., potential-driven rocksalt phase formation and decomposition, repeatedly occurs during cycling. The interfacial evolution induces electrolyte degradation and surface passivation, impeding the charge-transfer reactions. We further demonstrate that stabilizing the interface by electrolyte modification (e.g., EC exclusion) enables LNMO to possess a capacity retention of 91.0% after 100 cycles, an energy density of 715 Wh kg^{-1}, and a power density of 588 W kg^{-1} within the voltage range of 2.3–4.9 V. Our discovery of the prominent role of electrochemical interfaces on the cycling of LNMO proposes modulating the CEI stability as a promising strategy to develop high-energy and long-cycle-life RLB cathode materials of Mn-rich chemistries.

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11:15 AM CH01.12.10
Understanding Electrochemical Growth of Carbon Nanotubes from CO_2 Andrew B. Wong; National University of Singapore, Singapore

The development of new carbon-negative electrochemical processes are of paramount importance to the future sustainability of human civilization. This presentation will focus on the electrochemical growth of carbon nanostructures from CO_2. Previous works have pioneered the observation of carbon nanotube growth in molten $LiCO_3$ electrolytes from CO_2. However, in many past works, several CO_2-derived cathodic carbon morphologies were observed, which included carbon particles/spheres, graphite flakes, carbon nanofibers, CNTs, and graphene-like ultrathin carbon sheets. Moreover, these morphologies are often mixed, resulting in a low selectivity and difficult separation towards one single carbon morphology, and the factors leading to various morphologies are not currently well understood. In this talk, we will explore the fundamental growth mechanism to inform the broader long-term goal of improving the selectivity towards carbon nanotubes from CO_2. This present work studied the cathodic growth of carbon nanotubes by utilizing a simple three-electrode configuration consisting of pure Li_2CO_3 electrolyte, pure transition metal foil cathodes, Pt anode, and homemade Ag/Ag_2SO_4 reference electrode to determine the impact of tunable parameters on the resulting electroreduction products. These products are studied via potential-dependent studies as well as via ex-situ techniques such as TEM, XPS, XRD, and Raman spectroscopy to gain insights into the growth of these materials.

SESSION CH01.13: Advanced Material Development and Analytical Technique III
Session Chairs: Akihiro Kushima and Junjie Niu
Friday Afternoon, April 14, 2023
InterContinental, Fifth Floor, Ballroom C

1:30 PM CH01.13.01
Building 3D-organaized Nanocrystallites to Harness Grain-boundary Defects Myoung Hwan Oh[1,2,3]; [1]Korea Institute of Energy Technology, Korea (the Republic of); [2]UC Berkeley, United States; [3]Lawrence Berkeley National Laboratory, United States

Topological defects (i.e. dislocation, grain-boundaries) play an essential role in the properties of crystalline materials. When the size of the crystallite or functional domain of the materials decreases to the nanometer scale, the defects predominantly determine those properties. To date, however, neither bottom-up nor top-down methods for synthesizing nanocrystalline materials have been able to find a reliable way of controlling these defects. Herein, we demonstrate the delicate control of 3D heteroepitaxy using a lipid membrane-like synthetic system to grow various nanocrystallites, 3D organized with uniform grain-boundaries and related defects. In the resulting structures, the 3D-patterned strain field, which exists in the form of disclinations and dislocations, can be determined with atomic precision and even tailored. Through nano-to-macro crystallography and spectroscopy, we have also confirmed that the uniformity and dicreteness of the defects allow us to find a reliable correlation between the local strains/defects and collective electrochemical properties (i.e. catalytic activities for oxygen reduction reactions). These middle-entropy nanomaterials give us an opportunity to conduct nano-mechanics of 3D organizations of interconnected and symmetry-related functional domains and explore novel electronic states emerging from 3D coherent lattice and topological defects. Lastly, the current research focus to build next-generation functional nanomaterials for energy nanotechnology using 3D nano-mechanics will be discussed.

1:45 PM CH01.13.02
Chemical Crossover Accelerates Degradation of Lithium Electrode in High Energy Density Rechargeable Lithium-Oxygen Batteries Shoichi Matsuda and Manai Ono; National Institute for Materials Science, Japan

There has been considerable interest in developing rechargeable lithium oxygen batteries (LOBs) that have the potential to significantly exceed the energy density limit of a Li ion battery (approximately 300 Wh/kg). Although 500 Wh/kg LOB has been demonstrated and exhibited stable discharge/charge cycle at room temperature condition[1], their cyclability remains less than 10 cycle. For realizing the LOB with practically high energy density and long cycle life, the deep understanding of complicated reaction in LOBs has been highly demanded. Especially, the problems specifically associated with the limited electrolyte (“lean-electrolyte”) conditions need to be taken into account in LOBs.

Although the importance of investigating negative lithium electrodes in lean-electrolyte systems has been recognised in recent years[2], specific problems associated with the negative lithium electrode in a LOB has not been investigated so far. In particular, chemical crossover from the positive electrode to the negative electrode is a crucial factor that needs to be taken into consideration. Actually, recent studies have shown that LiOH is formed on the surface of a lithium-metal electrode through reaction with H_2O in the electrolyte[3,4]. This H_2O is generated by the decomposition of the tetraethylene glycol dimethyl ether (TEGDME) solvent at the positive oxygen electrode, which then migrates to the negative electrode side to react with the lithium-metal electrode. Consequently, problems related to chemical crossover are prominent in lean-electrolyte LOBs, where the effective water concentration in the electrolyte is much higher than that in an excess electrolyte system.

Despite the importance of investigating the reaction of negative lithium electrodes in LOB with appropriate technological parameters, mechanistic details remains unclear due to the technical difficulty for applying non-destructive analytical methods. In the present study, we investigated the reaction of a negative lithium electrode in a lean-electrolyte LOB operating under high areal capacity conditions. The use of advanced non-destructive analytical methods, including three-electrode electrochemical techniques and an in-situ analytical setup revealed that the reaction efficiency of the lithium electrode mostly decreases through chemical crossover from the positive oxygen electrode. In particular, the H_2O generated as a side-product at the positive oxygen electrode crosses over to the negative electrode side and reacts with the lithium-metal electrode to form a porous $LiOH/Li_2CO_3$ layer on the electrode surface. LiOH and Li_2CO_3 accumulates, and the porous layer thickens through repeated discharge/charge cycling, which supresses efficient Li-ion transport through the layer. In addition, the solvent decomposes rather than lithium peroxide during the final stage of charging at the positive oxygen electrode, and the generated CO_2 crosses over to the negative electrode side where it is further electrochemically reduced. This complicated LOB chemistry results in a significant decrease in reaction efficiency at the negative electrode. Importantly, the degradation behaviour observed for the lithium-metal electrode, which is due to chemical crossover from the positive electrode, is a common problem for next-generation rechargeable battery systems that use lithium electrodes. Hence, the methodology demonstrated in the present study, which combines non-destructive analytical techniques, effectively clarified the complicated hidden reaction mechanism associated with lithium-metal-based rechargeable batteries that operate under lean electrolyte conditions.

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2:00 PM CH01.13.03
Understanding the Effect of Low Temperature Degradation on Lithium-Ion Battery Performance and Safety Charlie R. Kirchner-Burles[1], Paul Shearing[1], Dan Brett[1] and Gareth Hinds[2]; [1]University College London, United Kingdom; [2]National Physical Laboratory, United Kingdom

As efforts to decarbonise the world economy ramp up, lithium-ion batteries have become a crucial component in facilitating the transition of key industries to clean energy. Successfully tackling this challenge requires continuous improvements in energy-density, longer cell lifetimes and better assurances in safe cell operation. In recent years, numerous high-profile failures of Li-ion batteries have been reported[1], contributing to wider concerns about the safety of high energy density cells. Inadequate management of such systems, in applications such as electric vehicles, aerospace, and portable commercial devices, can be costly in both human health and financial damages. Therefore, it is important to study battery safety in order to provide a reliable alternative to fossil fuels. Apprehensions in cell safety can mainly be attributed to a cell's ability to enter thermal runaway, a process that is most often caused by an internal short circuit (ISC). Such an event can be triggered by three different modes of abuse: thermal, mechanical, and electrical.

Conditions of thermal and mechanical abuse are mostly because of a cells external environment and can be controlled more easily; however, electrical abuse often originates from internal conditions that accelerate the growth of lithium dendrites that can pierce the separator – a mechanism that is more difficult to monitor or predict. At the anode, metallic lithium can precipitate onto the surface via three main conditions: overcharge, high charging currents, and low charging temperatures. Each of which create a saturation of intercalated lithium ions in the crystallographic active sites near the anode surface. This lowers the anodes surface potential until it is sufficiently low enough for lithium plating to occur. To better understand this process and how it affects battery safety, our work investigates the degradation of commercial cylindrical cells (with NCA cathodes) at low temperatures and how it changes their response to abusive conditions. Here we show that as the temperature is lowered, plating becomes more aggressive and pseudo-homogenous due to the reduced rate of lithium-ion diffusion into the bulk graphite.

By utilizing various *in-situ* lithium detection techniques, such as post-charge voltage relaxation, Electrochemical Impedance Spectroscopy, and Differential Capacity Analysis, the extent of a cell's degradation and its state of safety can be estimated by monitoring real-time electrochemical data. Further optimization of these techniques to generate quantitative measurements on the aforementioned parameters would greatly improve battery management systems and their predictive capabilities of cell failure. Moreover, subsequent Accelerated Rate Calorimetry (ARC) studies highlight that a cells thermal stability diminishes as degradation becomes more advanced. These findings demonstrate how lithium plating has an impact on battery safety and why more work is needed on developing real-time assessments of a battery's state of degradation. Insights into the mechanisms at play in such failures have been achieved through post-mortem X-ray computed tomography (CT) and *operando* ultra-high-speed tomography and radiography. Together, these techniques act as a valuable tool in elucidating failure behaviours.

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2:15 PM CH01.13.04
MALDI-TOF-MS as a Powerful Tool for Elucidating Nanocrystal Synthesis Mechanism Artur Feld[1,1], Agnes Weimer[1,1], Andreas Kornowski[1], Naomi Winckelmans[2], Jan-Philip Merkl[1], Hauke Kloust[1], Robert Zierold[1], Christian Schmidtke[1], Theo Schotten[3], Maria Riedner[1], Sara Bals[2] and Horst Weller[1,1,3]; [1]University of Hamburg, Germany; [2]University of Antwerp, Belgium; [3]Fraunhofer-CAN, Germany

The synthesis and development of colloidal nanocrystals still proceed by trial and error.[1] High-quality semiconductor quantum dots and iron oxide nanocrystals are synthesized in organic solvents using universally applicable ligands such as oleic acid. Thereby, starting from a few compounds, a highly complex reaction pathway is rapidly developing, whose essential aspects are still unknown. Insufficient knowledge of fundamental reaction mechanisms, especially the role of reaction intermediates during the formation of colloidal nanocrystals, prevents the expansion of the application potential of many nanoparticle systems.

Therefore, an essential goal of advanced nanocrystal synthesis is a comprehensive understanding of the reaction mechanisms in order to tailor and simultaneously control the triad of size, shape, and crystal structure. Since targeting this triad is hampered by numerous intertwined variables and severely limits the scope of synthetic results, unraveling the essential reaction mechanisms is of paramount importance.

We show exemplarily on the system - iron oxide - that significant aspects of the fundamental reaction mechanism can be elucidated by using matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF-MS). The combination of highly pure iron oleate and advanced mass spectrometry enabled us to gain a deep insight into the composition of iron oleate and elucidate a new cascade of redox reactions responsible for converting the individual complexes into each other already at low temperatures and early synthesis stages. Furthermore, we obtained evidence for the catalytic activity of iron in iron oleate by identifying many new complexes, thus essentially contributing to a more profound knowledge of the reaction conditions.[2]

This study serves as a template for the investigation of related systems[3,4] and reveals fundamental commonalities that will be exploited to unlock the missing tailored and simultaneous control of the triad of shape, size, and crystal structure.

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2:30 PM CH01.13.05
Mapping Distribution of Modern Binders in Graphitic Li-Ion Electrodes Enables Optimization of Electrodes Structure Stanislaw Zankowski[1,2] and Patrick Grant[1,2]; [1]University of Oxford, United Kingdom; [2]Faraday Institution, United Kingdom

Despite their low fraction (<5 % volume) in Li-ion electrodes, polymeric binders are a critical component of Li-ion batteries. Binders provide cohesion and adhesion of electrode particles to one another and to current collectors, and stabilize active particles against volume changes upon cycling. But binders also impede transport of Li^+ in the electrode pore space and, therefore, co-determine overall battery rate performance and lifetime. During high rate drying of cast electrodes, re-precipitated binder is prone to migrate from the current collector (where needed most) towards the electrode free surface (adding to ionic resistance). Consequently, slow electrode drying to maintain optimal binder distribution can become the bottleneck to high throughput, low-cost electrode fabrication. Up to now, however, practical binder optimization studies in negative Li-ion electrodes have been hindered by the lack of a convenient method to map the aqueous-processable binder used in most modern graphite electrodes that comprises a mixture of sodium-carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR).

We have developed two methods of independently labelling CMC and SBR using aqueous Cu^{2+} ions and gaseous Br_2 vapour, respectively, and tracing their distribution in electrodes using energy dispersive X-ray spectroscopy (EDX). Immersing electrodes in aqueous Cu^{2+} solution results in instant formation of an insoluble Cu-CMC complex, while exposing the electrodes to Br_2 vapour results in rapid bromination of SBR C=C bonds. Owing to the specificity of reactions, both binder components can be precisely mapped using EDX for copper and bromine. Additionally, bromination allows rapid (few seconds) detection of binder using backscattered electron imaging for quick assessment and feedback of binder distribution. Enabled by these new labelling techniques, we present two exemplary studies on binder agglomeration from sub-optimally mixed slurries, and on mitigating binder migration during fast electrode drying using a novel phase inversion approach. We show how improved CMC/SBR binder control can enhance the electrochemical performance of negative Li-ion electrodes.

2:45 PM BREAK

3:15 PM CH01.13.07
Quantifying Speciation and Degradation of Tin Anodes in Aqueous Batteries Sofia Catalina, Jianbo Wang, William C. Chueh and Tyler Mefford; Stanford University, United States

Aqueous batteries based on metal anodes (Zn, Al, Mg, Sn, etc.) present an attractive alternative to lithium-ion for long-duration energy storage due to their low-cost, high-safety, and theoretically high energy density. Still, despite many efforts towards development and commercialization, metal anode systems remain hampered by irreversible hydrogen evolution (HER), detrimental shape change, and passivation during cycling. Direct characterization of charge/discharge products and efficiency losses to parasitic side reactions are thus crucial to mitigate the degradation processes that limit the performance and applications of aqueous batteries.

Our work focuses on tin (Sn) as a largely unexplored alternative metal anode for aqueous systems. In alkaline electrolytes, Sn is reversibly electrodeposited from and anodically stripped to an aqueous $Sn(OH)_6^{2-}$ complex through an overall 4-electron process. This process is complicated by the generation of a soluble $Sn(OH)_3^-$ intermediate which limits the coulombic efficiency of the cell through crossover to the cathode. At high utilization, the limited solubility of $Sn(OH)_6^{2-}$ drives precipitation of an insulating SnO_2 product with limited reversibility. Additionally, while Sn has a high overpotential for HER, hydrogen generation during charge is still present at higher rates.

In this talk, we will describe our efforts to quantify these processes to understand the partitioning of charge/discharge current during cycling. Speciation between Sn(II) and Sn (IV) in the liquid phase is quantified using ^{117}Sn nuclear magnetic resonance (NMR). To investigate the solid plating behavior and reversibility of SnO_2 reduction, we perform *operando* XRD of Sn anode pouch cells. Lastly, we will describe the development of an *operando* gas detection method to quantify parasitic hydrogen and oxygen production using Clark type electrodes. The combination of these techniques may have wide applicability in aqueous battery development and help to explain commonalities in degradation processes that generate irreversible solid, liquid, and gaseous products.

3:30 PM CH01.13.08
New Diagnostic Technique to Characterize Electro-Kinetics in Redox Flow Battery Chao Zeng, Soowhan Kim, Yucheng Fu, Yunxiang Chen, Jie Bao and Zhijie Xu; Pacific Northwest National Lab, United States

As the fraction of electricity generated from intermittent renewable sources (such as solar and wind) grows, developing reliable energy storage technologies to store electrical energy in large scale is of increasing importance. Redox flow batteries (RFB) are regarded as a leading technology in providing a well-balanced solution for current daunting challenges of grid-scale energy storage. Cell-level resistive losses reduce RFB power density and originates from ohmic, kinetic, or mass transfer limitations. existing studies on electron and mass transfer rates are mostly performed in ex-situ conditions based on planar electrodes, so the obtained key parameters are difficult to make specific interference about the performance of a practical electrode in a battery. To address this limitation, an in-situ electroanalytical technique for RFB is proposed for the first time by a symmetrical cell design. For both cathodic and anodic reactions, the polarization curves at condition of a serious of flow rate are obtained on the symmetrical flow cell. The high frequency resistance is also obtained by electrochemical impedance spectroscopy (EIS) at open circuit condition. The ohmic, kinetic and mass transfer resistance can be decomposed from total polarization. Then, the corresponding key parameters, i.e., membrane conductivity, reaction rates, transfer coefficients and mass transfer rates, can be obtained by using a theoretical calculation of specific surface area. The extracted key parameters are validated on both vanadium redox flow battery and aqueous organic redox flow battery.

3:45 PM CH01.13.09
Magnifying Rate Capability and Efficiency of Li-Ion Storage Mechanism via Next-Generation Standalone Electrodes Enabled by $MoSe_2$ Nanosheets in SiOC High Aspect Ratio Structures Sonjoy Dey and Gurpreet Singh; Kansas State University, United States

Transition metal dichalcogenides (TMDs) such as $MoSe_2$ have continued to generate interest in the engineering community because of their unique layered morphology—the strong in-plane chemical bonding between transition metal atoms sandwiched between two chalcogen atoms and the weak physical attraction between adjacent TMD layers provides them with not only chemical versatility but also a range of electronic, optical, and chemical properties that can be unlocked upon exfoliation into individual TMD layers. Such a layered morphology is particularly suitable for ion intercalation as well as for conversion chemistry with alkali metal ions for electrochemical energy storage applications. Nonetheless, host of issues including fast capacity decay arising due to volume changes and from TMD's degradation reaction with electrolyte at low discharge potentials have restricted use in commercial batteries. One approach to overcome barriers associated with TMDs' chemical stability functionalization of TMD surfaces by chemically robust precursor-derived ceramics or PDC materials, such as silicon oxycarbide (SiOC). SiOC-functionalized TMDs have shown to curb capacity degradation in TMD and improve long term cycling as Li-ion battery (LIBs) electrodes. Herein, we report synthesis of such a composite in which MoSe2 nanosheets are in SiOC matrix in a self-standing fiber mat configuration. This was achieved via electrospinning of TMD nanosheets suspended in pre-ceramic polymer followed by high temperature pyrolysis. Morphology and chemical composition of synthesized material was established by use of electron microscopy and spectroscopic technique. When tested as LIB electrode, the SiOC/MoSe2 fiber mats showed improved cycling stability over neat $MoSe_2$ and neat SiOC electrodes. The freestanding composite electrode delivered a high charge capacity of 586 mAh g−1electrode with an initial coulombic efficiency of 58%. The composite electrode also showed good cycling stability over SiOC fiber mat electrode for over 100 cycles.

4:00 PM CH01.13.11
Correlative Multi-Microscopies Study of Electrodeposited Pt Nano-Assemblies as Precipitation Platforms for $Ni(OH)_2$ Nathaly Ortiz Peña[1], Louis Godeffroy[2], Jean-François Lemineur[2], Frédéric Kanoufi[2], Damien Alloyeau[1] and Jean-Marc Noël[2]; [1]Université Paris Cité, CNRS, Laboratoire Matériaux et Phénomènes Quantiques, France; [2]Université de Paris Cité, ITODYS, CNRS UMR 7086, France

Nanoscience involving nanoparticles (NPs) is a key element in the development of the next generation of efficient and safe systems enabling the conversion or storage of renewable energy. NPs being intrinsically heterogeneous in size, shape or composition, it is of prime importance to develop strategies able to investigate chemical processes at the single entity level or even at the sub-entity level. This will allow identifying structure-activity relationships that is fundamental to predict and control the activity of the NPs. Herein, we have harnessed the controlled monitoring of individual NPs electrodeposited on micrometric conductive surfaces to visualize operando by electrochemical transmission electron microscopy (EC-TEM) and post-mortem high-resolution TEM (HR-TEM) their electrocatalytic activity. It is exemplified herein by tracking the electrodeposition of platinum nano-assemblies (Pt-NA) and their modification by $Ni(OH)_2$. This electrochemical decoration of Pt nanostructures with metal hydroxides like $Ni(OH)_2$ is of great interest for the enhancement of hydrogen evolution reaction efficiency in alkaline media.[1] In this sense, we have been able to analyze the morphologies of the electrodeposited Pt-NA *post-mortem* by HR-TEM depending on the electrodeposition strategy, whereas the precipitation of $Ni(OH)_2$ was followed *operando* by EC-TEM. Complementary post-mortem analysis of the nano-assemblies by energy dispersive spectroscopy (EDS) and HR-TEM allowed determining the structure of the bifunctional material. Finally, the reactivity of the $Ni(OH)_2$/Pt for the hydrogen evolution reaction was investigated by EC-TEM.
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SESSION CH01.14: Virtual Session
Session Chair: Akihiro Kushima
Tuesday Morning, April 25, 2023
CH01-virtual

8:00 AM *CH01.14.01
Advances in the Characterisation of Honeycomb Layered Oxides Titus Masese[1], Yoshinobu Miyazaki[2], Godwill M. Kanyolo[3], Shintaro Tachibana[4], Yuki Orikasa[4], Hiroshi Senoh[1] and Tomohiro Saito[2]; [1]National Institute of Advanced Industrial Science and Technology (AIST), Japan; [2]Sumika Chemical Analysis Service (SCAS), Ltd., Japan; [3]The University of Electro-Communications, Japan; [4]Ritsumeikan University, Japan

Honeycomb layered oxides constitute a burgeoning class of materials with vast compositional and crystal structural versatility,[1] and with prospects in diverse fields spanning from electrochemistry, materials science, condensed matter physics and cosmology.[2-8] Despite the prospects envisioned in this class of materials, their augmentation is still encumbered by knowledge gaps that obscure the current understanding of their atomistic properties and behaviours. In this context, characterisation techniques are considered an efficient approach for accelerating the pace of discovery and optimisation of these materials through the elucidation of the atomic-level origins of material functionality and performance. In this talk, we introduce analytical techniques based on diffraction, microscopy and spectroscopy that have been applied to unravel various structural and electronic aspects of honeycomb layered oxides, particularly those that entail pnictogen or chalcogen atoms.[9-12]

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8:30 AM *CH01.14.02
High Spatial and Temporal Resolution Imaging for Advancing Fuel Cells and Electrolyzers Aimy Bazylak; University of Toronto, Canada

The transportation sector is responsible for 15% of global greenhouse gas emissions. In Canada, it is even more significant, i.e. 30% of country-wide emissions originate in the transportation sector, of which heavy-duty vehicles are an increasing contributor. Clean electrochemical energy conversion technologies, such as fuel cells and electrolyzers, are critical for reaching global net-zero 2050 decarbonization targets. However, cost and durability are key barriers to the widespread commercial adoption of fuel cells and electrolyzers, where these issues stem from inefficient transport of reactants and charge through materials and interfaces. Polymer electrolyte membrane (PEM) fuel cells and electrolyzers are composed of porous materials, including the catalyst layer, microporous layer, and substrate, and both material characteristics and associated multiphase flow behaviour have a significant impact on electrochemical performance. Commercial materials typically exhibit highly heterogeneous material and chemical properties, both of which are not fully resolved in the current literature. To reach cost targets for widespread commercial adoption, we must realize materials that enable more effective multiphase flow phenomena than what currently exists. Mass transport losses in PEM fuel cells and electrolyzers are both prohibitively significant, yet designing these materials requires the a priori knowledge of how the heterogeneous properties of the porous materials and their interfacial contacts influence electrochemical performance. In this talk, I will discuss our numerical and experimental methods of elucidating the complex multiphase flow behaviour in the porous materials of PEM fuel cells and electrolyzers and the critical impacts of material design.

9:00 AM *CH01.14.03
Visualization of Electrochemical Reactions in All-Solid-State Li-Ion Batteries by *Operando* Transmission Electron Microscopy Kazuo Yamamoto and Yuki Nomura; Japan Fine Ceramics Center, Japan

All-solid-state Li-ion batteries (ASS-LIBs) having incombustible solid-electrolytes are expected to be promising energy-storage devices because they have advantages of safety, long life-time, low cost and high energy density, compared with common liquid-based LIBs. However, there is a serious issue that needs to be solved for practical use, namely, large resistance of Li-ion transfer at the electrode/solid-electrolyte interfaces and/or in the electrodes. The high resistance of Li-ions drastically reduces the power density of the batteries. To overcome this issue, it is necessary to understand how Li-ions are transferred across the solid-solid interfaces during battery operation. We have so far developed a technique to operate ASS-LIBs in a transmission electron microscope (TEM) and succeeded in visualizing the electric potential distribution using electron holography [1, 2]. Moreover, to directly visualize the Li distribution, we have used electron energy-loss spectroscopy (EELS) in a scanning/transmission electron microscope (S/TEM) [3, 4]. Here, we report recent results of *operando* observation using S/TEM techniques.
We prepared a thin-film-type ASS-LIB having $LiCoO_2$-cathode/Al-, Si-, Ge-doped $LiTi_2(PO_4)_3$-solid-electrolyte (LATP)/*in-situ*-formed-anode structures. We used *operando* STEM-EELS to visualize the 2-dimensional Li maps in $LiCoO_2$ region [4, 5]. In a pristine state, the Li concentration was not uniform and the low concentration layers (20 nm) were observed near the interface. We found that mixture of Co_3O_4 and $LiCoO_2$ was formed, which is the origin of the large interfacial resistance of Li-ion transfer. In charge/discharge states, the Li concentration was changed in the $LiCoO_2$ as expected. To improve the time-resolution of *operando* STEM-EELS, we applied machine learning technique to obtain Li signals from EELS data set by reducing random noises. We succeeded in observing that Li-ions moved in not only perpendicular direction but also parallel direction to the interface [5]. If presentation time is permitted, we will show another result of Li observation in a bulk-type ASS-LIB having sulfide-based solid-electrolyte [6].
We would like to thank Dr. M. Fujii, Dr. T. Hirayama, Ms. E. Igaki, Prof./Dr. K. Saitoh and Prof./Dr. Y. Iriyama for valuable discussion in this study. This work was partially supported by JSPS KAKENHI (JP17H02792, JP19H05814).

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9:30 AM CH01.14.04
Proton-Conducting Composite Membranes with Graphene Oxide and (3-mercaptopropyl) Trimethoxysilanefor Hydrogen Fuel Cells Shahjahan K. Chowdury[1], Young Jin Cho[1], Sung Bum Park[2] and Yong-il Park[1]; [1]Kumoh National Institute of Technology, Korea (the Republic of); [2]Dongguk University Gyeongju, Korea (the Republic of)

Graphene oxide membrane (GOM) has outstanding electrolyte properties in electrochemical devices, such as fuel cells, electrolyzers, and batteries. In proton exchange membrane fuel cells (PEMFCs), perfluorinatedsulfonic acid (PFSA) membrane, i.e., Nafion®, is used as an electrolyte, which has disadvantages in the fuel cells application, such as fuel crossover, expensive, difficult manufacturing process, and many more. However, GOM has a much lower proton conductivity in through plane (σ_{th}) compared to Nafion® due to anisotropic properties of GOM, and the loss of surface functional groups due to reduction by hydrogen is accompanied by an increase in electron conductivity when in contact with hydrogen gas in a fuel cell. Therefore, in this study, an MPTS-modified GO composite (MGC) was synthesized using a high-viscosity GO solution (5 mg/ml) and a dilute (3-mercaptopropyl)trimethoxysilane(MPTS, $HS(CH_2)_3Si(OCH_3)_3$) (0.790 g/mL) (MPTS) and this was followed by impregnation of excess MPTS as a binding agent for MGC.The thiol group of the MPTS monomer is oxidized by hydrogen peroxide (H_2O_2) to a sulfonic acid group ($-HSO_3$), providing a fast proton conduction path with negative oxygen functional groups on the GO particle surface.The optimum weight of incorporation was analyzed by examining the amount of MPTS from 1 to 70 wt% in the GOM matrix. The physicochemical properties, gas crossover, chemical and thermal stability and proton conductivity of composite membranes were studied and compared with pristine GOM and Nafion®. In addition, hydrogen-permeable Pd was deposited on the surface of the MGC membrane to improve gas tightness and maintain high mechanical stability to prevent membrane degradation and reported the performance of hydrogen fuel cells using synthesized MGC membranes.

9:45 AM CH01.14.05

Addressing the Stability Challenges of Gas Diffusion Electrodes in the Presence of ILs-Based Solutions for the Continuous Electrochemical Reduction of CO_2 Federica Zammillo[1], Hilmar Guzmán[1], Danilo Candela[1], Stéphanie Narbey[2], Boyan Iliev[3] and Simelys Hernandez[1]; [1]Polytechnic University of Turin, Italy; [2]Solaronix SA, Switzerland; [3]IOLITEC, Germany

Nowadays, it has become clear that the ever-increasing concentration of carbon dioxide (CO_2) in the atmosphere is a threat to global security[1]. Therefore, the adverse climate events remind us that a transition towards a carbon neutral economy is more necessary than ever. Several approaches have been proposed to convert CO_2 to valuable products and, among these, the electrochemical reduction of CO_2 (ECR-CO_2) represents one of the most promising alternatives. Herein, the ECR-CO_2 has been carried out for the first-time employing silver based-gas diffusion electrodes (GDEs) within a continuous flow cell and in the presence of ionic liquids (ILs)-based solutions, which have been known to boost CO_2-derived products[2]. As reported in the literature, the instability of GDEs is initiated by the high overpotentials needed during the CO_2 reduction reactions and usually culminates in flooding[3]. This eventually has a negative impact on the product selectivity as well as limits the perspectives of scalability. In particular, in this work, different stability issues have been faced and visualized, for example, in the blackening of typical carbon-based gas diffusion layers (GDLs) and in the degradation/colour changes of ILs-electrolyte. Interestingly, by switching to non-carbon based GDLs it has been possible to reach and maintain a steady-state production of carbon monoxide (CO) both at -10 mA cm^{-2} and at -20 mA cm^{-2} for at least 40 minutes, with a H_2/CO ratio slightly above 2 in the former case. Field Emission Scanning Electron Microscopy (FESEM) and Electrochemical Impedance Spectroscopy (EIS) techniques have been employed to carry out the physicochemical characterization of the electrodes and to assess the electrochemical interfaces within the system, respectively. The observed findings definitely encourage us to proceeding with our study on GDL-supported catalyst for the continuous ECR-CO_2 in the presence of ILs solutions and offers openings for a large-scale deployment.

The financial support of the SUNCOCHEM project (Grant Agreement No 862192) of the European Union's Horizon 2020 Research and Innovation Action programme is acknowledged.

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10:00 AM CH01.14.06

Stabilizing Cobalt-free Li-rich Layered Oxide Cathodes through Oxygen Lattice Regulation by Two-phase Ru Doping Yameng Fan[1,2]; [1]University of Surrey, United Kingdom; [2]University of Wollongong, Australia

The limited theoretical capacity of traditional cathode materials solely based on transition metal (TM) redox has been a primary factor for the ceiling placed on the energy density of LIBs. In this regard, Li-rich layered oxides (LLOs) have received a great deal of attention, due to their high reversible capacity (> 250 mAh g^{-1}) and high energy density (900 Wh kg^{-1}), courtesy of the TM redox and the additional high-voltage O^{2-} redox.[1] Developing Co-free cathodes is inevitably a holy grail to overcome the limitations faced by conventional Co-containing LIB cathode materials (e.g., $LiCoO_2$, NMC) due to the high-cost, toxicity, and limited geological distribution of cobalt. Therefore, studies on Co-free LLOs are necessary for creating long-term benefits for the cathode industry. Like typical LLOs, Co-free LLOs suffer from dramatic voltage decay on cycling, which hinders their applications in commercial LIBs. It is well accepted that this voltage decay is primarily attributed to the irreversible anionic redox and structural degradation in LLOs. The doping strategy has been widely used to address the voltage decay of LLOs.[2] While the dopant is typically introduced to the layered Rm component, the lithium-rich component (C2/c) in the LLOs, which is the source of anionic redox, has always been ignored.

In this work, a small quantity (3%) of the electrochemically active 4*d* metal, Ruthenium (Ru), is successfully doped into TM octahedral sites in both hexagonal and monoclinic phases in the typical Co-free Li-rich LNMO cathode.[3] The effects of Ru doping on the structure and redox activities of the LNMO are investigated using various morphological, local structure, and crystallographic techniques. Neutron-based pair distribution function (PDF) analysis, neutron powder diffraction (NPD), and *in operando* synchrotron-based X-ray powder diffraction (XRPD) is employed to characterize the short- and long-range cation arrangement, the chemical environment of lattice oxygen, and the structural evolution on cycling. Post-mortem synchrotron-based near-edge X-ray absorption fine structure (NEXAFS) and X-ray absorption characterizations (XAS) are utilized to investigate the cationic/anionic redox process. The correlation between voltage decay with structural changes is reported in detail. Owing to enhanced structural stability, Ru-doped LNMO exhibits an extraordinarily low voltage decay (< 0.45 mV per cycle) and meanwhile retains a high reversible capacity (215 mAh g^{-1} at 1 C) contributed by both cationic and O^{2-} redox. This work unravels the role of heavier ions in modifying the structural evolution and suppressing the voltage decay and sheds light on improving the performance of cathodes for practical applications in LIBs.

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10:15 AM CH01.11.18

Material Development Strategy Guided by Degradation Analysis Under Dynamic Load in Proton Exchange Membrane Water Electrolysis

Anastasiia Voronova[1,2], Jong Hyun Jang[1,2], Hee-Young Park[1] and Bora Seo[1,2]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]University of Science and Technology, Korea (the Republic of)

To realize the hydrogen economy and achieve net-zero carbon emission, practical implementation of water electrolysis (WE) technique is of prime importance. Among the WE techniques, proton exchange membrane water electrolysis (PEMWE) has attracted much attention due to its high performance, compact design, and fast response. However, the lack of an appropriate evaluation protocol for durability, and the lack of understanding on degradation behavior of each component in PEMWE hinder its widespread application. In this presentation, degradation behavior under dynamic load-based accelerated stress test (AST) protocols will be discussed to guide material development strategy. Load ranges were varied by changing the low voltage limit (LVL) between 1.4 V and 1.9 V while fixing the high voltage limit at 2.2 V. The used AST protocols can simply mimic solar profiles characterized by high ramp rates and loads fluctuations. The AST protocols with LVL 1.4 V and LVL 1.5 V resulted in contrast degradation behaviors, showing an increase and decrease in performance after the test, respectively. The performance decrease, observed for the LVL 1.4, was ascribed to the fuel cell-like operation mode with reversal current occurrence, considered as additional stress factor for the cathode catalyst degradation. For the LVL 1.5, the slight performance increase is ascribed to the membrane thinning and/or catalyst dissolution at the anode/catalyst interface, which temporarily increases roughness, thereby exposing more active sites to the electrolyte. The AST protocols with LVL 1.7 and LVL 1.9 resulted in the substantial increases in mass transport overpotential. Given the cross-sectional SEM analyses, the results is presumably attributed to the bubble nucleation and subsequent degradation on membrane/catalyst and/or diffuse layer/catalyst interfaces together with decrease in catalyst layer porosity. Meanwhile, a comparative AST protocol with steady-state load (2.2 V) resulted in the performance decay, mostly attributed to the increase in ohmic overpotential due to the Ti porous layer passivation. The degradation study can suggest a practical guidance for understanding degradation behavior of each component, and for material development strategies in designing durable PEMWE system.

SESSION CH01.15: Virtual Session II
Session Chairs: Rosa Arrigo and Junjie Niu
Wednesday Morning, April 26, 2023
CH01-virtual

8:00 AM *CH01.15.01
Towards a Realistic Modelling of Electrified Interfaces the Nanoscale Clotilde Cucinotta; Imperial College London, United Kingdom

In this talk I will introduce some issues connected with the simulation of electrified interfaces at the nanoscale focusing on simulating the effect of an applied potential to an electrochemical (EC) cell, using realistic models for the charged electrode electrolyte interface. I will present some recent progress in the simulation of the double layer of the fundamental Pt-water interface and its response to changes of potential applied to the cell [1]; this is obtained applying a general ab initio electrode-charging approach we developed. If time allows, I will illustrate how combining knowledge from molecular electronics and DFT based methodologies to simulate atomic dynamics could lead to a more sophisticated description of EC phenomena.

8:30 AM *CH01.15.02
Development of Lab-on-a-Chip Platform for Electrocatalyst Screening, Electrochemical Testing, *In Situ* Probing of Product Chemical Composition and Morphology Evolution in Li-CO_2 Batteries Yunlong Zhao, Manman Wang and Kai Yang; University of Surrey, United Kingdom

Li-CO_2 batteries (LCBs) have received extensive attention as a promising alternative to solve both energy crises and CO_2 emission issues. However, the development of LCBs is still in its infancy, lacking efficient electrocatalysts, with unclear mechanisms and uncontrollable reaction pathways. Here, we developed a versatile on-chip electrochemical testing platform to simultaneously achieve efficient catalyst screening and in-situ probing of product chemical composition and morphology evolution. Among selected nine typical metal catalysts, the on-chip LCBs with screen-out optimal catalyst exhibited the smallest ultra-low overpotential (~0.55 V). Their high reversibility and reaction pathways were verified by the integrated functions of in-situ electrochemical Raman and atomic force microscopy and supported by the ab initio calculations. Following the on-chip platform guidance, LCB coin cells and pouch cells were fabricated, exhibiting large capacity with a superior energy efficiency of up to 90% and stability. These results demonstrate the practical competitive advantages of LCBs, and more generally, the demonstrated multimodal platform can be broadly applied to other systems (such as metal-air batteries, electrocatalysis, fuel cells and photoelectrochemical), opening new avenues for rapid catalyst screening, mechanism investigation and guiding macroscopic applications.

9:00 AM *CH01.15.03
New X-Ray Spectroscopy Techniques for Energy Materials Research Sofia Diaz-Moreno[1], Oliver Blackman[1,2], Armando Ibraliu[1,3,4], Andrea Russell[2], Daniel Bowron[3] and Christopher Hardacre[4]; [1]Diamond Light Source, United Kingdom; [2]University of Southampton, United Kingdom; [3]ISIS Pulsed Neutron and Muon Source, United Kingdom; [4]The University of Manchester, United Kingdom

X-ray Absorption Spectroscopy (XAS) is an established experimental technique that is used for the study of the electronic and local atomic structure of materials. The high sensitivity of the method together with its element selectivity make it very suitable for the study of energy materials. The technique is also frequently used for the study of processes in situ and under operando conditions.

In recent years, advanced spectroscopy techniques and analysis methods have been used to circunvent some of the shortcomings of traditional XAS. For example, X-ray Emission Spectroscopy at the Kb emission line can be used to perform spin-selective spectroscopy. In addition, the use of Modulation Excitation assisted by phase-sensitive detection (ME-PSD) analysis methods can significantly enhance the sensitivity of XAS by filtering out contributions of spectator species that are unaltered by the external stimulation.

In this contribution I will present two recent examples ilustrating the application of these new methodologies to the study of electrochochemical systems and energy materials. The changes in the structure of the iron metal centre in prussian blue and prussian blue analogues have been studied as a function of the applied potential, and the changes have been assigned to the iron in low and high spin. ME-PSD analysis has been applied to the study of the reversible ferrocyanide/ferricyanide couple using XAS.

9:30 AM *CH01.15.05
***In Situ* Spectroscopy-Guided Design of Synthesis and Processing—Bridging the Gap from Battery Innovation to Manufacturing** Feng Wang; Argonne National Laboratory, United States

Rechargeable batteries are among the key technologies for decarbonization with increasingly expanded applications in transportation and power grids. The demand for safer, longer-lasting, durable energy storage continues to fuel the need for battery innovation. This need, in turn, requires designing new materials, understanding how they function and developing scalable processes to manufacture them. Technical advances in characterization and computation have greatly facilitated materials design and discovery in the past decade. However, making battery materials to meet multifaceted performance needs (capacity, power, lifespan, and safety) has been nontrivial, often hindered by the practical engineering challenges encountered when optimizing the multiple intercorrelated steps – synthesis, processing, benchmarking, and upscaling.
We will present our effort to develop *in situ* spectroscopies applied to studying the synthesis/processing of battery materials, thereby gaining insights into the process design for addressing engineering challenges in battery materials manufacturing. Specifically, synchrotron X-ray based in situ spectroscopies are developed for real-time probing of the intermediate phases and their structural evolution as the materials are being synthesized and processed. The technique allows access to the details of the processes, elucidating how the processing parameters affect the kinetic reaction pathways and, consequently, the target material phases and their properties. Insights gained from such studies provide a basis for materials synthesis/processing by design – rationally selecting synthesis/processing parameters to improve performance and reduce cost. Specific examples will be provided to demonstrate the in situ spectroscopy-guided design of calcination and other scalable processes for processing nickel-based cathode active materials. We will conclude by discussing emerging opportunities in automated experimentation and digitalized process design, bridging the gap from battery innovation to manufacturing.

SYMPOSIUM

April 12 - April 14, 2023

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SESSION CH02.01: Advances in Cryogenic Transmission Electron Microscopy and Spectroscopy for Energy Materials I
Session Chairs: Shelly Michele Conroy and Jordan Hachtel
Wednesday Morning, April 12, 2023
InterContinental, Fifth Floor, Howard

8:15 AM *CH02.01.01
CryoTEM as a Tool for Investigating Crystallization in Aqueous Systems Jingshan S. Du[1], Jennifer A. Soltis[1], Elias Nakouzi[1], Guomin Zhu[2,1] and James J. De Yoreo[1,2]; [1]Pacific Northwest National Laboratory, United States; [2]University of Washington, United States

Solution based synthesis is a common method for production of energy-related materials and a pervasive process in environmental settings tied to energy technology through the impact on carbon emissions and climate. The realization that crystallization in aqueous systems occurs along diverse structural pathways has motivated extensive TEM-based investigations to understand the nature of those pathways, the associated dynamics, and the underlying thermodynamic and kinetic factors. Ex situ TEM studies of such systems suffer from the unknown impact of drying, as well as an inability to directly relate structures seen at one time point with those present at another, rendering an understanding of pathways nearly impossible. For systems amenable to in situ liquid phase TEM, these two problems can be readily circumvented, but the effect of the electron beam through the creation of radiolysis products that alter the solution chemistry and, in the case of organic compounds, the breakdown of the solutes themselves often cast doubt on the applicability of the results to synthetic processes outside the microscope. CryoTEM offers a middle ground that gives a true picture of crystallization at any given time point and allows for the construction of likely pathways per the ergodic principle by analyzing structures present over large areas as a substitute for following individual structures over time. Here we present two examples of crystallization processes for which cryoTEM provides critical information concerning the structural state. The first involves the process of crystal growth through repeated oriented attachment (OA) events, i.e., the growth of single crystals by repeated fusion of nanocrystals that adopt crystallographic coalignment prior to attachment. Using data from minerals aluminum and iron oxide growing by OA, we show that cryogenic high-resolution TEM (HRTEM) can provide definitive information on the temporal evolution of the growing crystals and the structural relationship of the primary particles. The second example involves the crystallization of the water itself. Visualizing the crystalline network of ice with atomic resolution in real space is challenging due to the weak directional hydrogen bonds between water molecules and the resulting instability of ice under an electron beam in vacuo. However, we find that crystallizing water encapsulated between amorphous carbon membranes and freezing it in liquid nitrogen to form hexagonal ice (Ih ice) enables successful HRTEM of the resulting ice sections. Even though the sections show overall single-crystallinity by diffraction standards, the crystal may exhibit structural variation and contain sub-domains ~ 10 nm in size. Quantitative strain and tilt mapping reveals the sub-surface flexibility of ice and is used to demonstrate the correlation between defect structures and strain accumulation. Both sharp low-angle grain boundaries and gradual lattice bending are associated with sub-domains with different crystal orientations. Taken together, this work shows promise in elucidating the molecular and defect structures of ice and may shed light on the physics of ice surfaces and their interfaces with substrates that promote ice nucleation.

8:45 AM *CH02.01.02

Cryo-Enabled Imaging of Interactions Between Airborne Pollution Particles and Human Cells Alexandra Porter[1], Victoria Garcia[1], Sharon Mumby[1], Gloria young[1], Prashant Kumar[2], Gopinath Kalaiarasan[2], Hisham Abubakar-Waziri[1], Iain M. Adcock[1], Kian Chung[1] and Maria Harkiolaki[3]; [1]Imperial College London, United Kingdom; [2]University of Surrey, United Kingdom; [3]Diamond Light Source, United Kingdom

Air pollution is becoming one of the most pressing issues because of the increasing levels of pollution around the world. Airborne particulate matter (PM) can trigger cellular oxidative stress and inflammation, which are the basis for respiratory diseases associated with pollution. Understanding the effects of PM pollution on respiratory system cells is key to develop strategies to reduce personal exposure, especially in congested areas. Currently, there is no correlated cell-level information about the effects of PM on primary human epithelial cells metabolism, the structural damage of cellular organelles and the size and chemistry fractions of PM that cause this cellular damage. In a collaboration with the National Heart and Lung Institute, we have been focusing on the impacts of pollution PM collected from a London Underground platform on the health of cell organelles and cellular metabolism. We have shown that the PM collected from the London Underground is composed of trace quantities of ultrafine particles composed of redox-active transition metals, including Cu, Cr, Fe and Mo that could damage respiratory cells by generating damaging free radicals[1]. We have exposed human nasal epithelial cells from healthy and asthmatic volunteers to this pollution PM. We have chemically fixed and stained the cells, embedded them in a resin and cut ultrathin sections for transmission electron microscopy and analysed the chemistry of intracellular nanoparticles of pollution using high resolution electron microscopy. In parallel, cryo soft X-ray tomography (cryo SXT) with structured illumination microscopy (cryo-SIM) (B24 Beamline, DLS, UK) was employed to generate whole-cell structural and metabolically relevant information about the cells (cell lines and human cells) exposed to PM in their near-native state. I will discuss the changes observed to ultrastructure and metabolism of cell organelles in cells exposed to London Underground pollution particles and the challenges of preparing and imaging human cells for correlative cryoSXT, cryo-SIM and cryo electron microscopy. I will also discuss how optimisation of cryo-focussed ion beam milling scanning electron microscopy (FIB-SEM) techniques could be used subsequently in specific areas for higher resolution imaging and complementary compositional analysis, as well as for lamella preparation for high-resolution cryo-TEM, where oxidation states and composition of damaging PM can be attained. In future, the development of this multidimensional workflow using human derived cells will bring together imaging of whole-cell structure and metabolism with chemical analysis of the PM to identify which chemistries are most damaging to intracellular cell organelles and their mechanisms of toxicity. This novel approach will offer new insights into how to mitigate the health effects of pollution PM.

[1.] Kumar P, Chung KF, Porter AEc et al, 2022, Characteristics of fine and ultrafine aerosols in the London underground., *Sci Total Environ*, Vol: 858

9:15 AM CH02.01.03

Local Chain Orientation and Alignment in All-Polymer Solar Cell Christina Cheng, Camila Cendra, Yilei Wu, Zhenan Bao and Alberto Salleo; Stanford University, United States

In recent years, all-polymer solar cell performance has accelerated, in part due to significant improvements in controlling microstructure by optimizing processing parameters. However, quantitative relationships between processing, microstructure, and performance remain weak. While charge generation in all-polymer blends is highly dependent on local chain orientation and local stacking structure, common microstructural characterization techniques only provide bulk average characteristics of film morphology. On the other hand, cryogenic High Resolution Transmission Electron Microscopy (cryo-HRTEM) has emerged as a promising method to image and quantify local polymer structure at sub-nanoscale resolutions.

In this study, we use cryo-HRTEM to analyze the structural organization of the fluorinated all-polymer blend PBDB-T-2F:F-N2200, and we show that donor microstructure can be selectively tuned with processing additives. By applying Fourier analysis and statistical methods, we map the local orientation of lamellar stacking, characterize donor/acceptor domains and interfaces, and quantify inter- and intra-species chain alignment. The results demonstrate how advances in quantitative analysis of cryo-HRTEM images can reveal new structural characteristics in polymer blends.

9:30 AM CH02.01.04

Structural Study of Hydrated Organic Mixed Ionic Electronic Conductors Using Cryogenic 4D-STEM Yael Tsarfati[1,2,3], Karen Bustillo[1], Benjamin Savitzky[1], Colin Ophus[1], Alberto Salleo[2] and Andrew M. Minor[1,3]; [1]National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory, United States; [2]Stanford University, United States; [3]University of California, Berkeley, United States

Organic mixed ionic–electronic conductors (OMIECs) are soft organic materials that are advantageous for varied bioelectronic devices, ranging from organic electrochemical transistors (OECTs) and biosensors to batteries and supercapacitors.[1] Their ability to operate in aqueous environments is an important virtue that qualifies them for these applications. One widely used successful strategy for obtaining OMIECs with enhanced water and ion uptake and hence increased capacitance, is placing ethylene glycol side chains on the polymer backbone.[2] However, the structural understanding of these glycolated OMIECs is still limited, particularly in operational states such as being hydrated in water, or used in aqueous electrolytes, or when electrochemically doped. One significant challenge in filling this gap is the challenge in characterizing hydrated or solvent swollen OMIECs, that is incompatible with many standard relevant techniques that involve high vacuum conditions.[3] Here we describe experiments where we used cryogenic vitrified solid-state samples and advanced scanning nanobeam diffraction (4D-STEM). We have previously applied 4D-STEM to study these materials in the dry solid-state, mining structural information from the molecular to the mesoscale level, providing a baseline and analysis pipeline for the more complex states. Applying this hybrid approach, we demonstrate the structural changes induced in glycolated OMIECs by hydration. The most prominent change is the lamellar expansion. Noteworthy, this is not an obviously predicted structural change, and theoretical simulation even predicted a lamellar contraction.[4] We believe this methodology can bring us one step closer to a deeper understanding of the structures of these materials in their operational modes. Our results show how cryogenic 4D-STEM can provide true structure-function relationships that can help improve our rational design of OMIECs thin films for more efficient devices.

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9:45 AM BREAK

10:15 AM *CH02.01.05

Development of a Stable Cryogenic *In Situ* Biasing System for Atomic Resolution (S)TEM Yevheniy Pivak[1], Hongyu Sun[1], Tijn Omme[1], Eva Bladt[1], Shelly Michele Conroy[2] and Leopoldo Molina-Luna[3]; [1]DENSsolutions, Netherlands; [2]Imperial College London, United Kingdom; [3]TU Darmstadt, Germany

The development of cryogenic electron microscopy started in the 1970s in order to study the structure of proteins and other biological material. However, only recent advances in detector technology and software algorithms have allowed the determination of biomolecular structure at atomic resolution [1]. The application of cryogenic transmission electron microscopy (cryo-TEM) methods to materials science and energy-related fields has been mainly limited to the study of beam sensitive materials such as lithium-ion batteries, organic semiconductors, perovskite-based solar cells, polymers and metal organic frameworks (MOFs). Most low-temperature in situ TEM experiments are carried out using cryogenic holders based on liquid nitrogen cooling and using 3-mm-sized TEM support grids. Despite their widespread use, grid-based cryogenic systems suffer from poor stability, making it challenging and time-consuming to obtain adequate atomic-resolution imaging [2]. Additionally, these systems often have the inability to set intermediate temperatures, which limits the experiments to be performed at either liquid nitrogen temperature or room temperature. Furthermore, such systems are limited in applications when understanding the structure, electronic and transport properties of materials under an applied electrical stimuli at low temperatures is of interest. For such applications, a system with low sample drift that combines liquid nitrogen cooling with an external voltage bias is needed. Such a development can enable a vast range of applications in the field of quantum materials [2], magnetic materials and nanostructures, ferroelectrics [3], topological insulators, metal-to-insulator transitions, superconductors.

In this talk, we will share our latest developments with respect to a combined in situ cooling and biasing system. The system includes a novel double-tilt cryogenic holder which is based on micro-electro-mechanical-systems (MEMS) technology, and uses liquid nitrogen for cooling. It has multiple electrical contacts and is compatible with the DENSsolutions heating and biasing Lightning Nano-Chips, enabling the setting of any intermediate temperature between LN2 and room temperature. Without the presence of the cooling agent, it is also possible to perform in situ heating experiments up to 1000oC. By exploiting the high stability of this system and its double tilt capability, we will demonstrate how atomic resolution imaging can be achieved while applying a bias to the sample and present a number of application examples, including ferroelectric focused ion beam (FIB) lamellas.

[1] Cheng Y et al, A primer to single-particle cryo-electron microscopy. Cell 2015 161 (3) (438).
[2] E. Tyukalova et al, Challenges and Applications to Operando and In situ TEMimaging and spectroscopic capabilities in a cryogenic temperature range. Accounts of Chemical Research 2021 54(16) (3125).
[3] JL Hart and JJ Cha, Seeing Quantum Materials with Cryogentic Transmission Electron Microscopy. Nano Lett 2021 21 (5449).
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10:45 AM CH02.01.06
Compressive Sensing for 4D-STEM Imaging Jacob Smith[1,2], Hoang Tran[2], Zhaiming Shen[3], Guannan Zhang[2] and Miaofang Chi[2]; [1]North Carolina State University, United States; [2]Oak Ridge National Laboratory, United States; [3]University of Georgia, United States

Quantum materials experience novel phenomena at low temperatures, either developing new structural or ferroelectric phases or new properties such as superconductivity and spin liquids. Because of its ability to simultaneously derive complex information about a material's electric field, charge density, and magnetic structures, four-dimensional scanning transmission electron microscopy (4D-STEM) has gained favor in cryogenic experiments to investigate a material's temperature dependent properties and phase transitions. However, 4D-STEM detectors usually require a per-pixel acquisition time in the region of a millisecond, resulting in a relatively lengthy acquisition time and potential sample damage due to excessive electron dose. One possible strategy is to only capture the probe positions required to recover the desired information. If a proper sampling method is taken and the data at redundant sites can be reconstructed using an algorithm, the total acquisition time and electron dose could be substantially reduced.

In this work, we developed a machine learning (ML) based compressive sensing algorithm to reconstruct 4D-STEM datasets from a limited subset of the available data. Our ML model consists of an autoencoder that extracts a low-dimensional feature space from the limited subset of the diffraction patterns, and a fully connected neural network to map from the integrated images, e.g., bright field, center of mass, to the extracted feature space. Once the neural networks are trained, for each missing pixel, i.e., the pixel that is not scanned during the acquisition, we can use compressive sensing to interpolate the pixel values in the integrated images, map the interpolated values to the feature space via the fully connected network, and then push the feature sample through the decoder to construct the missing diffraction pattern. [1]

Our 4D-STEM compressive sensing algorithm has been successfully implemented on a pair of datasets including different features in real space, including periodical atomic structural imaging as well as samples including interfaces and defects. Using this algorithm, we demonstrate significantly reduced sampling points (down to 25%) is sufficient to reconstruct STEM images retaining atomic-scale structural information.

Acknowledgments
[1] This research is supported by the U.S. Department of Energy, Office of Science, Office of Advanced Scientific Computing Research, the Scientific Machine Learning Program, and performed at Oak Ridge National Laboratory (ORNL). ORNL is operated by UT-Battelle, LLC, for the U.S. Department of Energy under Contract DE-AC05-00OR22725.
[2] The microscopy work was supported by an Early Career project supported by DOE Office of Science FWP #ERKCZ55–KC040304. All microscopy technique development was performed and supported by Oak Ridge National Laboratory's (ORNL) Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility.

11:00 AM CH02.01.07
Elucidating Phase Transition of Metal Trihalides using Cryogenic Scanning Transmission Electron Microscopy Hsin-Yun Chao and Miaofang Chi; Oak Ridge National Laboratory, United States

Transition metal trihalides are two-dimensional van der Waals interlayer-bonded quantum materials with complex phase transitions and intrinsic magnetic orderings at lower temperatures. For instance, $RuCl_3$ stirred up considerable interest due to its potential as a spin-1/2 honeycomb-lattice magnet, which is predicted to have characteristics of a spin liquid [1]. For these 2D materials, shifts in interlayer stacking can cause distinct transitions in magnetic properties [2]. However, atomic scale understanding of variations in layer-by-layer stacking arrangements of metal trihalides at relevant temperatures have yet to be empirically explored. Scanning transmission electron microscopy (STEM) is an exemplary technique to visualize changes in stacking structures. We select $CrCl_3$ as a model material as it is a relatively stable metal trihalide with an observed bulk phase transition at 240 K and ferromagnetic characteristics between 14 K and 17 K [3]. Cryogenic-STEM techniques are employed to examine low-dimensional $CrCl_3$ samples at varying thicknesses and temperatures from room temperature to 103 K. Unexpected stacking shifts deviating from expected phase transitions in the bulk are directly observed through high annular dark field (HAADF) imaging. Implications for these structural changes will be further discussed. [4]

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[4] Microscopy research was performed at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory, which is a US Department of Energy (DOE), Office of Science User Facility.

11:15 AM *CH02.01.08
Cryogenic EM Across Length Scales for Li Metal Anode Batteries Katherine L. Jungjohann[1], Laura C. Merrill[2], Renae N. Gannon[3], Steven J. Randolph[4] and Katharine Harrison[2]; [1]National Renewable Energy Laboratory, United States; [2]Sandia National Laboratories, United States; [3]Thermo Fisher Scientific, United States; [4]Oak Ridge National Laboratory, United States

An interfacial understanding is necessary for developing strategies to commercialize high-energy density rechargeable lithium metal anode batteries, as currently, the lithium anode/electrolyte interface is unstable with prolonged cycling. We have used several strategies to improve the cycling performance of lithium metal anodes, including reducing the parasitic reactions between lithium metal and the electrolyte, and improving the electrodeposited lithium metal morphology. These strategies have generated unconclusive electrochemical data, that has required the need for nanoscale interfacial characterization of these solid-liquid interfaces. Our team has used the cryogenic transfer workflow developed by Leica in collaboration with cryo-SEM/FIB tools by Thermo Fisher Scientific to cross-section lithium metal anodes and intact coin cell batteries to observe the interfacial structures, lithium morphology, and failure mechanisms relative to changes in electrode contract pressure, electrode coatings, and electrolyte chemistry. Cross-sectional SEM images and EDS maps of the lithium metal anodes have provided a better understanding of the electrodeposited lithium morphology, quantity of ‘dead’ lithium metal, and quantity of solid electrolyte interphase material that has formed alongside the lithium metal. In understanding lithium metal battery failure at the system level, we used a cryogenic stage in a laser plasma FIB to cross-section through the coin cell’s cap for imaging/mapping the entire battery stack under cryogenic conditions. The tools, methods, and results of these studies will be detailed in this presentation.

11:45 AM CH02.01.09
Event-based direct detection for transmission electron microscopy Barnaby D. Levin, Michael Spilman and Benjamin Bammes; Direct Electron LP, United States

The great majority of detectors currently used in electron microscopy are frame-based. Each time data is read from the sensor, a "frame" is generated by reading out all of the pixels on the sensor, or in a region of the sensor. In applications involving sparse signals, such as electron counting for imaging in cryogenic transmission electron microscopy, frame-based detectors are inefficient, as sparsity means that the majority of each frame does not contain signal, and therefore reading out frames of pixels involves large volumes of redundant data. In contrast, event-based detectors are an alternative technolgy in which pixels are read out asynchronously when they register a significant change in intensity. When event-based readout is employed on a direct detector with a very high single-electron signal to noise ratio, the detector can be designed such that pixels are only read out when they are excited by an incident electron. This strategy avoids the redundancy of reading out large numbers of pixels that contain no signal, and as a result, event-based direct detectors promise higher electron counting performance at a lower cost than frame-based detectors. In this presentation, we will review the development of event-based direct detectors, and their current and potential applications in transmission electron microscopy.

SESSION CH02.02: Advances in Cryogenic Transmission Electron Microscopy and Spectroscopy for Energy Materials II
Session Chairs: Shelly Michele Conroy and Jordan Hachtel
Wednesday Afternoon, April 12, 2023
InterContinental, Fifth Floor, Howard

1:30 PM *CH02.02.01
Cryo-TEM for Rechargeable Battery—Does Cooling Solve the Beam Sensitive Problem We Face? Chongmin N. Wang; Pacific Northwest National Laboratory, United States

An imaging process can exert an inadvertent effect on the object being observed. Consequently, what we observe does not necessarily represent what had been present before the observation. Normally, this effect can be ignored if the consequence of such a change is believed not to be significant. Electron beam based imaging and spectroscopic techniques appear to be one of the indispensable approaches for probing the characteristics of rechargeable batteries. Modification of battery materials by the electron beam during their imaging has been widely noticed, which, for some cases, appears to be not amendable for capturing any useful information. This is especially true for the case of dynamically formed entity during battery cycling, such as solid electrolyte interphase (SEI) layer, a thin layer formed on the electrode surface that is essential for electrochemical reactions in batteries and critically governs the battery stability. Recently, it has been demonstrated that, cooling of the battery sample, as termed as cryo-microscopy for materials science, can effectively mitigate the imaging electron induced modification effect, therefore to allow the capturing of structural features of beam sensitive battery materials at multi-scale down to atomic resolution. In this presentation, we will check into the latest advances of cryo-TEM and its application for probing into the structural and chemical evolution of rechargeable batteries, typically in the system of Si and Li anode and their SEI layers. In general, the pros and cons of cryo-TEM for material science will also be discussed.

2:00 PM *CH02.02.02
Cryogenic Electron Microscopy Imaging of Synthetic Soft Materials at the Atomic Level Xi Jiang[1], Tianyi Yu[1], Morgan E. Seidler[1,2], Xubo Luo[1], David Prendergast[1], Ronald Zuckermann[1] and Nitash Balsara[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

Atomic resolution imaging of soft materials using electron microscopy is challenging because of the radiation damage under the electron beam. By leveraging low-dose cryogenic transmission electron microscopy (cryo-TEM) and the sophisticated image processing approaches developed by the structural biology community, atomic-scale structural information can be obtained from the nanostructures formed by synthetic soft materials. Our experiments were conducted on crystalline nanosheets and nanofibrils formed by self-assembly of amphiphilic polypeptoid molecules. Low-dose cryo-TEM micrographs were obtained from vitrified nanosheets and nanofibrils. A combination of electron crystallographic and single particle analysis was used to obtain two-dimensional (2D) and three-dimensional (3D) high resolution images of crystal motifs and single molecules. 2D atomic-scale imaging reveals the importance of halogen bonds in the design of crystal motifs in self-assembled nanostructures. Moreover, the hidden lattice symmetry in halogenated nanosheets is clearly illustrated in 3D density map. In addition, 3D reconstruction of nanofibrils shows the direct view of chain conformation, the unique internal structures comprising two opposite layers and the effect of capping group interactions on the design of nanostructures. These discoveries thus allow us to explore the effect on inter/intra interactions on the self-assembled nanostructures at the atomic level.

2:30 PM *CH02.02.03
Development of Cryogenic Techniques for Characterizing Energy Storage Materials in Electrochemical Process Minghao Zhang[1] and Y. Shirley Meng[2]; [1]University of California, San Diego, United States; [2]The University of Chicago, United States

Lithium-ion batteries (LIBs) commercially dominate portable energy storage and have been extended to hybrid/electric vehicles by utilizing electrode materials with enhanced energy density. The energy density and cycling life of LIBs must extend beyond the current reach of commercial electrodes to meet the performance requirements for transportation applications. Recently, researchers proposed to use Li metal as the anode to achieve higher energy density. However, the dendritic growth of Li metal during cycling will result in low coulombic efficiency as well as safety issue which is detrimental for practical applications. It is proposed solid state electrolytes (SSE) are compatible with lithium metal because of lithium penetration resistance, which can be the ultimate choice to achieve the energy density of 500 Wh/kg. The performance of existing all-solid-state batteries is still not optimal, which is mainly attributed to the poor interfacial stability. Further improvements and developments of these energy storage materials rely on a fundamental understanding of their electrochemical cycling mechanisms at atomic level. Characterization of Li anodes and SSE/Li-metal interfaces remains difficult due to their sensitivity to beam damage, the nano-scale of interfacial decomposition products, and their buried nature. Our group has demonstrated the importance of cryogenic techniques for preparation (cryogenic focused ion beam, cryo-FIB) and characterization (cryogenic transmission electron microscopy, cryo-TEM), to preserve the morphology and structure of lithium metal. These breakthroughs enabled unprecedented characterization of plated Li metal and are currently being extended to all-solid-state batteries.

The first demonstration of the functionality of the cryo-TEM will focus on characterizing the morphology and crystallinity of electrochemically cycled lithium metal with different electrolytes. This work will also cover recent advances on cryo-EM development for Li/LiPON/LNMO interfaces. The combination of cryo-FIB and cryo-EM is necessary for quantitative structural and chemical analysis due to extreme susceptibility of both lithium metal and LiPON to air and beam damage. The obtained results provide new insights of decomposition, diffusion of chemical species, and chemical evolution along the interface, which leads to a better understanding of the cycling stability for Li metal batteries.

SESSION CH02.03: Advances in Cryogenic Transmission Electron Microscopy and Spectroscopy for Energy Materials III
Session Chairs: Shelly Michele Conroy and Leopoldo Molina-Luna
Wednesday Afternoon, April 12, 2023
InterContinental, Fifth Floor, Howard

3:30 PM CH02.03.03
Atomic-Scale Imaging of Exciton and Phonon Dynamics in Quantum Materials Sandhya Susarla; Arizona State University, United States

Accessing the atomic scale structural and electronic properties is crucial to understand fundamental correlated properties in quantum materials. In recent times, analytical electron microscopy techniques such as scanning transmission electron microscopy (STEM)-electron energy loss spectroscopy (EELS) under cryogenic conditions have been applied to image local bosonic states such as excitons and phonons. My talk will be focused on probing these bosonic states at low temperatures. I would start my talk with moiré two-dimensional transition metal dichalcogenides which have correlated electronic states resulting from atomically varying strains associated with the stacking configuration. I will talk about the recent progress that we have made in cryogenic imaging excitons in moiré two-dimensional transition metal dichalcogenide heterostructures at the atomic scale from barely detecting the moiré exciton signal in EELS [1] to imaging these excitonic states at the atomic scale [2] to recognizing the fine structure of the moiré excitons [3]. I would also elaborate on the future cryogenic experiments that could be performed on these systems. In the second part, I will take the example of a thin film $PbTiO_3$ layer grown on $DyScO_3$ substrate [4] and explain how the phonon properties vary near the domain walls. I hope to end my talk by provinding insights about future for cryogenic electron spectroscopy to be successful in accessing fundamental structural and electronic states in quantum materials with some of the pathways that our group is adopting to solve this problem.

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SESSION CH02.04 Poster Session
Session Chairs: Shelly Michele Conroy and Leopoldo Molina-Luna
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM CH02.04.01
Imaging Gas Adsorption in MOFs via 4D-STEM Sarah Karstens[1], Karen Bustillo[2], Jeffrey Long[1,1] and Andrew M. Minor[2,1]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Metal–organic frameworks (MOFs) are crystalline coordination networks composed of metal ions connected by organic linkers. One of the most prominent advantages of MOFs originates from interactions of the framework with small molecules; these are referred to as host-guest interactions. Visualizing interactions between host MOFs and guest molecules with cryoTEM enables us to explore their structure under different conditions. For example, it is possible to compare partial loading and visualize the nanostructural morphology of individual crystals, and ultimately optimize loading of MOFs.[1] Currently, host-guest interactions in MOFs are either understood via theoretical simulations or bulk characterizations using x-ray/neutron diffraction, in situ diffuse reflectance infrared spectroscopy, or nuclear magnetic resonance.[2] These experimental techniques average out information such as heterogeneity among adsorption sites.

MOFs are inherently electron beam-sensitive and typical electron irradiation causes collapse of the structure within seconds.[1] Since gas adsorption in a MOF is usually optimized to be reversible (so that the MOF can be cycled and reused), the host-guest interaction is ideally somewhat weak. At atmospheric pressure, small gas molecules and any other volatile solvent easily desorbs from the material. The high vacuum in the TEM further promotes desorption.[2]

For this project, a novel, air-free workflow to activate and gas dose metal-organic frameworks on a TEM grid has been devised. This is followed by cryogenic transfers that ensure that the gas molecules remain adsorbed in the pores of the material for imaging in the TEM.

This workflow was used on Co(bdp) (bdp^{2-} = 1,4-benzenedipyrazolate), a MOF in which adsorption induces a structural phase transition. Scanning nanodiffraction or “4D-STEM”[3] was employed to map the change in lattice parameters upon desorption. First, 4D-STEM at cryogenic temperature was used to image several crystals of CO2-dosed Co(bdp). To induce a phase transition, the sample was then heated to room temperature, and 4D-STEM was carried out on the same crystals. A change in lattice spacing was observed after warming, indicating the release of CO2 from the framework. Measured lattice spacings around 13 Angstroms suggest the framework itself, rather than dry ice, is being imaged. In the future, larger ensembles of crystals will be scanned to investigate the heterogeneity of adsorption, and the methodology will be used on an air-stable, industrially relevant framework that is isostructural to Co(bdp).

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5:00 PM CH02.04.02
Effect of Lithium Ion in Block Copolymer Electrolytes Phase Separation Process by using 4D-STEM Min Chen[1,2], Xi Jiang[2], Vivaan Patel[1], Karen Bustillo[2], Lorena Grundy[1], Nitash Balsara[1,2], Benjamin Savitzky[2], Steven Zeltmann[1,2], Ronald Zuckermann[2,2] and Andrew M. Minor[2,1]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Polymers that dissolve lithium ions are promising electrolyte materials for the next generation of rechargeable batteries. Both high mechanical stability and high ionic conductivity can be achieved through microphase separated block copolymer electrolytes by using one phase to conduct ions while the other provides rigidity[1]. The ion transport properties of such composite materials are not easily predicted solely from ion transport properties of the conducting domain alone [2], as the microphase and morphology play an important role in electrochemical performance [3, 4]. In previous research, heavy element staining bright field imaging and Energy-filtered transmission electron microscopy spectrum-imaging (EFTEM-SI) have been used to study PS-*b*-PEO [1, 2, 5]. Here, we utilize cryo-4D-STEM (four-dimensional scanning transmission electron microscopy) to investigate both the polymer morphology as well as the crystallinity as a function of Li concentration. 4D-STEM is a technique by which a nearly parallel electron nanoprobe is rastered across a sample (two dimensions in real space), recording the diffraction pattern (two dimensions in reciprocal space) at each scan point.[6] The diffraction patterns acquired form a 4D dataset provide real space information about the phase distribution and orientation of the polymer materials. It is a powerful tool to unveil the microphase of PS-*b*-PEO and provide further information about how the structure effects electrochemical performance.[2, 3]

Adding lithium salt into PS-*b*-PEO is a crucial step for real applications. Here we used mixtures of poly (styrene-block-ethylene oxide) copolymers (SEO) and bis(trifluoromethane)sulfonimide lithium salt (LiTFSI). By utilizing an air-free glove box and a cryo-transfer holder, we have established a workflow that avoids air exposure to these air-sensitive samples. 4D-STEM was later applied to show how the phase and DPs change when lithium concentrations change from r = 0 to 0.1. We calculated and carefully controlled the beam damage and successfully produced 4D-STEM results in cryo-condition. Compared with traditional RuO_4 staining 4D-STEM bright field imaging, 4D-STEM is shown to produce similar phase information without using toxic chemicals. Furthermore, 4D-STEM can provide additional phase distribution and orientation information inside the crystalline phase. The relation between the electrochemical performance and phase distribution, in relation to the crystallinity with and without the Li salt will also discussed.

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5:00 PM CH02.04.03
Carbon-Silica Hybrid Microporous Membranes for Gas Separations Jong Suk Lee, Hyun Jung Yu and Ju Ho Shin; Sogang University, Korea (the Republic of)

Membrane-based gas separation requires highly delicate engineering of molecular structures for the desired separation performance. For instance, natural gas processing including CO_2/CH_4 and N_2/CH_4 separations or olefin/paraffin separation involves a minimal molecular size difference of less than 0.5 Å. However, the extent of improvement in separation performance via engineering the chemical structure of polymeric membranes is very limited due to the trade-off relationship between permeability and selectivity. Moreover, most polymeric membranes are susceptible to condensable gas-induced plasticization at high pressures, suffering from significant selectivity loss. Carbon molecular sieve (CMS) membranes are promising molecular sieving candidates to overcome the intrinsic drawbacks of polymeric membranes including the limited separation performance and weak plasticization resistance. Recently, our group proposed a new approach to engineering the selective micropore structure of CMS membranes for various gas separations, including CO_2/CH_4, N_2/CH_4, or C_3H_6/C_3H_8 separation by pyrolyzing homogeneous blends of polyimide and ladder-structured polysilsesquioxanes. In particular, the SiOx phases in a carbonaceous matrix contributed to enhancing the molecular sieving ability of the resultant carbon-silica hybrid microporous membranes for various gas separations. In addition, our newly proposed approach enabled the formation of asymmetric CMS hollow fiber membranes with an excellent separation performance owing to the enhanced thermal stress resistance.

SESSION CH02.05: Advances in Cryogenic Transmission Electron Microscopy and Spectroscopy for Energy Materials IV
Session Chairs: Shelly Michele Conroy and Andrew Minor
Thursday Morning, April 13, 2023
InterContinental, Fifth Floor, Howard

8:30 AM *CH02.05.01
Recent Developments in S/TEM Technology Enabling Low-Dose, Low-Temperature, and Low-kV Observation of Beam-Sensitive Energy Materials Anahita Pakzad, Cory Czarnik and Ray Twesten; Gatan Incorporated, United States

Observing materials at atomic resolution gives us insight into how these systems operate and their failure mechanisms. This understanding is required to develop clean energy technology for a sustainable future on earth. In most cases, the key materials of the system under study (e.g., lithium batteries, perovskite solar cells, and MOFs/COFs) are sensitive to moisture, air, and electron beam irradiation, thus making it quite challenging, and in some cases, even impossible to succeed if conventional S/TEM methods are applied.
Using results from various materials, we will review some of these challenges. We will highlight how recent developments at Gatan in specimen holder (cryo-transfer vacuum holder), detection technology (high-speed electron counting direct detectors for imaging, diffraction, and EELS), and software (*in-situ* and multi-modal data acquisition and processing) enable the observation of such beam-sensitive materials at low dose, low temperature, and low accelerating voltage.

9:00 AM *CH02.05.02
Accessing the Solid-Liquid Interface of Materials at the Nanoscale Using Cryogenic Electron Microscopy and Spectroscopy Patricia Abellan[1], Helene Roberge[1,2], Aekta Upadhyay[1], Laura Samperisi[1], Eric Gautron[1], Baptiste Charbonnier[3], Angelique Galvani[3], Philippe Moreau[1], Jean Le Bideau[1], Pierre Weiss[3], Valérie Geoffroy[3], Estelle Couallier[2] and Jay LaVerne[4]; [1]Institute of Materials of Nantes (IMN) Jean Rouxel, Nantes University - CNRS, France; [2]Nantes Université-CNRS, France; [3]Nantes University, INSERM U1229, France; [4]University of Notre Dame, United States

Cryogenic transmission electron microscopy allows for the observation of samples in near native conditions and for higher electron beam tolerances than room temperature observations. Crucially, it provides the opportunity of obtaining quantified information from solid-liquid interfaces. In practice, accessing the solid-liquid interface at high-resolution represents specific challenges that are sample dependent and that must be addressed. Typically, sample preparation for cryo-(S)TEM is central and as a matter of fact, a significant bottleneck in many experiments. For the case of hard-soft interfaces in hydrated systems there are additional challenges which arise by the mismatch between the bio(chemical), mechanical and physical properties of both sides of the interface. Imaging conditions that are suitable for the different electron scattering produced by the different materials must be found and there can be limitations by the fact that a specific site within the sample (with a specific orientation) must be accessed. In this presentation, I will show our latest experimental results and discuss the specific challenges met on the application of 3D Cryo-FIB/SEM to the study of hard-soft tissue interfaces, to probe biomolecules fouled in polymeric filtration membranes and for the analysis of biomaterials interfaces. One specific challenge that is common to all experiments in hydrated samples is to understand the effect of the electron beam in our observations to disregard possible artefacts. Despite the more limited diffusion of secondary species at cryogenic temperatures, the high-energy electron beam used to probe the sample will unavoidably induces chemical processes due to radiolysis. Methods to directly probe the effects of radiation chemistry inside the EM have not been developed yet. In this talk, I will also present our investigations combining scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) on ice and discuss the effects of high-dose rate electron irradiation on water and on water-solid interfaces in the EM.

9:30 AM CH02.05.03
Dedicated Cryogenic Workflows for Atomic STEM Based Analysis on Lithium Based Battery Materials Paolo Longo[1], Zhao Liu[1], Maarten Wirix[1], Eric Van Cappellen[1], Minghao Zhang[2], David Foord[1] and Y. Shirley Meng[3]; [1]Thermo Fisher Scientific, United States; [2]University of California, San Diego, United States; [3]The University of Chicago, United States

In the past decade, the rapid growth of electric vehicles and consumer electronics market leads Li-ion batteries to attract significant attention. In order to further advance their performance for higher energy and better safety, fundamental understanding of battery materials structures and chemistry is essential. Nowadays, in order to pursue higher battery performance, more and more materials used in battery are beam sensitive and inherently air sensitive. This brings challenges to preserve their native structure and property via routine electron microscope practice.
Low-dose EELS STEM analysis carried out at cryogenic temperature on a Krios (S)TEM under cryogenic conditions has proven to be a very successful approach to study the solid electrolyte interface (SEI) in the Li metal anode region. The main challenges that until recently has limited the accurate investigation of SEI samples are the extreme sensitivity to air and probing sources such as the electron beam. However, by combining the cryo transfer approaches developed for life science tools and the extra stability of the dedicated cryo-stage in the Krios, it was possible to successfully carry out, morphological, chemical and tomography studies of the solid electrolyte interface region in Li-anodes [1].
Motivated by cryogenic electron microscope (Cryo-EM) technology in structural biology, the application and challenges of cryo-EM in battery research is discussed here.

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9:45 AM CH02.05.04
Cryogenic Analytical Transmission Electron Microscopy for Multivalent Ion Based Energy Storage Kevin R. Zavadil, Scott A. McClary, Kathryn Anderson Small and Paul Kotula; Sandia National Laboratories, United States

Limited knowledge of the chemistry and time dependent formation of Ca or Mg solid electrolyte interphases exists as current tools do not combine surface sensitivity, high spatial resolution, chemical specificity and preservation of the electrolyte environment. In response to this challenge, we have developed and demonstrated cryogenic transmission electron microscopy (cryo-TEM) combining the above attributes to determine the identity and properties of anode interphases that enable long cycle lifetimes in emergent Mg and Ca metal batteries. We find that a nanometric, heterogeneous oxide, not a hydride as previously thought, is the interphase responsible for reversible Ca cycling in a calcium borohydride - tetrahydrofuran electrolyte. Ca^{2+} conductivity in such a ubiquitous material, specifically along oxide, borate, and carbonate phase boundaries, raise the possibility of controlling SEI formation to support working cation conductivity in a broader class of chemistries. We demonstrate a strong dependence of SEI composition and properties on Ca and Mg cation solvation structure, highlighting the possibility of directing reactivity by controlling speciation within the electrolyte. In this presentation, we explore this concept of directing reactivity and correlate outcomes with SEI performance.

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10:00 AM BREAK

10:30 AM *CH02.05.05

Gas Injection System Free Cryogenic Focused Ion Beam Sample Preparation for Complementary Cryogenic Scanning Transmission Electron Microscopy and Atom Probe Tomography James O. Douglas[1], Shelly Michele Conroy[1], Finn Giuliani[1] and Baptiste Gault[1,2]; [1]Imperial College London, United Kingdom; [2]Max-Planck-Institut für Eisenforschung GmbH, Germany

The Imperial Centre for Cryo Microscopy of Materials (I(CM)^2) is a new facility at Imperial College London for the development and application of cryo microscopy to environmentally sensitive materials. The facility consists of the three state of the art microscopes (Cameca Local Electrode Atom Probe 5000 XR, FEI-Thermofisher Scientific Helios Hydra DualBeam with cryo-stage and FEI-Thermofisher Scientific Spectra 300 with cryo-holders) connected via an inert gas glovebox with cryo-vacuum transfer capability. By combining the complementary capabilities of these instruments, nanoscale compositional and structural analysis on environmentally sensitive materials of interest to a wide range of fields can be achieved.

Cryogenic focused ion beam (cryo-FIB) sample preparation for site specific liftout has significant challenges compared to the standard room temperature process flow. A number of applications that require cryo-FIB have successfully bypassed the requirement for liftout such as on-grid thinning for cryo electron microscopy (cryo-EM) [1] or “satellite dish” samples for Atom Probe Tomography (APT) [2]. However, there are many number of situations in life sciences and materials science where the cryo-FIB liftout stage is essential and so reliable and reproducible processes to enable this to become routine are required. Complementary Scanning Transmission Electron Microscopy (STEM) and APT analysis on the same sample [3] is increasingly commonplace and the application of this to materials requiring cryo-FIB is an emerging field of interest. This requires samples to be fabricated and mounted in a manner that is appropriate for the specific requirements for high yield and data quality from both techniques.

Room temperature FIB liftout generally uses site specific decomposition of an organometallic precursor gas supplied by a Gas Injection System (GIS) to provide protective layers and to attach liftout lamella to micromanipulators and support structures such as grids. If this gas is released into a FIB chamber with a cryogenically cooled stage then the gas immediately condenses. The thickness of this condensate is hard to control, it requires “curing” via an electron or ion beam to become conductive and using it significantly increases the difficulty of the liftout process [4]. GIS-free cryo-FIB liftout of TEM lamelle using redeposition methods has been shown to be viable [5] [6] and a cryo-FIB approach using a combined controlled cryogenic GIS deposition and redeposition has been demonstrated for APT samples [7] but has not been optimised for the extreme conditions experienced during APT analysis.

In this presentation, we demonstrate a reproducible, GIS-free, process flow for cryo-FIB liftout and mounting of APT samples using selective resputtering [8] of an in-situ tungsten micro-manipulator. APT samples made using cryo-FIB liftout from single crystal silicon using this method have been successfully analysed and the data collected was found to be comparable in quality to that collected from commercial pre-sharpened silicon calibration specimens (Cameca) [9]. Progress of this approach and applications of this process to facilitate cryo-FIB sample preparation for complementary cryo-STEM and APT on the same sample will be discussed along with the numerous challenges of cryo and vacuum transfer between instruments involved in this process.

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11:00 AM CH02.05.07

Imaging the Solid-Electrolyte Interphase in Lithium Metal Batteries with Cryogenic Electron and Ion Microscopy Hyeong-Jun Koh, Eric Detsi and Eric A. Stach; University of Pennsylvania, United States

The solid-electrolyte interphase (SEI) controls the transport of ions and electrons during battery operation. Thus, understanding its structure and chemistry is necessary to understand battery function. However, there are significant challenges in characterizing the SEI: it is nanoscale in dimension, heterogeneous in composition, and comprised of organic and inorganics species. The first two points suggest that electron and ion microscopy methods are needed, as they have the appropriate spatial resolution. However, organic materials present significant challenges to these approaches, as these materials are usually susceptible to irradiation damage.

Cryogenic transmission electron microscopy (cryo-TEM) has recently been used to observe lithium metals and their SEIs without electron beam damage. Most cryo-TEM research has probed lithium by electrochemically growing lithium on copper grids or extracting it from current collectors. These approaches necessitate removing liquid electrolytes from active materials by drying and washing before being characterized. However, it is unclear whether the structure and chemistry of the SEIs remain intact during such processes.

Vitrification is one way to observe the SEI: this is done by rapidly freezing liquid electrolyte media. However, as the vitreous liquid electrolytes that cover the active materials are often too thick, it is difficult to probe nanoscale assemblies of SEIs at high resolution through subsequent cryo-(S)TEM imaging. It is, therefore, crucial to develop a strategy to control the thickness of vitrified samples to obtain the desired electron transparency.

Cryogenic focused ion beam microscopy methods (cryo-FIB) allow thickness control through the cryogenic lift-out process; samples can be lifted out from specific sample areas and subsequently attached to TEM support grids for further thinning. Using the cryogenic lift-out process to characterize SEIs in energy storage materials has two advantages: (i) the thickness of the sample of interest can be carefully controlled through FIB milling and (ii) the configuration of battery structures can be preserved and selectively extracted without losing spatial information surrounding the region of interest.

In this work, we have used lithium and its SEI as a model material to identify how ion and electron beam damage can occur and how cryo-FIB can mitigate them. We also demonstrate the potential of cryo-TEM analysis for beam-sensitive battery materials using cryo-FIB.

In this talk, we will answer the following three critical questions:
1. We will answer how lithium gets damaged by ion beam milling at cryogenic temperatures.
2. We will discuss ion beam damage to SEIs.
3. We will finally show the structural alteration of SEIs before and after liquid electrolytes are removed, demonstrating the possibility of high-resolution imaging of nanoscale features in SEIs with vitrified electrolytes.

11:15 AM CH02.05.08
The True Role of Ethanol in Lithium-Mediated Ammonia Synthesis as revealed by Cryo-Electron Microscopy Olivia Westhead[1], Shelly Michele Conroy[1], Baptiste Gault[1,2], James O. Douglas[1] and Ifan E. Stephens[1]; [1]Imperial College London, United Kingdom; [2]Max-Planck-Institut für Eisenforschung GmbH, Germany

Ammonia is one of the highest value industrial chemicals, with 50% of global agriculture using industrially produced ammonia in fertiliser. However, the industrial method to make ammonia, the Haber-Bosch process, is extremely environmentally damaging. The requirement for extreme operating conditions and reliance on methane derived hydrogen results in an enormous energy and CO_2 penalty[1]. A better method of ammonia production would be distributed, powered by renewable energy, and carbon free. Electrochemical ammonia synthesis via the Nitrogen Reduction Reaction (NRR) could provide a solution. The only rigorously verified method of electrochemical ammonia synthesis is the lithium-mediated nitrogen reduction system[1,2]. This system utilises a lithium salt and organic electrolyte to catalyse the reaction between dinitrogen gas and a non-aqueous proton donor, which is often ostensibly sacrificial ethanol. While great strides have been made in terms of Faradaic efficiency, stability and activity[1,3], there are still numerous unanswered questions about exactly why this system is the sole example of efficient electrochemical ammonia synthesis.

One aspect of the lithium-mediated paradigm that could make it unique is the formation of the Solid Electrolyte Interphase (SEI) on the surface of the working electrode[1]. This electronically resistive but ionically conductive SEI is formed from the decomposition of the organic electrolyte and lithium salt on the application of the highly reductive lithium plating potential, analogous to that formed in lithium-ion batteries[1]. Recent work[4] reveals that the chemical makeup of the SEI is critical for system stability and controlling the access of reactants (Li^+, N_2 and protons) to the electrode surface. The role of ethanol as a proton donor has been recently disputed and it is proposed that it may in fact play a greater role in NRR-SEI formation[5,6]. It would be beneficial to be able to study NRR-SEI morphology changes with ethanol concentration via electron microscopy. However, the NRR-SEI is highly beam and air sensitive, making both analysis in and transport to the microscope complex. Therefore, a specialised air-free transfer system and cryogenic analysis is required.

While previous cryo-microscopy investigations suggest changes in NRR-SEI makeup with and without ethanol[6], we present a systematic study of the effect of changing ethanol concentration on NRR-SEI morphology via cryo-Scanning Electron Microscopy and cryo-Focussed Ion Beam milling, and propose how NRR-SEI morphology may affect Faradaic selectivity. Such work also paves the way for the future investigation of the SEI via cryo-Transmission Electron Microscopy. In addition, we present a novel method of cryogenic specimen preparation for Atom Probe Tomography (APT)[7]. APT will allow us to examine low atomic number elements, such as Li[8], as well as the effect of ethanol concentration on reactant transport through the SEI.

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SESSION CH02.06: Advances in Cryogenic Transmission Electron Microscopy and Spectroscopy for Quantum Materials V
Session Chairs: Miaofang Chi and Shelly Michele Conroy
Thursday Afternoon, April 13, 2023
InterContinental, Fifth Floor, Howard

1:30 PM *CH02.06.01
Vacuum Transfer System for EM Application Combined with a Cryogenic Technique Hiroya Miyazaki; Mel-Build Inc., Japan

Low-carbon efforts to realize a sustainable society are being vigorously pursued around the world. Rechargeable batteries, which are recognized as one of the most important nextgeneration energy technologies, are urgently needed not only for mobile applications such as cell phones and notebook PCs, but also for applications in transportation technology such as electric vehicles to promote low-carbon society.

Among these, lithium-ion battery materials, which are attracting attention because of their high energy density, react with water in the atmosphere when exposed to air, resulting in deterioration. In most cases, however, the sample is exposed to the atmosphere when it is transported to the electron microscope after preparation, making the observation itself difficult. Even if the sample can be transported to the electron microscope without being exposed to the atmosphere, it must be observed under cooled conditions because the crystal structure of the material tends to change due to electron irradiation during observation.

In order to conduct research on such samples, it is essential to develop a multifunctional system that can perform the entire transport process from sample preparation to electron microscopic observation under non-atmospheric conditions, as well as observation under cooled conditions. Against this background, Melville has been working on the development of non-atmospheric exposure and sample cooling techniques to meet the technical requirements of electron microscopy applications.

In this presentation, we will introduce our new TEM holder with non-exposure cooling and Peltier-cooled stage for FIB-SEM, which were developed based on the technologies we have developed so far.

2:00 PM *CH02.06.02

Cryogenic STEM Visualizations of Correlated Electronic Order Ismail El Baggari; Harvard University, United States

Scanning transmission electron microscopy (STEM) is highly sensitive to lattice degrees of freedom and enables tracking of lattice displacements with sub-Angstrom resolution and picometer precision. This has ushered novel visualizations and discoveries of functional atomic displacements in ferroelectric materials, magnetoelectric oxides, and 2D materials. Due to stringent stability requirements, the overwhelming majority of high-resolution STEM measurements are limited to room temperature or above. In many classes of correlated electronic materials, however, subtle and exotic ground states emerge exclusively below room temperature. Achieving cryogenic capabilities in STEM is therefore paramount to accessing and probing low temperature phases including high-temperature superconductivity, charge order, metal-insulator transitions, and more.

I will illustrate recent, successful applications of high-resolution cryogenic STEM for discovering and understanding novel correlated phases at low temperature (~90 K) [1,2,3]. I will focus on charge order, a state in which the electrons and the lattice form superstructures that break the translational symmetry of the atomic lattice. In an overdoped manganite, we directly visualize intrinsic topological defects and show how these local fluctuations alter the periodicity and long-range order of incommensurate charge order stripes [1]. In a half-doped manganite, we address the long-standing question of whether charge order resides on the sites or bonds, discover an exotic intermediate state which breaks inversion symmetry, and find that non-linear couplings between distinct lattice distortion modes locally determine phase competition [3]. These cryogenic STEM results pave a clear path to imaging low temperature electronic phases with high resolution and precision.

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2:30 PM BREAK

3:30 PM CH02.06.03

Observation of Charge Ordering in $EuAl_4$ via Cryogenic Scanning Transmission Electron Microscopy Haoyang Ni[1,2], Jian-Min Zuo[1] and Miaofang Chi[2]; [1]University of Illinois, Urbana-Champaignaign, United States; [2]Oak Ridge National Laboratory, United States

$EuAl_4$ is one of charge density wave materials where the lowering of the crystal symmetry at a phase transition give rise to incommensurate modulation[1–4]. CDW transition occurs below 145.1 K and exhibits four successive magnetic transitions below 16 K[2]. Very recently, a chiral spin skyrmion structure was reported, making it a rare case where one could observe the co-exitance of exotic magnetic order and charge order[5,6]. CDW phase transition is accompanied by symmetry-breaking atomic displacement in general. Knowledge of the atomic structure, especially which and how atoms are displaced and how CDW gives rise to these exotic physical properties, is thus of utmost importance for understanding nontrivial quantum properties.

Here, we combine atomic resolution Scanning Transmission Electron Microscopy (STEM) combined with scanning convergent beam electron diffraction (SCBED) at cryogenic temperature, enabled by the development of a new liquid nitrogen holder. We show this combination allows for the visualization and determination of the atomic structure in $EuAl_4$. SCBED is achieved by acquiring electron diffraction patterns formed by a highly coherent nanometer-size electron probe at different specimen locations. With the high-speed direct electron detector, diffraction patterns from a field-of-view of 200 nm with sub-nanometer sampling can be achieved, this powerful technique allows the mapping of interatomic distances in real space. This talk will show that the atomic displacement changes the intensity of Bragg reflection, and CDW can be visualized by diffraction contrast. Analysis of CBED patterns shows a reduction of inversion symmetry, and dominant displacement modes can be identified. Imperfections of CDW, such as dislocations and phase boundaries, can be revealed by interatomic distance mapping. Further, whether a relatively higher temperature CDW phase could be a precursor of the lower magnetic phases remains an open question.

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3:45 PM *CH02.06.04

Taking Low Energy Excitations at High Spatial Resolution to Low Temperatures Jordan A. Hachtel; Oak Ridge National Laboratory, United States

Over the last decade, modern monochromated electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) has achieved the ability to combine ultrahigh energy and spatial resolution simultaneously. As a result, a new wave of experiments on ultralow energy excitations, such as phonons, phonon-polaritons, molecular vibrations, shallow electronic structure, and infrared optical excitations have achieved exciting results in the STEM.

The emergence of monochromators that can reach the mid-infrared has largely coincided with the development of stable cryogenic TEM holders that can reach ultralow temperatures. However, due to the relative recency of both techniques achieving consistency and accessibility only limited opportunities have been available to combine them on the same materials systems. Here, I will show recent work at ORNL on the combining cryo-STEM and monochromated EELS. Focusing on cryogenic phase changes, emergent behavior at cryo-temperatures, and the effect of low-temperatures on beam-sensitive materials.

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4:15 PM *CH02.06.05
Electron Spectroscopy at Cryogenic Temperatures for Nano-Optics Luiz H. Galvao Tizei; Centre National de la Recherche Scientifique, France

Fast electrons spectroscopies have had huge success for nano-optics [1]. For phase-locked excitations (e. g. surface plasmons) electron energy loss spectroscopy (EELS) is an optical extinction analogue and cathodoluminescence (CL) that of optical scattering [2]. For "incoherent" excitations, EELS also measures optical extinction for atomically thin materials [3,4,5], while CL measures spectra similar to off-resonance CL [3]. For many technologically and fundamentally interesting materials, including semiconductors, experiments at cyrogenic temperatures is a requirement. For example, many quasi-particles (such as excitons and trions) are only stable at low temperatures, due to their low binding energy. This will be discussed in this contribution, including variable temperature measurements down to about 100 K. This will be used as a motivation for still colder experiments (to be realized).

Despite clear benefits (link to structural and chemical information, atomic-scale spatial resolution and broadband excitation), electron spectroscopies have some penalties which limit applications to nano-optics: lack of resonant excitation and polarization degrees of freedom and still limited spectral resolution (EELS). In this seminar, we will discuss how temporally resolved spectroscopies can mitigate some of these issues.

The lack of excitation energy control can be circumvented by measuring the energy lost by each electron in time coincidence EELS-CL experiments. This has been achieved using a nanosecond-resolved direct electron detector (Timepix3) [6], correlation electronics and a PMT. The information retrieved here is analogous to that of photoluminescence excitation spectroscopy (PLE), hence we name it cathodoluminescence excitation spectroscopy (CLE) [7]. With it, we explored the relative quantum efficiency of different excitation energies and decay pathways towards 4.1 eV defect photon emission in h-BN flakes [7].

The current impressive energy resolution achieved with electron beams (~meV range) is still orders of magnitude away from the necessary one to access the physics of lifetime-limited high quality factor optical modes, such as cavity modes in dielectric spheres [8]. As proposed more than a decade ago [9], electron energy gain spectroscopy (EEGS) should easily overcome this limitation. Here, we will discuss EEGS experiments using fast electron blankers (~ns) in a continuous-gun electron microscope, allowing energy resolution delivered by laser beams compatible with a state-of-the-art electron microscope performance. As an example, we will show measurements of whispering gallery modes in dielectric spheres separated by a few hundreds μeV with energy sampling in the μeV scale [10].

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SESSION CH02.07: Advances in Cryogenic Transmission Electron Microscopy and Spectroscopy for Quantum Materials VI
Session Chairs: Miaofang Chi and Shelly Michele Conroy
Friday Morning, April 14, 2023
InterContinental, Fifth Floor, Howard

8:30 AM *CH02.07.01
Probing Properties and Dynamic Behaviors of Topological Polar States by 4D STEM Xiaoqing Pan; University of California, United States

Topological polar solitions such as domain walls, polar voritices, skyrmions, etc, in ferroelectrics have attracted much attention owing to their unique functionalities and potential applications in electronic devices. Recent advances in transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS) provides powerful tools to study the structure, properties, and dynamic behaviors of nanostructures with atomic resolution. In this talk, I will show how ferroelectric domains nucleate and evolve under applied electric field in TEM. Using quantitative TEM, we can measure and map the electric polarization of nanodomains, vortices and other polar solitons with the atomic resolution. Recently, we have developed a novel four-dimensional STEM (4D STEM) method that can directly map the local electric field and charge density of crystalline materials in real space with sub-angstrom resolution.[1]. I will also show that skyrmion-like polar nanodomains can be created in lead titanate/strontium titanate bilayers transferred onto silicon and can be switched from one type to another by an applied electric field, which substantially modifies their resistive behaviours.[2] The polar-configuration-modulated resistance is ascribed to the distinct band bending and charge carrier distribution in the core of the two types of polar texture. The integration of high-density (more than 200 gigabits per square inch) switchable skyrmion-like polar nanodomains on silicon may enable non-volatile memory applications using topological polar structures in oxides.

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9:00 AM *CH02.07.02
Phase Contrast Imaging of Non-Collinear Spin Textures with Lorentz Microscopy Robert Streubel; University of Nebraska-Lincoln, United States

Transmission electron microscopy is a critical asset to basic and applied sciences research as it enables the characterization of, e.g., structural order on the atomic scale. This includes not only crystalline structures and orientation, but also their temporal evolution, behavior at and across interfaces, and disordered, amorphous materials leveraging tomographic imaging. To date, the vast majority of electron microscopy harnesses the superior spatial resolution owing to a de Broglie wavelength of a few picometers. Taking advantage of the wave properties of coherent electrons and their interaction with electromagnetic fields, e.g., matter, allows for enhancing sensitivity and resolution and visualizing the spin degrees of freedom in the form of the in-plane magnetic induction. These experiments are based on the detection of the electron phase using off-axis or in-line holography. The former requires a biprism, the latter works in Fresnel mode/Lorentz mode with post processing involving a phase retrieval algorithm, such as transport-of-intensity or Gerchberg-Saxton. I will discuss the fundamentals, including pros and cons, of phase contrast imaging and review recent applications to visualize non-collinear spin textures in magnetic films in the presence of magnetic bias fields and cryogenic temperatures triggering magnetic phase transitions and spin fluctuations. One focus will be on chiral spin textures in amorphous materials where exit wave reconstruction allows to disentangle electrostatic, magnetization, and magnetic field contributions to the phase shift [1,2].

[1] RS et al., Adv. Mater. DOI: 10.1002/adma.201800199
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9:30 AM *CH02.07.03
Cryogenic Lorentz Transmission Electron Microscopy of van der Waals Ferromagnetic Heterostructures Charudatta Phatak[1], Arthur McCray[1,2], Yue Li[1], Rabindra Basnet[3], Krishna Pandey[3], Jin Hu[3], Daniel Phelan[1], Wei Wang[1], Xuedan Ma[1] and Amanda Petford-Long[1,2]; [1]Argonne National Laboratory, United States; [2]Northwestern University, United States; [3]University of Arkansas, Fayetteville, United States

Magnetic skyrmions are topologically protected magnetic spin textures that can exist both as individuals and in dense quasiparticle lattices. Manipulation of skyrmions then requires a detailed understanding of their stability. While individual skyrmions have been studied extensively, their collective behavior in skyrmion lattices is poorly understood, both on the micron-scale where lattice ordering is observed and the nanoscale where inter-skyrmion interactions occur. In this work, we will present the observation of Néel skyrmion lattice ordering in the van der Waals (vdW) ferromagnet Fe3GeTe2 (FGT) using cryo-Lorentz transmission electron microscopy (LTEM). We will discuss the magnetic domains formed in FGT under various conditions of applied field and as a function of temperature. We will discuss the stability of skyrmions under applied fields and formation of domains with higher topological charge. In order to understand the collective behavior of these Néel skyrmions, when imaged with LTEM, we performed imaging of skyrmion lattices over a large field of view and employed a machine learning algorithm which applies a convolutional neural network (CNN) to identify skyrmion centers. We will discuss the local and global lattice order, and the observed thermal hysteresis in the order. Based on an analytical model, we can elucidate the collective behavior of skyrmion lattices to be dependent on the competition between the Zeeman energy and the domain energy.

10:00 AM BREAK

10:30 AM *CH02.07.04
Cryogenic Electron Holography and Differential Phase Contrast Imaging of Quantum Materials and Electron-Beam-Sensitive Materials Rafal E. Dunin-Borkowski, Penghan Lu, Fengshan Zheng, Lei Jin, András Kovács, Thibaud Denneulin, Qianqian Lan, Luyan Yang, Michael Feuerbacher, Joseph Vas, Michael Faley and Amir H. Tavabi; Forschungszentrum Juelich, Germany

Cryogenic transmission electron microscopy offers new prospects for studying quantum materials and electron-beam-sensitive materials. Here, we describe recent progress in the use of phase contrast techniques in the (scanning) transmission electron microscope, in combination with liquid nitrogen and liquid helium cooling, to obtain quantitative information about electromagnetic fields in nanoscale materials and to generate improved contrast at low electron dose from materials that are affected by irradiation damage.

The first examples involve the use of off-axis electron holography and Lorentz imaging at low temperature to study magnetic skyrmions in crystallographically chiral materials such as FeGe and magnetic flux vortices in superconducting materials such as NbN in focused ion beam milled samples that provide geometrical lateral confinement. The influence on the measurements of sample preparation damage, the direction and strength of an applied magnetic field and electrical current, as well as the presence of electron-beam-induced specimen charging, will be discussed.

The second examples involve the use of (integrated) differential phase contrast imaging in the scanning transmission electron microscope at low temperature to record atomic-resolution images of electron-beam-sensitive materials, including metal-organic frameworks, organic materials and minerals. The use of event-driven detectors, automation of experimental workflows and non-standard electron beam scanning protocols will be discussed.

Finally, new concepts for improved instrumentation for such experiments, including liquid-helium-cooled specimen stages, advanced magnetizing units, specimen holders for high frequency experiments, sample transfer cartridges and capabilities for in situ laser irradiation of the sample in the electron microscope, will be presented.

11:00 AM *CH02.07.05
Cryogenic Electron Microscopy for Quantum Materials Yimei Zhu; Brookhaven National Laboratory, United States

Quantum materials refers to a class of materials with exotic properties that arise from the quantum mechanical nature of their constituent electrons, exhibiting, for example, high-temperature superconductivity, colossal magnetoresistivity, multiferroicity, and topological characteristics. Quantum materials often have incompletely filled d- or f-electron shells with narrow energy bands and the behavior of their electrons is strongly correlated. One distinct characteristic of the materials is that their electronic states are often spatially inhomogeneous, thus is well suited for study using spatially resolved electron beams with its great scattering power and sensitivity to atomic ionicity. Furthermore, most of these exotic properties only manifest at very low temperatures, posing a challenge to modern electron microscopy. It requires extraordinary instrument stabilities at cryogenic temperatures with critical spatial, temporal, and energy resolutions in both static and dynamic manner to probe these materials. On the other hand, the ability to directly visualize the atomic, electronic and spin structures and inhomogeneities of quantum materials and correlate them to their functionalities creates enormous opportunities. At the most elementary levels of condensed matter physics, understanding the competing orders of electron, spin, orbital, and lattice and their degrees of freedom, the impacts of defects and interfaces, and the site-specific quantum phenomena and phase transitions that give rise to the emergent behaviors allows us to discover and control novel materials for quantum information science and technologies [1].

In this presentation, several of our research examples are selected to highlight the use of Cryo-EM to study strongly correlated quantum materials. We focus on the critical roles of heterogeneity, interfaces, and disorder in crystal structure, electronic structure, and spin structure to understand the physical properties of the materials. We show how electron diffraction and diffuse scattering analysis at low temperatures empowers us to reveal the nature of structural disorder and phonons under thermal equilibrium and far-from equilibrium [1]; how atomically resolved imaging and electron energy-loss spectroscopy at 10K can be used to understand the interface-enhanced superconductivity (Fig.1); and how to use Lorentz phase microscopy to explore the intriguing transformations among various topological chiral spin states under applied magnetic field at various cryogenic temperatures (Fig.2). Finally, we review our recent unprecedented development of a closed-cycle cryocooler for Cryo-EM without the need of refilling liquid He. The system is designed to reach a temperature as low as 4k with temperature stability and control better than a few mK.

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Acknowledgement

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11:30 AM *CH02.07.06
The Quest for New Frontiers in Cryo Electron Microscopy for Materials Sciences Juan C. Idrobo; University of Washington, United States

Modern scanning and transmission electron microscopes (S/TEM) are now almost ubiquitous in materials and biological sciences laboratories. They have radically enhanced our understanding matter at the atomic level, bringing unique information of structure, chemical composition, and electronic properties of materials. Moreover, the recent development of stable cryogenic TEM holders at temperatures ranging from liquid N_2 (100 K) to 300 K with electrical contacts, combined with aberration-corrected and monochromated electron optics has allowed S/TEM to study magnetic, structural and electronic phase transitions with unprecedented spatial and energy resolutions.

In this talk, I will present two examples of cryogenic STEM measurements done in a set of two-dimensional (2D) transition metal dichalcogenides (TMDs) samples. In the first example I will address excitonic dephasing in MoS_2. I will present experimental results that show how monochromated electron-energy-loss spectroscopy (EELS) can reveal the exciton-phonon coupling of a few layers of MoS_2 encapsulated in hexagonal boron nitride (hBN). The measurements are spatial localized beyond the diffraction limit of the associated optical excitation, indicated how STEM can be complementary to conventional optical probes. In the second example I will present measurements that show a spatial dependence of a moiré-exitonic coupling in a hBN/WSe_2/WS_2 heterostructure at LN_2 cryogenic temperatures. I will also present a geometrical phase analysis of the moiré structure that allows to reveal the strain on the lattice at large field of views (>30 x 30 nm^2) while still maintaining atomic resolution. Prospects and limitations of future experiment will be discussed in the detail during the talk.

SYMPOSIUM

April 11 - April 25, 2023

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SESSION CH03.01: Neutrons for the Study of Energy Materials
Session Chairs: Valeska Ting and Helen Walker
Tuesday Morning, April 11, 2023
InterContinental, Fifth Floor, Fremont

10:30 AM *CH03.01.01
Structure & Dynamics in Sustainable Energy Materials: The Crucial Role of Large-Scale Facilities Martin Mansson; KTH Royal Institute of

Technology, Sweden

Establishing a sustainable society is our century's grand challenge. Here, one of the main obstacles is how to efficiently harvest, store and utilize green energy. To facilitate such transition new generations of advanced functional energy and quantum materials needs to be developed. This includes understanding and controlling material properties on an atomic, or even subatomic, length-scale. Only recently, technological advancement in materials synthesis and characterization techniques have opened new possibilities for studying both structural and dynamic material properties on the length- and time-scales necessary for advancing the field. Here a new generation of large-scale research infrastructures with more powerful neutron, x-ray and muon sources have played an important role. This state-of-the-art research landscape is the main platform for the SMaRT research group at the KTH Royal Institute of Technology. We run a comprehensive scientific program for advanced development of sustainable energy materials as well as novel quantum materials, studied mainly by large-scale techniques **[1]**.

In this talk I will give the general background as well as a few examples that show that neutron scattering, and complementary techniques are both crucial and optimal techniques for advancing this important field. I will show our recent work on Li-/Na-/K-ion battery materials that reveal new possibilities to improve battery performance using strain/pressure as well as surface coating **[2-6]**. I will further show how *in-operando* measurements of porous carbon reveal novel insight into the synergy effect between structure and dynamics in H-storage materials **[7-10]**. Finally, I will showcase our more fundamental efforts into organic quantum materials that could be a key development towards future energy efficient information and communication technologies **[11]**.

In summary, I aim to show that our current research program has established an innovative and detailed insight into the atomic structure and ion-diffusion mechanisms, as well as their synergy. This now allow us to actively consider tuning of future energy related materials with improved functional properties. In our quest, the use of neutron scattering has clearly been a crucial component. To support continuous breakthroughs for science and technology, Sweden and Europe are currently making unprecedented investments with the development and construction of the European Spallation Source (ESS) **[12]**. We are in parallel also building the next generation of neutron users/experts within the Swedish national graduate school in neutron scattering (SwedNess) **[13]**.

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11:00 AM *CH03.01.03
Direct Observation of Dynamic Lithium Diffusion Behaviour in Nickel-Rich Cathodes Using *Operando* Muon Spectroscopy Serena Cussen[1], Innes McClelland[1] and Peter Baker[2]; [1]University of Sheffield, United Kingdom; [2]ISIS Pulsed Neutron and Muon Source, United Kingdom

Efficient and sustainable energy storage technologies will form a core element in decarbonising our energy system and batteries are one of those technologies which will enable that transition. Central to this is the development of new materials and methods which, for example, enable stable interfaces to improve power densities or mitigate degradation processes to improve energy densities. This talk details the use of muon spin relaxation spectroscopy as a local probe of diffusion dynamics in battery materials.
In this talk, I will discuss a new *operando* muon spectroscopy (μSR) method which can be applied to investigate how local Å-length scale diffusion and internal field properties change in the high nickel content cathode NMC811 during cycling. Our design of a new Battery Analysis by Muon (BAM) cell allows monitoring of diffusional properties with highly correlated structural changes in the unit cell during operating conditions.
The nature of μSR as a local probe means it reflects the diffusion rates at specific sites and from a site-to-site basis, in contrast with bulk measurements such as electrochemical impedance spectroscopy (EIS) which provides information on resistive interfaces and long-range charge transfer. In the case of the high nickel content cathode NMC811, we find that Li^+ dynamics increase most rapidly at the beginning of charge, before decreasing above 75% state of charge (SOC). We also interestingly observe a sensitivity of the static field distribution width parameter Δ, obtainable by μSR, to the TM redox activity and resultant TM-O bond length changes, with a correlation between the trends observed in dQ/dV, cyclic voltammetry and Δ. This observed sensitivity to changes in TM-O bond length is particularly intriguing for investigating anion redox in next-generation cathodes, where μSR can provide additional insights into ongoing challenges in stabilising anion redox behaviour.

SESSION CH03.02: Materials for Energy Conversion and Storage

Session Chairs: Alexander O'Malley and Valeska Ting
Tuesday Afternoon, April 11, 2023
InterContinental, Fifth Floor, Fremont

1:30 PM *CH03.02.01
Inelastic Neutron Scattering, A Unique Tool to Study Hydrogen In Materials Anibal J. Ramirez-Cuesta, Rafael Balderas and Yongqiang Cheng; Oak Ridge National Laboratory, United States

Inelastic neutron scattering can measure the vibrational spectra of materials on the whole range of vibrational motions (0-4400 cm−1) and effectively open up the field of neutron spectroscopy [1]. INS is a technique mainly used to study hydrogen-containing materials due to the high cross-section of hydrogen

[2].
The VISION spectrometer at the SNS in Oak Ridge, Tennessee, has increased overall flux at low energy transfers up to 40 times over its competitors and has unprecedented sensitivity.
In this paper, the author will present examples of the technique's unique capabilities for studying metal hydrides and molecular hydrogen in confinement.
In $ZrVH_2$, the inelastic neutron scattering spectra analysis reveals that these structures originate from hydrogen vibrations confined by neighboring hydrogens, partially at distances as short as 1.6 Å. This is an experimental demonstration of the violation of Switendick's criterion, which predicts the minimal possible hydrogen-hydrogen distance in a metal hydride is around 2.1Å.[3]
Inelastic neutron scattering (INS) and neutron diffraction (ND) experiments were performed at the VISION beamline, demonstrating the existence of rapid and efficient hydrogen clathrate hydrate formation in a confined nanospace. It shows that specially designed activated carbon materials can surpass these obstacles of hydrogen clathrate formation by acting as nanoreactors promoting the nucleation and growth of H2 hydrates. The confinement effects in the inner cavities promote massive growth of hydrogen hydrates at moderate temperatures, using pure water, with high-speed kinetics, and at lower pressures than the bulk system. [4]
Adsorption on various adsorbents of hydrogen and helium at temperatures close to their boiling points shows, in some cases, unusually high monolayer capacities. Theoretical and INS studies of molecular hydrogen on mesoporous silica demonstrate the formation of such a super-dense phase. [5]

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2:00 PM *CH03.02.02
Adsorption and Separations Processes Within Metal-Organic Frameworks Through Neutron Scattering Craig Brown[1], Hayden A. Evans[1] and Ryan A. Klein[2,1]; [1]National Institute of Standards and Technology, United States; [2]NREL, United States

Metal organic frameworks (MOFs) are crystalline materials that contain metal-ions or metal-ion clusters as nodes and organic ligands as linkers to form 1-, 2-, and 3-D structures. Their structural versatility and multifunctional properties have sparked much interest in advanced materials synthesis. Due to their modular nature, many of these materials can be constructed by design. Over the last decade there are several MOFs that reportedly have high surface areas allowing them to physically adsorb significant amounts of gas and/or exhibit significant separations performance. Adsorption of molecules in functionalized and high surface area microporous materials is of technological importance in a multitude of areas ranging from catalysis, drug delivery, chemical separations, and energy storage to personal care products. Through careful selection of the ligand and metal, which control pore size/shape and MOF-adsorbate interactions, their uptake properties can be tuned. Over the past several years we have focused our research efforts on understanding the properties of gas interactions within a variety of microporous materials with the goal of improving new optimal storage and separation materials.

2:30 PM BREAK

3:00 PM *CH03.02.03
Probing the Hydrogen Interaction with Supported Pt and Pd Catalysts by Inelastic Neutron Scattering Andrea Piovano[1], Eleonora Vottero[2], Riccardo Pellegrini[3] and Elena Groppo[2]; [1]Institut Laue-Langevin, France; [2]University of Torino, Italy; [3]Chimet SpA, Italy

Pt and Pd nanoparticles on carbonaceous supports are widely employed as heterogeneous catalysts for hydrogenation reactions, and find application in fundamental industrial sectors such as fine chemistry or as fuel cell electrocatalysts. Carbonaceous materials are also largely investigated as hydrogen storage materials, and the introduction of metal nanoparticles was demonstrated to be able to increase the hydrogen uptake of the material. Albeit their routine use, many details about their interaction with H_2, and hence on their hydrogenation catalytic activity, are still not completely understood.
In this presentation, I will make a journey into the recent advances we made on the understanding of several key aspects of these catalysts: the influence of the carbon activation method and possible post-treatment on the catalytic activity [1,2]; the morphology of the H-terminated graphenic domains [3]; identification and quantification of functional groups [4]; the active hydrogen species in the catalytic process [5]; the dynamical nature of the active species [6,7,8]; the catalysts support interaction including spillover effects [5,8]; the differences in behavior between gas and liquid phase [7,9]. All such effects are those that together finally shape catalytic activity and selectivity.
In this respect, Inelastic Neutron Scattering played a major role thanks to its high sensitivity to hydrogen. INS spectra display an unprecedented quality, allowing the detection of extremely small changes on real catalysts. The data obtained for this same set of carbons and catalysts from other laboratory techniques, offered us the possibility to critically compare the results without the issue of sample reproducibility. When necessary, measurements were made on the same catalysts supported on alumina, to be able separate effects due to active phase or support.
Overall, our findings provide important insights for better understanding the complex nature of the support-catalysts system and the interaction between hydrogen and Pt and Pd-loaded catalysts.

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3:30 PM CH03.02.05
***In Situ* Small-Angle Neutron Scattering Study of Hydrogen Physisorption in Nanoporous Carbons** Sebastian Stock[1,2], Malina Seyffertitz[1], Bruno Demé[2], Viviana Cristiglio[2], Nikolaous Kostoglou[3] and Oskar Paris[1]; [1]Montanuniversität Leoben, Chair of Physics, Austria; [2]Institute Laue Langevin, France; [3]Montanuniversität Leoben, Chair of functional materials and materials systems, Austria

When produced with renewable energy, molecular hydrogen (H_2) is considered an environmentally beneficial alternative to carbon-rich fossil fuels. However, one of the major challenges to the widespread use of H_2 as a fuel is its efficient and secure storage. Physisorption of molecular H_2 in high-surface area nanoporous materials is regarded as an alternative volume-efficient solution as compared to high-pressure tanks [1]. Due to the low binding energy between the gas molecules and solid surfaces, it is associated with quick adsorption/desorption kinetics and complete reversibility. H_2 adsorbs preferentially within very small, sub-nanometer-sized pores due to their overlapping potentials from opposing pore walls [2,3]. Experimental observations of the underlying mechanisms during physisorption can be facilitated by neutron scattering techniques, as neutrons strongly interact with the hydrogen nucleus. In this study, we employed in-situ small angle neutron scattering (SANS) during gas sorption to investigate the physisorption of H_2 and D_2 in a micro-/mesoporous activated carbon material at cryogenic temperatures. The SANS measurements were carried out with the high resolution diffractometer D16 at the Institute Laue-Langevin, which allowed covering a wide range of the scattering vector. The SANS data indicate that H_2 fills the small micropores at very low pressures, and with increasing pressure a densification of the adsorbed gas in the micropores, as well as a filling of the larger mesopores takes place. Using established models for the scattering from nanoporous carbons [4], with strong emphasis towards different contrast scenarios to analyze the scattering data [5,6], allowed to quantify the density evolution as a function of pressure within the two distinct pore size regimes [7]. The strong interaction of neutrons with the hydrogen nucleus and the different interaction with D_2 enabled us to probe the density of gas molecules in their confined spatial arrangement, as well as to evaluate isotope effects .Our results suggest that the isotope substitution of H_2 with D_2 has a significant effect on the adsorption behaviour in nanoporous carbons, with the capacity of D_2 being higher than the one of H_2 due to a preferred adsorption of D_2 in even smaller pores.

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3:45 PM CH03.02.06
Poster Spotlight: Designing Next Generation Compositionally Complex Oxide Emissions Abatement Catalysts Using *In Situ* Neutron Total Scattering Sreya Paladugu[1], Palani Jothi[2], Cheng Li[3], Stephen Purdy[3] and Katharine Page[1]; [1]University of Tennessee, Knoxville, United States; [2]JTEC Energy, United States; [3]Oak Ridge National Laboratory, United States

Integration of renewable feedstocks into the current energy infrastructure will require the development of catalysts and sorbents that can maintain high surface area and catalytic activity under challenging thermal/hydrothermal environments and acid gas exposure Studying the time-resolved structural evolution of materials under gas flow conditions is key to understanding catalytic performance under real-world operating conditions with the end goal of extracting design strategies for industrially relevant catalysts. Total scattering, including both Bragg and diffuse scattering signals, enables the study of structural evolution in catalysts and can provide key insights into how long-range, nanoscale, and local atomic structure motifs differ and deliver unique properties. We have designed a new high temperature sample environment capable of hazardous gas flow (HGHS) at the Nanoscale Ordered Materials Diffractometer (NOMAD) at Oak Ridge National Lab, that will result in the capability to study acid gas interactions with sorbents and catalysts *in-situ* by neutron total scattering. The HGHS will deliver *in-situ* exposure to industrially relevant acid gas at NOMAD, enabling investigations of acid gas interactions with sorbents and catalysts, which will be a unique capability among neutron sources in the world and will aid in the design of new materials and processes with higher energy efficiency and a smaller emissions footprint. We have developed compositionally complex oxide (CCO) cerate/zirconate-based fluorite catalysts hypothesized to have high sinter resistance and improved low temperature activity compared to the single component oxide analogue. We will discuss the design, commissioning, and proof-of-concept demonstration of the capabilities of the HGHS using cerate/zirconate fluorite catalysts. Overall, this study will offer crucial structural insights into the suitability of CCO catalysts for industrial applications in comparison with traditional single component oxides, thus informing design strategies for next generation emissions abatement catalysts.

SESSION CH03.03: Characterization of Energy Materials
Session Chairs: Ke An and Mi Tian
Wednesday Morning, April 12, 2023
InterContinental, Fifth Floor, Fremont

8:30 AM *CH03.03.01
Understanding Molecular Behaviour in Industrial Microporous Catalysts Alexander O'Malley[1,2]; [1]University of Bath, United Kingdom; [2]UK Catalysis Hub, United Kingdom

The contributions of neutron spectroscopy techniques (INS and QENS) to the study of active species behaviour in microporous catalysts relevant to established industrial chemical processes have become more and more significant in recent years. Vibrational spectra obtained using INS can give great insight into the interactions between the active species and the catalyst active sites, while QENS may allow for the probing of a range of timescales of molecular behaviour. These include short timescale motions local to the active site, on the scale of ~10-100 ps such as rotations and confined translations, all the way through to long range diffusion processes throughout the framework structure.

Recent studies have included the uncovering of primary steps in the ZSM-5 catalysed Methanol to Hydrocarbons (MTH) process thanks to access to low energy vibrational modes (showing surface methoxylation at room temperature)[1] while accurately measuring rotation/diffusion dynamics of methanol and dimethylether using the QENS obtained elastic incoherent structure factor, showing a switch from isotropic methanol rotation to confined diffusion at higher temperatures, even alluding to the preferred channel siting in the catalyst micropores[2], and how this may change as a function of catalyst usage and the associated pore blockage and framework destruction.

QENS has also been used to show how the uniaxial rotation, and intramolecular methyl rotations of common fluid catalytic cracking species (n-octane and dimethyl hexane) in industrial zeolite catalysts are hindered when more acidic sites in the catalyst are present.[3] More emerging fuel/chemical production processes employing lignicellulosic biomass as a feedstock have also been probed with QENS, showing how the isotropic rotation of phenol[4] in potential zeolite catalysts is of a similar rate compared to catechol, but a significantly higher proportion of catechol is static on the instrumental timescale due to the presence of the extra hydroxyl group on catechol.[5]

The work presented highlights the unique insight that neutron spectroscopy techniques bring to microporous catalyst design, particularly when combined with molecular simulations, either for the direct reproduction of neutron scattering observables, or as complementary simulations taking place over different timescales to build a detailed picture of molecular behaviour in these industrially important catalytic systems.

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9:00 AM CH03.03.02

Cooperative Water Dynamics Investigated by Joint Approach of TOF Polarization Spectroscopy and Polarization Analysis Using Neutron Spin Echo Margarita Russina[1], Gerrit Gunther[1], Bela Farago[2], Earl Babkock[3], Zahir Salhi[3], Alexander Ioffe[3] and Ferenc Mezei[4]; [1]Helmholtz-Zentrum Berlin, Germany; [2]Institut Laue-Langevin, France; [3]Forschungszentrum Julich GmbH, Germany; [4]Institute for Solid State Physics and Optics, Hungary

Water is the most abundant liquid on Earth and is chemically a very active substance. Liquid water can act as a solvent and as a solute, as reactant and as catalyst and has therefore a broad importance for energy relevant technologies. The presence of hydrogen bonds, which control the local water structure and water tetrahedrality, leads to many unique and anomalous water properties setting it aside from other molecular liquids. Therefore, the understanding of hydrogen bonds formation and criteria governing the molecular mobility at nanoscale is of high importance for a broad range of applications. In general, the formation of hydrogen-bonded networks and / or rearrangements of molecular ensembles is a highly cooperative process. However, due to the absence of pronounced long-range order the elucidation of the local structure in water is non-trivial and investigations of cooperative phenomena have been extremely difficult and limited to very few studies.
Here we report the results of our investigation of the cooperative nanoscale dynamics in bulk water using polarized neutron spectroscopy. Polarization spectroscopy can be used in non-magnetic systems for the separation of coherent from incoherent scattering signals, which are associated with cooperative and self-particle dynamics respectively. For our study we have used a polarization spectroscopy option implemented on TOF spectrometer NEAT in Berlin [1]-[3]. Furthermore, to broaden the experimental time scale we have developed a new approach for polarization analysis using neutron spin echo spectrometer WASP at ILL, Grenoble [4]. Using a combination of these two experimental methods we observed a dynamic process on the picosecond time scale in addition to the previously observed relaxation processes which are usually associated with a long-range self-diffusion and molecular rotational diffusion. The process is visible in coherent signal and must be of cooperative nature. We also observe some fine differences in H_2O and D_2O which will be also discussed here.

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[4] Margarita Russina, Gerrit Günther, Bella Farago, Earl Babcock, Zahir Salhi, Alexander Ioffe and Ferenc Mezei, submitted

9:15 AM BREAK

9:45 AM CH03.03.03

Crystal Growth, Thermal Transport Properties and Neutron Scattering Study of Single Crystal Garnet Electrolyte $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ Yitian Wang[1], Yaokun Su[1], Youming Xu[1], Qingan Cai[1], Travis Williams[2], Chen Li[1,1] and Xi Chen[1,1]; [1]University of California, Riverside, United States; [2]Oak Ridge National Laboratory, United States

Li-ion batteries with solid-state electrolytes (SSEs), known as all-solid-state batteries, have gained great interest due to their improved safety with high energy density. One of the promising SSEs is the garnet-type lithium ionic conductor $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (LLZTO), which exhibits excellent chemical stability against lithium metal and high ionic conductivity. Although there have been many studies on its ionic properties, the thermal properties and phonon dynamic of LLZTO are not fully understood. Here we synthesize millimeter-size LLZTO single crystals using the infrared-heating floating zone method. The crystal quality and chemical composition are checked by Laue X-ray diffraction, electron microscopy and Raman scattering. The thermal and mechanical properties are also measured on the single crystal samples. Furthermore, we investigate the phonon dispersion of LLZTO using inelastic neutron scattering. In addition, quasielastic neutron scattering is used to reveal the important information about the Li ion diffusion behavior. These results provide useful insights into the thermal transport and phonon dynamics in solid ionic conductors.

10:00 AM CH03.03.04

Cation Short Range Ordering of $MgAl_2O_4$ and $NiAl_2O_4$ Spinel Oxides Studied via *In Situ* Neutron Total Scattering John M. Hirtz[1], Eric O'Quinn[1], Igor Gussev[1], Joerg C. Neuefeind[2] and Maik K. Lang[1]; [1]University of Tennessee, Knoxville, United States; [2]Oak Ridge National Laboratory, United States

Complex oxides that adopt the isometric spinel structure (AB_2O_4) are regularly used in energy storage technologies. Their performance in these applications can be drastically different depending on the defect structure present in the material. Using total neutron scattering experiments at the Spallation Neutron Source (Oak Ridge National Laboratory), we elucidated both the long-range repeating structure and the short-range local atomic arrangements of disordered and defective spinels. We have performed this technique on $MgAl_2O_4$ and $NiAl_2O_4$ disordered through chemical substitution ($Mg_{1-x}Ni_xAl_2O_4$), external heating (up to 1000°C), and dense electronic excitation through swift heavy ion irradiation (2.2-GeV Au ions). In the case of chemical substitution and external heating, the induced anti-site defects and associate inversion create a heterogeneous structure where the long-range structure is different from the short-range order. Locally, the isometric [endif]-->*m* spinel structure re-arranges to a tetragonal $P4_122$ atomic arrangement in order to maintain local charge balance, which can be rationalized by Pauling's rules. The local phase fraction is directly linked to the amount of inversion, whether it is intrinsic (chemical substitution) or external (heating). Interestingly, this behavior is modified for spinels that are disordered through far-from-equilibrium swift heavy ion irradiation. In addition to the local phase changes, the resulting defect structure includes cations trapped at vacant sites that are unoccupied when the structure is ordered or disordered by less extreme conditions. These results demonstrate that disordering in spinel oxides is highly heterogeneous across length scales and strongly dependent on the processing method; neutron total scattering with pair distribution function analysis and sensitivity to the anion sublattice provides an ideal approach to experimentally interrogate this complex behavior.

10:15 AM *CH03.03.05
Using Neutron Scattering to Reveal Complex Dynamics of Ions in Energy Materials Olivier Delaire; Duke University, United States

A better understanding of atomic motions in solids is critical to design improved materials for a wide range of energy applications. Neutron scattering provides us with key insights into a wide range of atomic dynamics in solids, from fast ionic diffusion in solid-state electrolytes to phonon propagation and thermal transport in thermoelectrics, or electron-phonon coupling and phase transitions in metal-halide perovskites for photovoltaics and optoelectronics. Our group combines state-of-the-art neutron and x-ray scattering techniques together with atomistic materials modeling to probe and rationalize atomic dynamics. This presentation will highlight results from our investigations of atomic dynamics in several classes of materials impacted by strong anharmonicity and a proximity to lattice instabilities, such as halide perovskite photovoltaics, thermoelectrics, and superionic conductors [1-6]. In these materials, we have found that one needs to properly account for the effect of strong anharmonicity, which disrupts the quasiharmonic phonon gas model through large phonon-phonon coupling terms. Large phonon amplitudes can also amplify the electron-phonon interaction and lead to renormalization of a material's electronic structure. Similarly, phonons of the host framework couple with hopping of mobile ions in superionic conductors, and significantly impact the bulk diffusivity. Such interactions, often neglected in textbooks, remain insufficiently understood but could open the door to new and improved material functionalities. By mapping spatio-temporal correlations throughout reciprocal space, complex atomic dynamics can be studied in detail. Our first-principles simulations enable the quantitative rationalization of these effects, for example with ab-initio molecular dynamics simulations and machine-learning accelerated simulations.

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SESSION CH03.04: Neutron Investigation of Energy Conversion Materials
Session Chairs: Anibal Ramirez-Cuesta and Helen Walker
Wednesday Afternoon, April 12, 2023
InterContinental, Fifth Floor, Fremont

1:30 PM *CH03.04.01
Elucidating the Mechanism of the Magnetocaloric Effect in Compounds of the Series $Mn_{5-x}Fe_xSi_3$ Karen Friese[1,2], Karin Schmalzl[1], Jörg Voigt[1], Nikolaos Biniskos[1], Stephane Raymond[3], Andrzej Grzechnik[1,2], Flaviano Jose dos Santos[4,1] and Thomas Brückel[1]; [1]Forschungszentrum Jülich GmbH, Germany; [2]RWTH Aachen University, Germany; [3]Université Grenoble Alpes, France; [4]École Polytechnique Fédérale de Lausanne, Switzerland

Domestic and industrial refrigeration applications contribute a substantial part to mankind's energy consumption. New technologies based on solid state caloric effects promise considerable efficiency gains as compared to today's vapor compression technology. In caloric materials, applied fields (e.g. magnetic, electric, pressure, strain) lead to changes in entropy and in the adiabatic temperature. The observed caloric effects form the basis of the caloric refrigeration cycles. Within our research we aim at a better understanding of the relation between the structure and the dynamics of the materials to guide a sustainable material design.

We focused our research on the magnetocaloric effect in the family of compounds $Mn_{5-x}Fe_xSi_3$. Within the series the magnetocaloric behavior changes from an inverse MCE below 100 K for the end member Mn_5Si_3 (x=0) to a moderately high direct MCE close to room temperature for $MnFe_4Si_3$ (x=4) [1,2]. We performed macroscopic magnetization measurements in static and pulsed fields which provide a basis to quantify and explain phenomenologically the MCE and to elucidate its anisotropy [3,4]. Crystal structures were investigated using powder and single crystal x-ray and neutron diffraction studies under varying temperatures and pressures [5].

Neutron diffraction experiments were of particular importance here as - on one hand - they allow to unambiguously characterize the preferred ordering of Mn and Fe on the two symmetry independent sites available for the paramagnetic ions and thus help elucidating the site dependence of the magnetocaloric effect [6]. On the other hand, they are mandatory for the determination of the magnetic structures in the system [2,6].

The underlying spin dynamics of the system was studied by a combination of inelastic neutron scattering and density functional theory calculations [7,8]. The parent compound Mn_5Si_3 (x=0), undergoes two first order phase transitions to a collinear AFM2 phase (60K<T<100K) and a non-collinear AFM1 phase (T<60K) with the transition from AFM1-AFM2 being related to an inverse MCE. The spin excitation spectrum of the AFM1 phase consists only of propagating spin waves, in contrast to the AFM2 phase where propagative spin waves coexist with diffuse spin fluctuations [9].

For the ferromagnetic compound $MnFe_4Si_3$ (x=4), which exhibits a direct MCE, we observed a strong anisotropy between in- and out-of-plane magnetic exchange interactions in the magnon spectrum which is also reflected in the *q*-dependent line-widths in the paramagnetic state. The obtained correlation lengths of this system indicate a short-range order and the in- and out-of-plane spin-fluctuations around T_c are found to be isotropic [10].

Furthermore, we performed inelastic neutron scattering investigations under external magnetic field on Mn_5Si_3 (x=0) and $MnFe_4Si_3$ (x=4). We could show that the inverse MCE which is observed in Mn_5Si_3 is related to field-induced spin fluctuations [9], while on the contrary the direct MCE observed in $MnFe_4Si_3$ is associated to the usual suppression of fluctuations by magnetic field [10].

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2:00 PM *CH03.04.02
Caloric Materials for Decarbonisation of Heating and Cooling Xavier Moya; University of Cambridge, United Kingdom

Half of the world's CO_2 emissions can be attributed to heating and cooling [1]. This is primarily due to heating with natural gas and cooling with compression of greenhouse gases, which are neither environmentally friendly nor energy efficient. Therefore there is great interest in developing energy-efficient solid-state heat pumps that can replace these environmentally damaging technologies. Caloric materials are at the core of novel solid-state heat-pump technologies, and neutron scattering provides a unique tool for their in-operando study of structure and dynamics. During this talk I will describe our work on field-driven phase transitions in caloric materials, by combining calorimetric and neutron scattering techniques.

[1] Climate change: science and solutions low-carbon heating and cooling, Royal Society, 2021.

2:30 PM BREAK

3:00 PM *CH03.04.03
Dynamics in the Metal Halide Perovskites $FAPbI_3$ and $CsPbI_3$ Investigated Using Neutron Scattering Techniques Maths Karlsson[1], Rasmus Lavén[1], Lorenzo Malavasi[2], Adrien Perrichon[3], Michael M. Koza[4], Fanni Juranyi[5], Markus Appel[4] and Garrett Granroth[6]; [1]Chalmers Univ of Technology, Sweden; [2]University of Pavia, Italy; [3]ISIS Pulsed Neutron and Muon Source, United Kingdom; [4]Institut Laue-Langevin, France; [5]Paul Scherrer Institute, Switzerland; [6]Oak Ridge National Laboratory, United States

Metal halide perovskites are currently attracting considerable attention because of their photovoltaic and photoluminescent properties and concomitant promise for use both in solar cells and in light emitting diodes. Understanding the local structure and dynamics in these materials is critical to future breakthroughs in the optimization of their performance in such devices, however, the impact of local structure and dynamics on the performance of metal halide perovskite is, in general, insufficiently understood. In this contribution I will report on new insight into the dynamics of metal halide perovskites, as obtained from recent quasielastic and inelastic neutron scattering experiments on the prototypical hybrid organic-inorganic perovskite formamidinium lead iodide $HC[NH_2]_2PbI_3$($FAPbI_3$), its methylammonium (MA, CH_3NH_3) substituted variant $FA_{0.6}MA_{0.4}PbI_3$, and the all-inorganic counterpart $CsPbI_3$.

The study on $FAPbI_3$ focused on the dynamical nature of the organic FA cation and how it changes with temperature, using quasielastic neutron scattering by the time-of-flight and backscattering techniques. The phase diagram of $FAPbI_3$ is relatively well understood, and the analysis of the quasielastic neutron scattering data established that the FA cation dynamics evolve from nearly isotropic rotations in the high-temperature (T > 280 K) cubic phase, to reorientational motions with preferred orientations related to the symmetry of the distorted tetragonal phase at intermediate temperatures (140 K < T < 280 K), to even more complex dynamics in the lower-temperature (T < 140 K) tetragonal phase. The study on $FA_{0.6}MA_{0.4}PbI_3$, a composition which was selected due to its excellent performance when used in a solar cell device, reveals strikingly different organic cation dynamics with respect to the single-organic-cation systems $FAPbI_3$ and $MAPbI_3$. It follows that tuning of the MA/FA concentration ratio represents a promising gateway to tune the dynamical properties of the mixed-cation system $FA_{1-x}MA_xPbI_3$ and hence, possibly, its performance in devices.

The study on $CsPbI_3$ focused on the nature of vibrational dynamics and how it changes with temperature, using inelastic neutron scattering. The results unraveled a quasi-harmonic and almost temperature-independent lattice dynamics from 10 K all the way up to the orthorhombic-to-cubic phase transition around 600 K. In the cubic perovskite phase (T > 600 K) of $CsPbI_3$, the dynamics are, conversely, highly anharmonic and overdamped, which are due to anharmonic rattling motions of the Cs^+ ions with the "perovskite cage" and spatially coherent, yet overdamped dynamics of Pb-I perovskite sub-lattice. Since the overdamping of vibrational dynamics in metal halide perovskites have been suggested to reduce the interaction with charge carriers and hence lead to an increase of the charge carrier lifetime and diffusion lengths, which are critical factors affecting the performance of metal halide perovskites in actual devices, this new insight can be expected to help in the rational design of new metal halide perovskites towards specific applications.

3:30 PM *CH03.04.04
Local Order and Dynamics in Hybrid Metal Halide Perovskites Nicholas J. Weadock; University of Colorado at Boulder, United States

Hybrid metal halide perovskites (MHPs) are a rediscovered class of semiconductor with remarkable optoelectronic performance in applications such as solar absorbers, radiation detectors, spintronics, and light emitting diodes. Recent computational results have demonstrated that the optoelectronic properties of MHPs are not explained by classic semiconductor models, instead it is the large structural fluctuations, driven by strong anharmonicities, which govern the behavior [1,2]. Despite recent progress in understanding the fundamental physics underlying thermal and charge carrier transport in these

materials, there still exist detrimental issues like lead toxicity and halide migration which hinder widespread deployment of MHP-based devices [2].
In this talk I will present two studies which highlight the uniqueness of neutron scattering to investigate (i) the lattice dynamics contributions to thermal conductivity in lead-free MHPs, and (ii) the two-dimensional dynamic local order in the prototypical MHPs, $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$. In the first study, we use triple-axis neutron spectroscopy to measure the acoustic phonon lifetimes in $Cs_2AgBiBr_6$ and find that the acoustic mode contributions to the lattice thermal conductivity are larger than in other MHPs. In the second study, we utilize neutron and X-ray single crystal total scattering to reveal that the simple cubic structure of $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ is in fact and assembly of two-dimensional tilted regions of PbX_6 octahedra which induce further correlations on the $CH_3NH_3^+$ sublattice. I will connect this dynamic local structure to unresolved questions surrounding the optoelectronic properties and halide migration in these materials.

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[2] D. A. Egger, A. Bera, D. Cahen, G. Hodes, T. Kirchartz, L. Kronik, R. Lovrincic, A. M. Rappe, D. R. Reichman, and O. Yaffe, *What Remains Unexplained about the Properties of Halide Perovskites?*, Advanced Materials **30**, 1800691 (2018).

4:00 PM CH03.04.05
Tunable Phase Transitions in a Two-Dimensional Superionic Conductor Alex Rettie; University College London, United Kingdom

Superionic conductors (SICs) possess liquid-like ionic diffusivity in the solid state, finding wide applicability from electrolytes in energy storage to materials for thermoelectric energy conversion. Type I SICs, where high ionic diffusivity is linked to the crystal structure *via* a first-order transition and is therefore either on or off, are attractive for energy storage and conversion applications providing the transition temperature can be controlled. However, such SICs (e.g., AgI, Ag_2Se, etc.) have been found exclusively in 3D crystal structures so far, limiting existing approaches to applied pressure and nanoscale size effects – which affect the transition temperature in one direction – while the effects of chemical substitution cannot be easily decoupled from 3D ion-conducting pathways. Layered materials have spatially separated mobile and immobile sublattices, potentially facilitating wide tunability and functioning as platforms to study two-dimensional superionic conduction.

We previously identified a first-order, order-disorder phase transition in 2D KAg_3Se_2 – a dimensionally-reduced derivative of 3D Ag_2Se – at ~695 K using in-situ XRD and DSC [1]. Here, we use quasi-elastic neutron scattering and AIMD simulations reveal that a-KAg_3Se_2 is a type I SIC with a highly disordered Ag sublattice restricted to 4 Å thick layers [2]. The superionic local structure was probed by in-situ XPDF analysis, confirming the defect dynamics from AIMD simulations (Fig. 1b). Thermal analyses of cation-substituted AAg_3Se_2 (A = Li-Cs) compounds indicate that the superionic transition temperature can be tuned by the composition of the immobile charge-balancing layers (Fig. 1c). Our work extends the known classes of superionic conductors and points the way to the design of new materials, in bulk, single-/few-layer and thin film forms, with tailored ionic conductivities and phase transitions.

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SESSION CH03.05: Poster Session
Session Chairs: Ke An and Valeska Ting
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM CH03.05.02
Poster Spotlight: Designing Next Generation Compositionally Complex Oxide Emissions Abatement Catalysts Using *In Situ* Neutron Total Scattering Sreya Paladugu[1], Palani Jothi[2], Cheng Li[3], Stephen Purdy[3] and Katharine Page[1]; [1]University of Tennessee, Knoxville, United States; [2]JTEC Energy, United States; [3]Oak Ridge National Laboratory, United States

Integration of renewable feedstocks into the current energy infrastructure will require the development of catalysts and sorbents that can maintain high surface area and catalytic activity under challenging thermal/hydrothermal environments and acid gas exposure Studying the time-resolved structural evolution of materials under gas flow conditions is key to understanding catalytic performance under real-world operating conditions with the end goal of extracting design strategies for industrially relevant catalysts. Total scattering, including both Bragg and diffuse scattering signals, enables the study of structural evolution in catalysts and can provide key insights into how long-range, nanoscale, and local atomic structure motifs differ and deliver unique properties. We have designed a new high temperature sample environment capable of hazardous gas flow (HGHS) at the Nanoscale Ordered Materials Diffractometer (NOMAD) at Oak Ridge National Lab, that will result in the capability to study acid gas interactions with sorbents and catalysts *in-situ* by neutron total scattering. The HGHS will deliver *in-situ* exposure to industrially relevant acid gas at NOMAD, enabling investigations of acid gas interactions with sorbents and catalysts, which will be a unique capability among neutron sources in the world and will aid in the design of new materials and processes with higher energy efficiency and a smaller emissions footprint. We have developed compositionally complex oxide (CCO) cerate/zirconate-based fluorite catalysts hypothesized to have high sinter resistance and improved low temperature activity compared to the single component oxide analogue. We will discuss the design, commissioning, and proof-of-concept demonstration of the capabilities of the HGHS using cerate/zirconate fluorite catalysts. Overall, this study will offer crucial structural insights into the suitability of CCO catalysts for industrial applications in comparison with traditional single component oxides, thus informing design strategies for next generation emissions abatement catalysts.

SESSION CH03.06: Neutron Techniques for Energy Materials
Session Chairs: Ke An and Margarita Russina
Thursday Morning, April 13, 2023
InterContinental, Fifth Floor, Fremont

8:30 AM *CH03.06.01
Probing Defect Fluorite Catalysts and their Interfaces with Operando Total Scattering Studies Katharine Page[1,2]; [1]The University of Tennessee,

Knoxville, United States; [2]Oak Ridge National Laboratory, United States

Integration of renewable feedstocks into the current energy infrastructure will require the development of heterogenous catalysts that can maintain high surface areas and selective catalytic activities under a variety of challenging chemical and environmental conditions. Recently, a number of compositionally complex oxides have been reported with intriguing and tunable thermal stabilities and catalytic properties. As with traditional catalysts, the all-important atomic structure details of their gas-solid and liquid-solid interfaces, which are aperiodic and transient nature, remain almost entirely out of reach by traditional structural probes. The ability to capture chemically reactive catalyst surfaces, including correlated defects and chemical short-range order, in real time and at elevated temperatures, represents a modern frontier in the field of crystallography. We will demonstrate how neutron total scattering methods, including both Bragg and diffuse scattering signals, can provide information on local atomic structure motifs and the unique properties they provide to nanomaterial platforms with significant surface to volume ratios. Neutrons offer advantages of light atom sensitivity, distinguishing neighboring atoms in the periodic table, and superior penetration of sample environments for *operando* studies. We present studies following multiple length-scales of interest in two cerate-based catalytic material systems with these probes: (1) the oxidation and reduction behaviors of ceria and Pt-decorated ceria nanorods at elevated temperatures, specifically following the evolution of oxygen vacancy correlations; and (2) the unique compositional complexity and nanoscale heterogeneities leading to increased stability and selectivity in novel, compositionally complex Rare Earth cerate and cerate zirconate emissions abatement catalysts. These examples highlight the importance but also the current limitations of studying nanocatalyst candidates and their structure-property characteristics under real-world reaction conditions. Emerging opportunities for *operando* investigations of industrially relevant catalytic and chemical separations processes with a hazardous gas handling system currently under construction at the Nanoscale Ordered Materials Diffractometer (NOMAD) and planned capabilities at the proposed DISCOVER beamline at the Spallation Neutron Source at Oak Ridge National Laboratory will be presented.

9:00 AM *CH03.06.02
Evaluating Structural Anisotropy from Neutron Pair Distribution Function Analysis of Uniaxially-Loaded Sustainable Cement Undergoing Viscoelastic Relaxation Nishant Garg[1], Brendan Kehoe[2], Daniel Olds[3], Joseph Vocaturo[2], Michelle Everett[4], Katharine Page[5], Joerg C. Neuefeind[4] and Claire White[2]; [1]University of Illinois Urbana-Champaign, United States; [2]Princeton University, United States; [3]Brookhaven National Laboratory, United States; [4]Oak Ridge National Laboratory, United States; [5]The University of Tennessee, Knoxville, United States

Pair distribution function analysis (PDF) is well-suited for determining time-dependent local atomic structure changes occurring in amorphous and disordered systems. Sustainable cements, with reduced CO_2 emissions compared with Portland cement, fall into this category due to multiple amorphous phases that are known to evolve concurrently during initial formation and over the service life of the material. Viscoelastic relaxation of cement-based systems is known to control macroscopic creep, but the underlying mechanisms responsible for this viscoelastic behavior are still to be fully reconciled. Due to the high penetrating power of neutrons and their sensitivity to hydrated materials, neutron PDF analysis is ideal for uncovering these mechanisms. However, typically PDF analysis assumes isotropic scattering which may not be applicable to cement systems subjected to uniaxial loads.

In this talk we will discuss a unique sample environment setup and data reduction approach that were used on the NOMAD instrument at the Spallation Neutron Source, Oak Ridge National Laboratory, to obtain directional-dependent total scattering patterns and associated PDFs. Alkali-activated slag and hydrated tricalcium silicate cement cylinders were subjected to 40% of their ultimate strength while data were collected in situ for the initial 24 hours, and then at 1, 2, 4, 8, 16 and ~32 weeks. As part of this talk uniaxial structural anisotropy will be assessed from neutron PDFs parallel and perpendicular to the loading direction, and mechanistic insights on cement viscoelasticity will be discussed. Key challenges that were faced as part of the investigation will also be outlined.

9:30 AM BREAK

10:00 AM CH03.06.03
Designing CENTAUR for Understanding *In Situ/Operando* Structure Evolution from Atomic to Meso Scale Shuo Qian and Cristina Boone; Oak Ridge National Laboratory, United States

CENTAUR is one of the first eight instruments to be first built for the Second Target Station of Spallation Neutron Source at Oak Ridge National Laboratory. As a work-horse SANS instrument, its capabilities are extended to cover wide-angle scattering and diffraction, therefore provide a simultaneous measurement for structures from atomic scale to hundreds of nanometers. This will fill a gap in the US neutron scattering capability. The large dynamic range coupled with high flux provides an ideal tool for *in-situ/operando* energy materials research, especially for kinetic and/or out-of-equilibrium studies of phenomena with time-resolution down to seconds.
In this presentation, I will go through the progress and the current design of CENTAUR. Highlighted features will be presented to seek feedbacks from a broader materials research community. For example, CENTAUR will have a broad wavelength band and 4 arrays of large detector coverage to enable wide Q coverage simultaneously. The optimized yet fixed-position detector arrangement maximizes the output with high data rate. A flexible optics system provides different collimation lengths for adjustable instrument resolution. We also emphasis the design on an open, spacious, and easy to access sample area with modular sample environment setups. Additionally, the spectrometer mode extends the momentum transfer and energy transfer to a lower Q than those typically covered by other spectrometers and provides a unique capability for inelastic SANS experiment. Also beam polarization will enable detailed structural and dynamical investigations of magnetic materials and quantum materials. We hope those features will enable better future materials research. With this presentation, we invite the energy materials research community to engage with us during the design phase so any additional important requirement especially the *in-situ/operando* sample environment can be captured and reflected in the next iteration of the design process.

10:15 AM CH03.06.04
Neutron Scattering Aiding to Understand Material Processing for Energy Storage Applications Yan Chen and Ke An; Oak Ridge National Laboratory, United States

Clean energy innovation is seeing drastic increase in demand, and a key step is to develop advanced renewable energy materials with high efficiency, reliability and safety. Given the right selection of compositions, the crystal structures plus various defects such as atom disordering, vacancies and incoherent boundaries usually act as determinative factors of materials performance. The understanding and controls of those factors in multiple length scales in the structure are highly desired in the design of material synthesis and manufacturing. However, the dynamic and sometimes reversible structure evolution during material processing makes the trial-and-error paradigm less effective to reveal the full mechanisms. Neutron scattering is a powerful characterization tool for the studies of energy storage materials. It possesses unique capabilities of detecting vacancies of light-weight elements and ordered arrangement of transition-metal-elements in lattice. Neutrons' high penetration in materials facilitates equipping various sample environments that mimic material processing. Over the structure evolution, the neutron scattering reveals the processing mechanisms towards superior performance. This presentation takes an example of high-energy ball milling on the high-voltage $LiNi_{0.5}Mn_{1.5}O_4$ spinel cathode of Li-ion battery. Neutron scattering reveals the ball-milling effects on structure breakdown, defect generation and atom disordering. By employing in-situ neutron diffraction, the kinetics of the structure recovery during the subsequent annealing are visualized and resolved in multiple length scales. The ball milling is also found to influence Mn^{3+} formation, Mn/Ni ordering, and the rock-salt phase transition during annealing. In addition, another example of the synthesis mechanism study on the garnet-type solid-state electrolyte is given. The in-situ neutron diffraction reveals how the element doping and the synthesis control manipulate the Li vacancy quantity and distribution to facilitate the fast-ion transport network in the solid $Li_7La_3Zr_2O_{12}$ garnet. The studies illustrate neutron scattering aiding understandings of mechanisms to advance materials processing for energy storage applications.

10:30 AM CH03.06.05

INS Characterization of Defect Sites in Metal Organic Frameworks Lucas Cavalcante[1], Makena Dettmann[1], Luke L. Daemen[2], Bruce C. Gates[1], Ambarish Kulkarni[1] and Adam J. Moule[1]; [1]University of California, Davis, United States; [2]Oak Ridge National Laboratory, United States

Metal Organic Frameworks (MOFs) that incorporate metal oxide cluster nodes, exemplified by UiO-66, have been widely studied, especially in terms of their deviations from the ideal, defect-free crystalline structures. Although defects such as missing linkers, missing nodes, and the presence of adventitious synthesis-derived node ligands (such as acetates and formates) have been proposed, their exact structures remain unknown. Previously, it was demonstrated that defects are correlated and span multiple unit cells. The highly specialized techniques used in these studies are not easily applicable to other MOFs. Thus, there is a need to develop new experimental and computational approaches to understand the structure and properties of defects in a wider variety of MOFs. Here, we show how low-frequency phonon modes measured by inelastic neutron scattering (INS) spectroscopy can be combined with density functional theory (DFT) simulations to provide unprecedented insights into the defect structure of UiO-66. We are able to identify and assign peaks in the fingerprint region ($< 100\ cm^{-1}$) which correspond to phonon modes only present in certain defective topologies. Specifically, this analysis suggests that our sample of UiO-66 consists of predominantly defect-free fcu regions with smaller domains corresponding to a defective bcu topology with 4 and 2 acetate ligands bound to the Zr_6O_8 nodes. Importantly, the INS/DFT approach provides detailed structural insights (e.g., relative positions and numbers of acetate ligands) that are not accessible with microscopy-based techniques. The quantitative agreement between DFT simulations and the experimental INS spectrum combined with the relative simplicity of sample preparation, suggests that this methodology may become part of the standard and preferred protocol for the characterization of MOFs, and, in particular, for elucidating the structure defects in these materials.

10:45 AM CH03.06.06

Nanoscale Characterisation and Neutron Damage Testing of Organic Semiconductors for New Generation Photovoltaics Giuseppe M. Paternò[1], Franco Cacialli[2] and Victoria Garcia Sakai[3]; [1]Politecnico di Milano, Department of Physics, Italy; [2]Free University of Bozen-Bolzano, Italy; [3]ISIS Pulsed Neutron and Muon Source, United Kingdom

The work I will present here involves acquiring a comprehensive insight into the nanoscale arrangements of organic semiconductors used as active materials in photovoltaics, by combining neutron scattering techniques and fast neutron irradiation.[1]
Neutron scattering is a powerful and versatile tool to investigate these highly hydrogenated materials, since hydrogen shows the highest neutron scattering cross section among the isotope.
In the first part, I will go through the investigation of the nano-morphology of conjugated polymers/fullerene photovoltaic blends by means of quasi-elastic neutron scattering and reflectivity.[2–5] The large neutron scattering contrast between these two functional materials (usually around one order of magnitude), allows one to obtain detailed information about the nano-morphology in these blends that is complementary to the information acquired via electron-sensitive techniques, such as electron microscopies and X-ray scattering techniques. This is crucial, as their arrangement at the microscale is ultimately linked to the process of exciton splitting and charge generation.

Furthermore, intense and broadband neutron pulses can be used to study the effect of neutron irradiation on organic electronics, of importance when used in space and avionic applications. In particular, I will show that the different neutron radiation tolerance exhibited by two polythiophene derivatives stems from their different crystallinity and assembly features, which in turn is induced by a combination of different molecular design features.[6,7]

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[2] G. Paternó, F. Cacialli, V. García-Sakai, *Chem. Phys.* **2013**, *427*, 142.
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SESSION CH03.07: Virtual Session
Session Chairs: Ke An and Yan Chen
Tuesday Morning, April 25, 2023
CH03-virtual

8:00 AM *CH03.07.01

Investigation on Ionomer Structure in Catalyst Layer of Polymer Electrolyte Fuel Cell Masashi Harada[1], Shin-ichi Takata[2], Hiroki Iwase[3], Hiroyuki Aoki[2,4] and Norifumi Yamada[4]; [1]Toyota Central R&D Labs., Inc., Japan; [2]Japan Atomic Energy Agency, Japan; [3]Comprehensive Research Organization for Science and Society, Japan; [4]High Energy Accelerator Research Organization, Japan

A polymer electrolyte fuel cell (PEFC) generates electric current by an electrochemical reaction of hydrogen and oxygen in a porous composite material called a catalyst layer, consisting of platinum nanoparticles, carbon aggregates, and a fluorinated polymer having sulphonic acid groups (ionomer). In the catalyst layers, the platinum catalyst is loaded on the carbon support (Pt/C) and the Pt/C is coated with the ionomer binder. Because the ionomer coating on the Pt/C plays important roles in the transport of the hydrogen ions and oxygen molecules to the platinum surface, the structure of the ionomer in the catalyst layers has a great influence on the performance of a PEFC. Thus, analysis of the ionomer structure has been indispensable for PEFC development while electron microscopy and X-ray scattering hardly distinguish carbon particles and ionomer films in the catalyst layer. In this presentation, some examples of neutron application to the catalyst layer of PEFC will be shown, enabling us to reveal ionomer distribution in the inhomogeneous multi-component system through the unique interaction of neutrons with isotopes.
First, we present an example of contrast-variation small-angle neutron scattering to separate the ionomer in the catalyst layer into two types:

homogeneously adsorbed and heterogeneously deposited ionomer against Pt/C [1]. The catalyst layers were soaked in aqueous ethanol with different H/D ratios to separately analyze the scattering components of the ionomer and Pt/C. The obtained scattering curves were modeled with a fractal aggregate of polydisperse core-shell spheres, and the thickness of adsorption and the amount of deposition were evaluated.

Next, we present an example of the analysis on the interface structure between ionomer and Pt/C in a model thin film by the double-contrast neutron reflectometry method [2, 3]. The difference in the depth profiles of the scattering length density at humidity (80% RH) in H_2O and D_2O vapor reflects the water distribution in the ionomer exchanged in the vapor, and the distribution of ionomers can be evaluated subsequently. Comparing the concentration of the ionomer on a platinum surface with that on a carbon surface, it was found that the ionomer concentration was higher at the interface with platinum than at the interface with carbon, indicating the different interactions of the ionomer with the substrate.

In summary, neutrons have the potential for observing the inhomogeneous ionomer structure in the catalyst layer by utilizing the contrast between H and D. The distribution of the ionomer is separated into two types and the interfacial concentration is extracted for the platinum and carbon surfaces. These parameters of the ionomer will be introduced into advanced simulation models of catalyst layers to design optimal performance from their structure.

Acknowledgment: The neutron experiments were performed in J-PARC with the support of the instrument scientists.

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8:30 AM *CH03.07.03

Enhancement of Thermoelectric Performance in *n*-type Bi_2Te_3 Based Samples and its Correlation with Topological Insulating Properties Aritra Banerjee; University of Calcutta, India

Bi_2Te_3, a room temperature thermoelectric material, is also well known for its bulk (3D) topologically insulating properties. We report enhancement of thermoelectric performance in *n*-type Bi_2Te_3 based compounds and its correlation with topologically insulating properties. The case of nanostructured Bi_2Te_3/graphite composite and Co doped Bi_2Te_3, *viz.*, $Bi_{2-x}Co_xTe_3$ samples will be discussed. In-depth thermoelectric properties of the samples are probed both microscopically and macroscopically using x-ray diffraction, Raman spectroscopy, temperature dependent thermal conductivity κ, Seebeck coefficient S, resistivity ρ, and carrier concentration n_H. Further the results obtained for inelastic neutron scattering experiment on Bi_2Te_3/graphite nanocomposites and magneto-resistance (MR), as well as magnetization measurements performed on Cobalt-doped Bi_2Te_3, *viz.*, $Bi_{2-x}Co_xTe_3$ (x = 0, 0.05, and 0.1) samples will also be highlighted.

Raman spectroscopic analysis confirms that graphite introduces defects and disorder in the system. A large (~17%) decrease of κ with Graphite addition has been observed, which originates from strong phonon scattering effect. A low lattice thermal conductivity (κ_L) value of $0.77 Wm^{-1}K^{-1}$ is reported for Bi_2Te_3 + 1.0 wt. % graphite sample. Interestingly, this low value of κ_L tends towards the κ_{min} value estimated using the Cahill–Pohl model. Also improvements in other thermoelectric parameters, viz., Seebeck coefficient and resistivity, is observed with graphite addition in Bi_2Te_3 nanocomposite samples. Inelastic neutron scattering experiment performed at ISIS, STFC, UK (Instrument: MARI) depicts that Graphite dispersion alters the low-energy inelastic neutron scattering spectrum providing evidence for modification of the Bi_2Te_3 phonon density of states.

On the other hand for $Bi_{2-x}Co_xTe_3$ samples, the power factor, PF ($=S^2/\rho$) a measure of thermoelectric performance is found to increase by around 47% with Co doping. The MR measurements at low field and low temperature, depicting positive linear MR and nearly cusp like behavior, followed by fitting of the Magnetoconductance data with Hikami-Larkin-Nagaoka (HLN) equation confirms the presence of 2D weak anti-localization (WAL) effects in both the pristine and Co-doped Bi_2Te_3 samples. The field-dependent magnetization showing a cusp-like nature in the susceptibility data around zero field regions (± 5 kOe) signifies the existence of topological surface state (TSS). MR along with magnetization data confirms the robustness of TSS with Co doping. In this context, the case of highly anisotropic single crystalline Bi_2Se_3 sample exhibiting high thermoelectric PF along with anisotropic magnetization and topological insulating properties will also be highlighted. Our investigation unveils that Co doping can trigger the thermoelectric performance of Bi_2Te_3 keeping the TSS intact, which gives the dual advantages of being a good thermoelectric material along with a Topological Insulator from the application point of view.

9:00 AM *CH03.07.04

Pressure-Functionalized Glassy Crystals Bing Li[1], Dehong Yu[2] and Jiangshui Luo[3]; [1]Chinese Academy of Sciences, China; [2]ANSTO, Australia; [3]Sichuan University, China

As a nontrivial solid state of matter, the glassy-crystal state embraces physical features of both crystalline and amorphous solids, where a long-range ordered periodic structure formed by the mass centers of constituent molecules accommodates orientational glasses [1-3]. Here, we discover and validate a glassy-crystal state in 2-amino-2-methyl-1,3-propanediol (AMP, $C_4H_{11}NO_2$) by neutron scattering and complementary broadband dielectric spectroscopy (BDS) measurements. The freezing process of the dynamic orientational disorder is manifested at relaxation times well described by the Vogel-Fulcher-Tammann (VFT) law and the strongly frequency-dependent freezing temperature ranging from around 225 K at 0.1 Hz to above room temperature in the GHz region. At room temperature, the supercooled state is extremely sensitive to pressure such that a few MPa pressure can induce crystallization to the ordered crystal state, eventually leading to a temperature increase by 48 K within 20 s, a significant reduction of visible light transmittance from about 95% to a few percentages, and a remarkable decrease of electrical conductivity by three orders of magnitude. These ultrasensitive baroresponsivities might find their applications in low-grade waste heat recycling, pressure sensors and non-volatile memory devices. It is expected that glassy crystals serve as an emerging platform for exploiting exotic states of matter and the associated fantastic applications [4].

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April 11 - April 26, 2023

Symposium Organizers
Syed Ghazi Sarwat, IBM
Stefania Privitera, CNR
Carlos Ríos, University of Maryland
Matthias Wuttig, RWTH Aachen University

* Invited Paper
\+ Distinguished Invited

SESSION EL01.01: Materials Science and Engineering of Phase Change Materials I

Session Chairs: Bart Kooi, Stefania Privitera and Wei Zhang
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3001

10:30 AM *EL01.01.01
Phase-Change and Ovonic Chalcogenide Materials for Innovative Electronic and Photonic Devices Pierre Noé; CEA-LETI, France

Chalcogenide materials have attracted a lot of attention over the years due to their wide range of applications. Among them, some compounds such as Ge-Sb-Te based alloys exhibit a unique portfolio of properties, which has led to their wide use for non-volatile memory applications such as optical data storage or more recently resistive phase change memory (PCM) [1,2]. In addition to a high IR transparency window and large optical nonlinearities [3], some chalcogenide glasses such as Se-based compounds exhibit an uncommon conductivity behavior under high electric field, called ovonic threshold switching effect (OTS) [4].
In this talk, I will show that materials science research through the coupling of advanced characterization tools, device characterization, and state-of-the-art simulation methods provides a powerful tool to correlate the complex structure, from long-range to local nanoscale/atomic order, and properties of prototypical chalcogenide compounds and heterostructures [5-9]. I will illustrate how such an approach applied to various chalcogenide materials used in PC memories, OTS selection devices, or photonics, provides valuable clues to understand the origin of their unique properties widely exploited so far in state-of-the-art memory devices, as well as the possibilities to go far beyond. Finally, based on this basic knowledge, we will propose new technological avenues to tailor the properties of chalcogenides, from atomic engineering to nanostructuring [10-12], to improve some of their macroscopic properties and overcome the many current technological challenges they face in many applications, while opening up new fields of application [13].

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11:00 AM *EL01.01.02
A Machine-Learning Interatomic Potential for the $Ge_2Sb_2Te_5$ Phase Change Compound Omar Abou El Kheir[1], Luigi Bonati[2], Michele Parrinello[2] and Marco Bernasconi[1]; [1]Università di Milano-Bicocca, Italy; [2]Istituto Italiano di Tecnologia, Italy

In the last fifteen years atomistic simulations based on density functional theory (DFT) have provided useful insights on the structural and functional properties of phase change materials. However, several key issues such as the effect of confinement and nanostructuring on the crystallization kinetics, just to name a few, are presently beyond the reach of DFT simulations. A route to overcome the limitations in system size and time scale and enlarge the scope of DFT methods is the exploitation of machine learning techniques trained on a DFT database to generate interatomic potentials for large scale molecular dynamics simulations. The first example of the application of such an approach to the study of phase change compounds dates back to 2012 when an interatomic potential for GeTe [1] was devised within the neural network (NN) framework proposed by Behler and Parrinello [2]. The same scheme was also applied to elemental Sb [3]. The NN potentials were then used to address several issues such as the crystallization in ultrathin films [3] and nanowires, and the thermal conductivity and aging of the amorphous phase [4]. More recently, a different machine learning technique within the Gaussian approximation potential (GAP) framework was exploited to generate an interatomic potential for $Ge_2Sb_2Te_5$ [5].

In this talk, we report on the generation of an interatomic potential for the $Ge_2Sb_2Te_5$ compound within the neural network framework implemented in the DeePMD-kit package [6]. The interatomic potential allows simulating several tens of thousands of atoms for tens of ns at a modest computational cost. The validation of the potential and its application to the study of the crystallization kinetics in the bulk phase will be discussed.

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11:30 AM EL01.01.03
Simulation of Phase Transformations Occurring in Ge-Rich GeSbTe Phase Change Memories—Coupling of Multi-Phase Field and Thermal Models Robin Miquel[1,2,3], Thomas Cabout[1], Olga CUETO[2], Mathis Plapp[3] and Benoit Sklénard[2]; [1]STMicroelectronics, France; [2]CEA-Leti, Univ. Grenoble Alpes, France; [3]Lab. Physique de la Matière Condensée, Ecole Polytechnique, CNRS, IP Paris, France

Phase change memories (PCM) rely on phase-change materials to store information. During memory operations (write and erase), the PCM cell undergoes Joule heating during the application of appropriate electrical pulses. Thanks to a highly resistive electrode in contact with the PCM layer, phase change occurs in a dome-shaped active zone of the phase change material located above this electrode [1]. Depending on heating and cooling profiles, the dome ends up in the amorphous or in the crystalline state, both states having different electrical resistivities.
The stoichiometric ternary compound Ge2Sb2Te5 (GST) is widely used in PCM technologies thanks to its interesting physical properties (ovonic switching, fast and congruent crystallization, large resistivity difference between the two states) [2]. However, because of its relatively low crystallization temperature, at which the amorphous state spontaneously crystallizes (effectively losing the stored information), GST is not suited for some industrial applications that require high operating temperatures, such as automotive microcontrollers [3]. To increase the crystallization temperature, GST can be enriched with germanium [4]. However, this leads to segregation during crystallization: two types of crystalline phases appear, germanium-rich phases and phases close to pure GST. The crystallization of GST is congruent, but that of Ge-rich GST is not.

In order to simulate the crystallization of the material after the microfabrication process and during memory operations, we have developed a multi-phase field model coupled with an orientation model [5]. This model is able to reproduce the segregation effect and to perform memory operations. However, it makes substantial approximations for the couplings to the thermal field and the electrical current that accompany memory operations.
In this work, we couple the multi-phase field approach with a thermal model that takes into account the multi-phase character of the material. Physical parameters such as thermal conductivities and specific heat have been determined with available experimental data, they are phase and temperature dependent when it is relevant. Such dependence is especially important for thermal conductivities because there are more than two orders of magnitude between their values in the different phases. Latent heats that were not taken into account by the previous model are also included to account for the heat produced during crystallization and absorbed during melting.
Chemical species diffusion and thermal diffusion are phenomena occurring at different time scales. This leads to a numerically stiff problem when they are coupled in simulations. We combine multiple numerical approaches and optimizations to keep our results accurate and simulation times low.
With this thermal multi-phase field model and with a heat source provided by an electrical model, first simulations are proposed and discussed. We investigate different electrical pulses and their effects on crystallization scenarios. While our model remains qualitative in nature, it can give insight on the crystallization mechanism occurring during memory operations.

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11:45 AM EL01.01.04
Encapsulation Effects on Ge-rich GeSbTe Alloys at High Temperature Oumaima Daoudi, Emmanuel Nolot, Mélanie Dartois, Magali Tessaire, François Aussenac, Névine Rochat, Van-Hoan Le and Gabriele Navarro; CEA-Leti, Univ. Grenoble Alpes, F-38000 Grenoble, France, France

Phase–Change Memory (PCM) is a mature technology based on chalcogenide alloys, which has proven its suitability for next generation of non–volatile memory, in particular targeting embedded applications [1]. This result was achieved thanks to the intrinsic features of PCM in terms of scalability, fast programming and high endurance. Enrichment of GeSbTe (GST) alloys by Ge and doping by light elements demonstrated to be a successful solution to enhance the data retention in PCM, opening the possibility for this technology to target automotive applications featuring strict specifications in terms of stability in high temperature environment [2–4].
It has been shown that even a partial oxidation of the chalcogenide layer can affect the properties of the material and its evolution once exposed to high temperature, likely leading to a modification of the final device performances. Indeed, the oxidation phenomena in $Ge_2Sb_2Te_5$ and GeTe films lead to a reduction of their crystallization temperature [5]. Recently, a comparison between TiN encapsulated and air–exposed N–doped Ge–rich GeSbTe (GGST) layers, highlighted the appearance of heterogeneous interfacial phenomena in the air–exposed sample [6].
In this work, we propose the study of the interfacial effects on GGST alloys at high temperature, comparing different encapsulation materials: Carbon (C), Tantalum Nitride (TaN) and Titanium Nitride (TiN) and specific combination of them. The results are compared to the ones obtained from an air-exposed sample.
Carbon is interesting for its transparency in IR and Raman spectroscopy in the range of frequency of interest. Moreover, it has been used in devices to hinder the electrode/chalcogenide material intermixing [7]. TaN has a high chemical resistance [8] and it has been already integrated in memory devices [9]. Finally, TiN was studied as reference because of its adoption in state of the art PCM devices.
We show how carbon layer faces instability at around 400°C, while TaN encapsulated sample presents stress induced phenomena at high temperature and accelerated crystallization of the chalcogenide layer. Encapsulation by TiN electrode preserves up to high temperature (more than 450°C) the properties of the GGST layer.
We compared the results coming from different techniques in order to highlight the main properties of the samples upon annealing:
- Raman spectroscopy to follow the evolution of Ge atoms vibrations;
- IR spectroscopy to observe the evolution of Ge–N and Ge–O bonds;

- Transmission Electron Microscopy (TEM) after annealing at 500°C;
- X-ray diffraction (XRD) to compare the crystallization dynamics.

The investigations were performed at several increasing temperatures up to 500°C, in order to highlight the intermixing phenomena along with the segregation and crystallization of Ge and GeSbTe phases into the GGST layer. The thickness of TaN layer should be optimized to have the compromise between a good oxidation barrier and low stress effects.
In conclusion, we compared the evolution of different samples in terms of oxidation, interfacial diffusion and stress effects to highlight the advantage and drawbacks of each encapsulating material with respect to GGST alloys evolution in temperature.

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SESSION EL01.02: Materials Science and Engineering of Phase Change Materials II
Session Chairs: Marco Bernasconi, Valeria Bragaglia, Andriy Lotnyk and Pierre Noé
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3001

1:30 PM *EL01.02.01
Structure and Properties of Ultra-Confined Phase-Change Thin Films—The Important Role Played by Peierls Distortion Bart J. Kooi, Daniel Yimam, Jesse Luchtenveld and Majid Ahmadi; Univ of Groningen, Netherlands

In the present work GeTe and Sb films were grown using molecular beam epitaxy and pulsed laser deposition. Their structures have been analysed at atomic scale using scanning transmission electron microscopy (STEM). Optical properties of the films and their crystallization temperature were assessed by spectroscopic and dynamic ellipsometry, respectively. The properties of ultrathin GeTe and Sb films (grown on amorphous oxides or nitrides), like crystallization temperature and optical properties, turned out to depend strongly on film thickness. For Sb_2Te_3 and GeSbTe films this dependence was found to be more moderate. This difference in thickness dependence can be coupled to a Peierls-like distortion (PD) being present in GeTe and Sb and absent in Sb_2Te_3 and GeSbTe. The PD in crystalline GeTe and Sb films, as measured using STEM, was found to vary across the film thickness, being overall larger for thinner films. For crystalline films of about 10 nm or thicker the PD is sufficiently small such that films behave metallic (due to metavalent bonding). In the ultrathin crystalline films, the PD is larger, opens up the bandgap and crystalline films behave more insulating (due to covalent bonding like in the amorphous films). Moreover, it will be shown that in thicker GeTe films the PD is downward in the film close to the substrate and upward in the film close to the surface with the presence of a concrete antiphase boundary (APB) running largely parallel to the interface and surface. This shows that the PD is closely associated with passivating the interface and surface and also demonstrates that the ferroelectricity of GeTe cannot be a significant effect, because such APB should not exist in ferroelectric materials.

2:00 PM EL01.02.02
Crystallization in Carbon-doped $Ge_2Sb_2Te_5$ (C-GST) via Temperature Dependent Raman Scattering and DFT-Based Molecular Dynamics Thomas Beechem[1], Robert J. Appleton[1], Arihant Kaul[1], Jenna Smith[1], Fernando Vega[1], Alejandro Strachan[1] and David P. Adams[2]; [1]Purdue University, United States; [2]Sandia National Laboratories, United States

Doping $Ge_2Sb_2Te_5$ (GST) modifies its phase change and thus the performance of any device based upon its use. Assessing the physical mechanisms belying the interplay between doping and phase change in GST, therefore, provides a path to faster, more energy efficient, and robust phase change microelectronics and photonics. With this motivation, phase-change in carbon-doped GST (C-GST) was examined using a combination of temperature dependent Raman spectroscopy and density functional theory (DFT) based molecular dynamics (DFT-based MD). Practically, Raman spectra of C-GST films synthesized with carbon concentrations ranging from 0 to 12% were collected at temperatures spanning 80 to 300 K, which allowed the undoped material to progress from its amorphous state through the metastable rock-salt phase and finally into its trigonal form. Observed changes in the Raman responses were then compared to the vibrational density of states projected onto individual atomic species. This comparison, in turn, identified those bonds most impacted by carbon-doping.

Carbon doping increases the amount of tetrahedrally bonded Ge-atoms in GST. Increased tetrahedral bonding, in turn, delays crystallization as the metastable rock-salt phase requires octahedral bonding arrangements. This deduction is supported by both observations of increased spectral weight of the tetrahedrally bonded Raman signal of Ge near 220 cm^{-1} and analysis of the coordination numbers of Ge-atoms in the simulation. Carbon doping also slows the atomic ordering necessary for crystallization. Experimentally, this is seen by not just the higher temperatures required for crystallization but the increase in disorder as the crystallization initiates, as evidenced by broader Raman features. These results are corroborated computationally in a decrease in the number of primitive rings with the presence of doping. Taken together, carbon therefore affects the phase change of GST not just by altering bonding within the amorphous material but also serving as an impediment to the atomic movement necessary for the ordering implicit in crystallization.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

2:15 PM EL01.02.03
Effects of Carbon Concentration on the Local Atomic Structure of Amorphous GST Robert J. Appleton[1], Zachary D. McClure[1], Thomas Beechem[1], David P. Adams[2] and Alejandro Strachan[1]; [1]Purdue University, United States; [2]Sandia National Laboratories, United States

Ge-Sb-Te (GST) alloys are the phase-change materials of choice for data storage due to their fast phase transition between amorphous and crystalline states. To accommodate the data storage devices of the future, the stability of the amorphous phase must be enhanced. Experiments have shown that introducing carbon results in increased crystallization temperatures up to 50% higher than pure $Ge_2Sb_2Te_5$. Previous simulations have shown that carbon alters the local atomic environment in the amorphous phase favoring tetrahedral coordination, especially with Ge. Here we use density functional theory-based molecular dynamics to study the evolution of the atomic structure of amorphous GST-C with increasing carbon concentrations. We find that carbon increases the number of Ge atoms with tetrahedral bonding, stabilizing the amorphous structure. However, this effect saturates between 5% and 10% carbon where the additional carbons aggregate on long chains. This indicates that both changes in the atomic environment and the formation of long chains contribute to the hindering of crystallization. The relative potency is not known.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

2:30 PM BREAK

3:00 PM EL01.02.04
Influence of Film Thickness on the Crystallization Kinetics of Ge-rich Ge-Sb-Te Thin Films Philipp Hans[1,2], Cristian Mocuta[3], Yann Le-Friec[4], Philippe Boivin[4], Roberto Simola[4] and Olivier Thomas[1,2]; [1]Aix Marseille Universite, France; [2]CNRS IM2NP, France; [3]Synchrotron SOLEIL, France; [4]STMicroelectronics, France

Phase-Change Memory is a very promising non-volatile memory that is being considered by several companies for a wide range of applications (storage-class memory, in-memory computing, neuromorphic computing, eNVM for microcontrollers …). At STMicroelectronics a new Ge-rich Ge-Sb-Te alloy (GGST) has been developed with a crystallization temperature above 350°C [1] for addressing the specific needs of the automotive market where high operating temperatures are needed. To investigate the crystallization behavior of these GGST alloys we use X-ray diffraction as a function of temperature during annealing. Capped thin films are heated *in situ* under nitrogen atmosphere on the DiffAbs beamline of SOLEIL synchrotron facility. The incident beam is monochromatic (18 keV) and the incidence is fixed. A bidimensional detector collects the diffraction pattern and is corrected and integrated [2] to yield a 1D diffraction pattern. The diffraction peaks are then fitted with a Voigt function [3] that allows extracting the integrated intensity, integral breadth and position of the Bragg peaks. In a previous work [4] we have shown that crystallization proceeds in two stages with Ge crystallization preceding the crystallization of cubic $Ge_2Sb_2Te_5$. In the present study we have investigated the kinetics of crystallization by performing isothermal in situ diffraction measurements on films with thickness in the range (5 nm – 50 nm). A three-stage crystallization process is identified with very different activation energies (1.7 to 3 eV). Evolution of these parameters with film thickness will be presented and discussed. These results bear important consequences for the understanding of the crystallization process in memory cells.

Acknowledgments:
The authors gratefully acknowledge the SOLEIL Synchrotron for allocating beam time. P. Joly, is acknowledged for excellent technical support during the experimental campaign at SOLEIL Synchrotron on DiffAbs beamline. This research was supported by IPCEI/Nano 2022 program.

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3:15 PM DISCUSSION TIME

3:30 PM EL01.02.06
Revealing Hidden Phases and Self-Healing in Antimony Trichalcogenides and Chalcoiodides Subila K. Balakrishnan[1], Priyakumari C. Parambil[2] and Eran Edri[1]; [1]Ben-Gurion University of the Negev, Israel; [2]Indian Institute of Technology Palakkad, India

The prevalence of self-healing semiconductors is restricted to a few selected cases, limiting understanding of the phenomenon. Herein, we report self-healing following photoinduced damage in antimony trichalcogenides and chalcoiodides—quasi-one-dimensional semiconductors with prospective applications in photovoltaics and other electronic devices. We relate the self-healing to photoinduced phase transition (PIPT) and the 'damaged' state to a hidden phase from which the 'damaged' semiconductors recover ('self-heal'). We elucidated intermediate species in the reaction and reaction dynamics using vibrational spectroscopy. Comparing four different materials with a similar crystal structure enabled us to uncover the common structural feature that leads to self-healing in these materials. By analyzing the chemical bonding, we rationalize the chemical reaction and point to bonding states at the bottom of the conduction band as central origins in propelling the hidden phase. Expanding the type and number of self-healing materials and uncovering the underlying solid-state reactions will facilitate the development of self-healing electronic building blocks for making animate electronic devices.

3:45 PM EL01.02.07
Exploring In_3SbTe_2 Chalcogenide Material for Multi-Bit Phase Change Memory Applications Anushmita Pathak and Shivendra K. Pandey; National Institute of Technology Silchar, India

Any information processing system must be able to store both temporary and permanent data, and SRAM, DRAM, and Flash memory, all being CMOS-based memories, have done this to date. However, in recent years, due to the massive global expansion of data and the practical limitation of the conventional transistor (CMOS) scaling, enormous efforts have been dedicated in delivering highly efficient storage memory. Phase change memory (PCM) technology is one of the possible contenders for the next generation emerging memory devices [1]. It uses the concept of differences in optical reflectance and electrical resistance between crystalline (low-resistance or SET state) and amorphous (high-resistance or RESET state) phases of chalcogenides/phase change material to record digital information. $Ge_2Sb_2Te_5$ (GST) ternary alloy, has been extensively utilized in both optical and electronic (PCM) data storage applications due to its ideal conditions [2]. However, this material shows some significant drawbacks such as a low crystallization temperature of ~160 °C, causing stability issues in devices [3] and a limited capacity for multi-bit storage. The scalability of PCM and the device optimization for the intended application such as determining the appropriate speed, retention, and durability tradeoff rely heavily on the phase change material characteristics. As a result, several attempts have been undertaken to explore novel chalcogenide materials and investigating their characteristics. This idea served as the foundation for investigating $In_3Sb_1Te_2$ (IST) chalcogenide alloy. IST has demonstrated high crystallization temperature of ~290 °C, proposing better thermal stability and a difference of six orders of magnitude in phases resistance, imparting the multiple bit storing potential for the PCM applications [3]. Therefore, it is essential to look at the viability of using IST material in PCM applications. The goal of this work is to investigate the optical properties such as optical bandgap and associated structural disorder of IST material during phase transition by the use of UV-Vis-NIR spectroscopy method. Amorphous phase of IST show an optical bandgap value of 0.998 eV whereas the crystalline phase show 0.449 eV, revealing IST bandgap is higher than widely used GST. A significant contrast in optical bandgap values contributes lesser threshold current and a higher signal-to-noise ratio, favourable for multiple data storing applications. Structural disorder, determined by the Tauc parameter slope, exhibit 22.7 % increment during transition to crystalline phase, revealing the ordered SET phase of IST. These results are assisted by X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy findings showing atomic bonding modification upon crystallization. In_2Te_3, InSb, and InTe bonds present in the amorphous IST sample. Annealing of the amorphous sample at 300 °C reveals the phases splitting into crystalline InSb and InTe species having vibration modes associated with TO phonons with Γ_{15} symmetry and B_{1g} symmetry respectively. Further annealing at 400 °C led to the formation of stable cubic In_3SbTe_2 with Γ phonons vibration mode. A PCM device is fabricated using IST as the active layer and W (tungsten) as both bottom and top electrodes. A threshold voltage of 2.94±0.10 V is obtained upon applying a triangular pulse with 0 to 6 V sweep. The device change to conducting state at the threshold voltage and the device current rise sharply around 4.86±0.10 V upon further rising of applied voltage. These experimental results would aid in identifying the essential characteristics of IST phase change material and would be helpful in designing thermally stable, longer data retaining and multi-bit data storage PCM devices.

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4:00 PM EL01.02.08
The Impact of Hyperbonding on the Static and Dynamic Properties of Amorphous Chalcogenides Taehoon Lee[1] and Stephen Elliott[2]; [1]Kyungpook National University, Korea (the Republic of); [2]University of Cambridge, United Kingdom

The spectrum of the application area of amorphous and crystalline chalcogenide materials is very broad. Among others, the phase-change (PC) tellurides are considered an important class of chalcogenide materials due to their unique properties inexplicable within conventional chemical bonding theories. In an effort to understand PC materials, the nature of chemical bonding has been intensively investigated recently. The hyperbonding concept provides a theoretical framework from which the structure and properties of PC chalcogenides can be comprehensively understood. The significance of this theory relies on its capability of establishing the structure-property relationships found in PC materials. In this talk, we extend the applicability of this theory to other amorphous chalcogenide materials, including pure chalcogens, binary, and ternary, alloys. The new concept of hypervalency, proposed based on multi-center hyperbonding theory, enables systematic classification of short-range structural order (or structural building motifs) and offers a theoretical basis for elucidating the static properties of many chalcogenide materials. Their dynamic properties will be also discussed based on the dynamic behaviour of constituting structural building motifs.

4:15 PM EL01.02.09
Raman Spectroscopy of Quasi-One-Dimensional $NbTe_4$ Weyl Semimetal Nanowires Zahra Ebrahimnatajmalekshah[1], Fariborz Kargar[1], Subhajit Ghosh[1], Sergiy Krylyuk[2], Albert Davydov[2] and Alexander A. Balandin[1]; [1]University of California, Riverside, United States; [2]National Institute of Standards and Technology, United States

Recently a new research field of quasi-one-dimensional (1D) van der Waals quantum materials has emerged from earlier work on low-dimensional systems [1-2]. The quasi-1D van der Waals materials have 1D motifs in their crystal structure [1]. Many of these materials reveal strongly correlated phenomena such as charge density waves (CDW) [1-2]. The CDW phase is a periodic modulation of the electronic charge density, accompanied by distortions in the underlying crystal lattice. Potential uses for CDW materials include memory storage and oscillators [3]. Raman spectroscopy can identify the CDW transitions to different phases via the appearance of phonon peaks due to emerging superstructure or the disappearance of certain peaks due to the loss of translation symmetry in the crystal lattice [3]. In this presentation, we report the results of the angle and temperature-dependent Raman scattering spectroscopy investigation of the mechanically exfoliated nanowires of the quasi-1D Nb van der Waals material. It is known that Nb forms in a tetragonal crystal structure with space group 124 (P4/mcc). Recently, this material attracted attention as a CDW material with multiple phase transitions, some of them, possibly, near room temperature. Little information is known on the Raman characteristics of this material. Our Raman data for different polarization angles show strong anisotropy in the response depending on the crystal direction. The most pronounced Raman peaks reveal strong temperature dependence. The results of the measurements will be compared with the theoretical predictions. Our data is important for further investigation of this quasi-1D CDW material for possible applications in phase-change memory and reconfigurable devices.

A.A.B. acknowledges the support of the Vannevar Bush Faculty Fellowship (VBFF) from the Office of Naval Research (ONR) contract N00014-21-1-2947 “One-Dimensional Quantum Materials” and the National Science Foundation (NSF) program Designing Materials to Revolutionize and Engineer our Future (DMREF) via a project DMR-1921958 “Data-Driven Discovery of Synthesis Pathways and Distinguishing Electronic Phenomena of 1D van der Waals Bonded Solids”. A. D. and S. K. acknowledge support through the Material Genome Initiative funding allocated to the National Institute of Standards and Technology.

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SESSION EL01.03: Nanoelectronic Phase Change Devices I
Session Chairs: Kotaro Makino, Sharon Weiss and Nathan Youngblood
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3001

9:00 AM *EL01.03.01
Materials Design of OTS Selectors and Phase-Change Materials for 3D Cross-Point Memory Technology Huai-Yu Cheng[1,2], Wei-Chih Chien[1,2], Alexander Grun[1,2], Matthew BrightSky[1,3] and Hsiang-Lan Lung[1,2]; [1]IBM/Macronix PCRAM Joint Project, United States; [2]Macronix International Co., United States; [3]IBM T. J. Watson Research Center, United States

With the increasing demand for high-capacity and high- performance memory, storage class memory (SCM) technology has aimed to fill the gap between storage and memory in the computer storage hierarchy of a modern system. The capability to fast read and write data in SCM is very important for big data analysis and AI applications. However, to boost the memory density, SCM technology requires NVM densely packed in “crosspoint” arrays to achieve $4F^2$

footprint with selecting devices capable of delivering high current and power. In addition, it is possible to integrating a repeating sequence of phase change memory layer and selector layer, achieving a 3D stackable structure increasing dramatically the density of SCM technology. Ovonic Threshold Switching (OTS) material/device show potential to meet all the selector requirements both from electrical and 3D integration point of view.
In the first part of this paper, we will discuss the role that the OTS selector plays in minimizing the leakage current through the many non-selected cells, while also delivering the right voltages and currents to the selected cell. We will focus on how to design OTS materials to meet the selector criteria enabling cross-point memory operation. OTS material based on Te-As-Ge-Si system have been demonstrated for a selector device since 1968 [1] and have been the primarily studied materials. However, insufficient cycling endurance and low thermal stability remains a key hurdle that inhibits these materials to be used in a large cross-point array. Different Ge, Si and As concentrations in Te-As-Ge-Si system [2] are tuned and optimal composition is proposed to reach endurance performance to 10^{11} cycles. However, the high leakage current (I_{OFF}) and high threshold voltage (V_{th}) drift are still the main concerns for TeAsGeSi-based materials. Se- based chalcogenides have demonstrated to be good selectors [3]. The doping effect of B, C, S, Si as well as In dopants into AsSeGe chalcogenide will be systematically discussed [4] where it will be providing the guideline for material engineering of OTS for 3D crosspoint memory.
In the second part of this paper, we will discuss the phase-change materials (PCM) suitable for storage-class memory with fast switching speed and high endurance. We will also focus on the need for researching new PCM material with uniform and stable V_{tS} (system threshold voltage when PCM is in SET state) and V_{tR} (system threshold voltage when PCM is in RESET state) distribution as well as lack of degradation of V_{tS} and V_{tR} memory window during the write cycling operation. The materials design for PCM based on the crosspoint memory specification will be reviewed and discussed, together with the impact that OTS have on PCM materials during programming operation and how it may affect V_{tS} and V_{tR} drift performance [5]. Therefore, it is desirable to find new PCM which can be matched with candidate OTS selector to optimize the 3D crosspoint memory performance.

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[5] H.-Y. Cheng et al. Dig.- Int. Electron Devices Meet, 18.5 (2022).

9:30 AM EL01.03.02
Physics-Based Machine Learning for the Electronic Structure of Phase Change Materials Qunfei Zhou[1,2], Suvo Banik[3], Srilok Srinivasan[2], Subramanian Sankaranarayanan[2] and Pierre T. Darancet[2]; [1]Northwestern University, United States; [2]Argonne National Laboratory, United States; [3]University of Illinois Chicago, United States

Computing the electronic properties of amorphous and disordered materials is challenging but of great importance to accelerate the discovery and design of phase change materials for high-efficient in-memory computing. While first-principles calculations based on Density Functional Theory (DFT) have demonstrated the numerical accuracy required for most nanoelectronics applications, amorphous and polycrystalline systems represent a particular challenge due to their heterogeneity and the associated size of their structural approximants. Tight-binding methods offer the scalability required, but rely on their prior parametrization, a complex tax for multivalent and phase changing materials. In this work, we use machine learning to parameterize a tight-binding ansatz for the electronic structure of complex phase change materials. Using the DFT results for small unit cells of single and multivalent GexSbyTez (0< x,y,z<1) alloys, we map the complex atomic configurations to a tight-binding Hamiltonian using an atom-centered basis set and the local overlap matrix. This atomic-configuration-dependent tight-binding Hamiltonian allows us to evaluate the electronic structure of large-scale phase change materials in both crystalline, amorphous, and mixed phases.

9:45 AM EL01.03.03
Reduction of Switching Current on GeSbTe Through Atomic Local Structure Engineering with Carbon Co-Doping Young Jae Kang[1], Changyup Park[2], Ha-Jun Sung[1], Donggeon Koo[2], Jongbong Park[1], Kiyeon Yang[1], Yongnam Ham[1], Minwoo Choi[1], Bonwon Koo[1], Wooyoung Yang[1], Yongyoung Park[1], Dongho Ahn[2], Kwangmin Park[2] and Chang Seung Lee[1]; [1]Samsung Advanced Institute of Technology, Samsung Electronics, Korea (the Republic of); [2]Semiconductor R&D Center, Samsung Electronics, Korea (the Republic of)

There is high demand for non-volatile memory technologies such as MRAM(magnetic random-access memory), PRAM(phase change random-access memory), RRAM(resistive random-access memory), thanks to high capacity and low power consumption.[1] Among all non-volatile memories, 3D cross-point phase change memory demonstrates long time of data retention, scalable array architecture and low costs, which device consisting of OTS(Ovonic threshold switch) and phase change materials can be switched between amorphous and crystalline phase of chalcogenide.[2,3] Considerable research efforts have been focused on the reduction of switching current and endurance improvement in the next generation of 3D cross-point PRAM device. It can be imagined that phase change properties should be modified by introducing new dopants.
With carbon doping, the reset current of GeSbTe can be reduced with increasing set resistance.[4] In this presentation, we will report the co-doping effects to improve switching current and reliability of GeSbTe. From the ab-initio calculations, we revealed that doped X element can decrease the number of Ge-Ge and Te-Te homopolar bonding. The X-dopant can suppress electron hopping sites, resulted in the set resistance increase of GeSbTe. From experimental works, we show co-substitution in GeSbTe can significantly reduce switching current (~38%) compared to carbon doped GeSbTe. Also, Carbon/X co-doped GeSbTe shows high cycling endurances of 10^6. We found that Carbon/X doped GeSbTe should be promising candidate materials for a next generation of 3D-cross point PRAM device.

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10:00 AM BREAK

10:30 AM *EL01.03.04
An Analytical Approach to Understanding Mushroom-Type Phase Change Memories Stephan Menzel[1,2], Benedikt Kersting[1], Abu Sebastian[1] and Syed Ghazi Sarwat[1]; [1]IBM Research-Zurich, Switzerland; [2]Forschungszentrum Juelich, Germany

Mushroom-type phase change memories have been investigated for memory and computing-in-memory applications due to their non-volatility, good retention properties and compatibility to CMOS processing [1]. Phase change memory device can be programmed to analog resistance states, which makes

the highly interesting for analog computing-in-memory applications. The resistance states are encoded in the shape and size of the amorphous volume within the crystalline phase change material (PCM). The size of this amorphous volume determines further device characteristics such as the threshold voltages, the resistance drift, and the retention characteristics. To capture these properties accurately a suitable model should also contain the information about the size and shape of the phase-configuration. So far, most groups used physical continuum simulations, which accounts for the exact shape. Moreover, often the investigations were limited to large amorphous volumes (i.e the full RESET states). The drawback of this method, however, is the long computation time, which makes it unsuitable for circuit simulation.
In this work, an analytical model is presented for mushroom-type PCM cells that is based on the shape and size of the amorphous mark under different programming conditions. The model is framed for both projecting and non-projecting devices [2]. To this end, analytical equations for the differently shaped amorphous and crystalline regions are derived. One of the main features of the model is the inclusion of a current 'leakage' path which injects the current directly at the outer edge of the heater. It is shown that the model reproduces well the experimental programming curve and drift data of a PCM mushroom cell. The state-dependent drift observed in experiment can be well explained within the model due to the current flowing through amorphous and crystalline regions. The drift coefficient for the amorphous and crystalline regions remains constant. The model accounts also for the asymmetry of the current conduction with respect to voltage [3] and includes the field-dependent conductivity of the amorphous material. To simulate the threshold switching, the resistance model is coupled with two ordinary differential equations describing the temperature in the leaky path and the main current path. To this end, all resistance elements of the model are modeled as temperature dependent. The simulation results show that the initial threshold switching is triggered in the leaky path and then extends to the main current path. The model allows us to simulate the threshold switching behavior and the retention behavior as a function of the phase configuration. For example, the typical trends of the threshold switching such as switching delay, sweep rate-dependence or state dependence can be well reproduced. Our work provides a simple framework for understanding the characteristics of PCM devices and lays the basis for a fully dynamic compact model.

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11:00 AM *EL01.03.05
Analog In-Memory Computing for Deep Neural Network Acceleration Andrea Fasoli[1], Geoffrey W. Burr[1], Hsinyu Tsai[1], Pritish Narayanan[1], Stefano Ambrogio[1], Kohji Hosokawa[2], Masatoshi Ishii[2], Charles Mackin[1], Atsuya Okazaki[2], Akiyo Nomura[2], Takeo Yasuda[2], Alexander Friz[1], Yasuteru Kohda[2], An Chen[1] and Jose Luquin[1]; [1]IBM Research–Almaden, United States; [2]IBM Tokyo Research Laboratory, Japan

Multiply-accumulate (MAC) operations are at the core of Deep Neural Network (DNN) workloads. In-Memory Computing (IMC) enables hardware accelerators that achieve very high-throughput and energy-efficient MAC, thus tackling the issue of exploding computational costs in ever growing DNNs. In particular, non-volatile memory (NVM)-based analog accelerators materialize massively parallelized compute by leveraging Ohm's law and Kirchhoff's current law on arrays of resistive memory devices. Provided that weights are accurately programmed onto NVM devices and MAC operations are sufficiently linear, competitive end-to-end DNN accuracies can be achieved via this approach.
In this presentation, we describe an analog IMC chip consisting of more than 35 million Phase-Change Memory devices, analog peripheral circuitry, and massive parallel routing to accelerate communication between inputs, outputs, and analog cores. We demonstrate the speed and power advantages of analog computing when applied to multiple DNN inference benchmarks, with tasks ranging from image classification to natural language processing, and show that high accuracy can be retained by a careful combination of materials, circuit, architecture, and operational choices.

11:30 AM EL01.03.06
Realizing of a Selector Function in Hf-O-Te Amorphous Films with Modified Conduction Mechanism by Adjusting the Te Content Shogo Hatayama, Yuta Saito and Noriyuki Uchida; National Institute of Advanced Industrial Science and Technology, Japan

The non-linear current (*I*)-voltage (*V*) characteristics of an Ovonic threshold switch (OTS) material plays an important role for X-point device architecture. The *I-V* behavior of OTS material is characterized by Poole-Frenkel (PF) conduction and atomic rearrangement originating from chalcogen defects; thus, most OTS materials contain Se and/or Te. To avoid crystallization, in addition to these chalcogen elements, As is usually added to form rigid amorphous networks. However, since As and Se are toxic, the development of As- and Se-free OTS materials is strongly desired. To this end, a new strategy for material development to realize As- and Se-free OTS materials with a comparable or even superior performance should be established. In this work, we aimed to realize a selector function by introducing Te to a HfO_2 to modify the electric conduction mechanism from insulator to PF conduction. The optical and electrical characteristics of Hf–O–Te ternary amorphous films with various Te contents were investigated. The physical properties of the films showed a strong compositional dependence. The optical bandgap was found to be tuned in the range of 0.46–5 eV along with the modification of electrical properties by changing the Te content. The $Hf_{0.24}O_{0.55}Te_{0.21}$ film was revealed to exhibit PF conduction, resulting in a selector function with a selectivity of roughly two orders of magnitude. These results indicate that the inclusion of a heavy chalcogen, such as Te, is effective in altering the conduction mechanism of transition-metal oxides and realizing a selector function. The present findings will pave a way for developing novel As- and Se-free OTS materials [1].
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11:45 AM EL01.03.07
Identification of Structural Phases in Al Doped HfO_2-Based Ferroelectric Films by DFT-Assisted EXAFS Analysis Mehmet A. Sahiner[1], Rory Vander Valk[1], Eric Kurywczak[1], Joshua Steier[1], Stephen Kelty[1], Bruce Ravel[2], Joseph Woicik[2], Jean Jordan-Sweet[3], Christian Lavoie[3] and Martin Frank[3]; [1]Seton Hall Univ, United States; [2]National Institute of Standards and Technology, United States; [3]IBM T.J. Watson Research Center, United States

HfO_2-based ferroelectrics have become important for future applications in CMOS technology such as negative capacitance low-power field effect transistor (FET) logic, FeRAM or FeFET memory, and FeFET- or ferroelectric tunnel junction (FTJ)-based neural network accelerators.
In our previous studies, we have used density-functional theory (DFT)-assisted extended X-ray absorption fine-structure spectroscopy (EXAFS) to identify the crystalline phases in the films of ($Hf_{0.46}Zr_{0.54}O_2$) as grown by atomic layer deposition [1]. In these films, Ferroelectric switching in TiN/$Hf_{0.46}Zr_{0.54}O_2$/TiN metal-insulator-metal capacitors is verified. We confirmed that the frequently invoked polar orthorhombic $Pca2_1$ phase is present in ferroelectric hafnium zirconium oxide, along with an equal amount of the non-polar monoclinic $P2_1/c$ phase. For comparison, we verified that paraelectric HfO_2 films exhibit the $P2_1/c$ phase. In this study we are extending our studies to identify the crystalline phases in Al-doped HfO_2 thin films. We have again used density functional theory (DFT)-assisted extended X-ray absorption fine-structure spectroscopy (EXAFS) to determine the structural symmetry of Al doped HfO_2 thin films. The 8-nm thick HfO2-based films were grown by atomic layer deposition in a metal-insulator-metal (MIM) stack configuration with varying doping levels Al and annealing temperatures. Grazing-incidence fluorescence-yield mode Hf L_3 and Zr K absorption edge EXAFS experiments were performed at the 6-BM beamline at the National Synchrotron Light Source II of Brookhaven National Laboratory. The results of the

EXAFS multiphase fitting and the effect of Al doping levels to crystalline phases will be discussed in conjunction with the electrical properties.

[1] M.A. Sahiner et al., Appl. Phys. Lett. **118**, 092903 (2021)

SESSION EL01.04: Nanoelectronic Phase Change Devices II
Session Chairs: Huai-Yu Cheng, Syed Ghazi Sarwat and Wei Zhang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3001

1:30 PM *EL01.04.01

Epitaxial Layered Phase Change Thin Films for Memory and Neuromorphic Applications Hagen Bryja[1], Jürgen Gerlach[1] and Andriy Lotnyk[1,2,3]; [1]Leibniz Institute of Surface Engineering, Germany; [2]Research Institute of Advanced Technologies, Ningbo University, China; [3]College of Physics and Optoelectronic Engineering, Harbin Engineering University, China

Chalcogenide-based phase change alloys are promising materials for optical and electronic memory applications. In this work, we propose to use epitaxial layered 2D-like Sb_2Te_3 thin films for memory and neuromorphic applications [1]. High-quality Sb_2Te_3 thin films were directly deposited on microelectronics-relevant Si(111) substrates by pulsed laser deposition (PLD) using low deposition temperature of 200°C. This offers an industry applicable large-scale method for the fabrication of memory devices, circumventing major challenges in the integration of 2D-like materials. Different top electrode metals were utilized to prepare vertical memory device structures.

The switching characteristics of Sb_2Te_3 -based cells were dependent on the used top electrode metals. The use of Ag and Cu electrodes showed pronounced bipolar memristive switching of memory devices. The devices utilizing Ag top electrode revealed analog programmability, stable multilevel retention, and endurance performance with a memory window larger than one order of magnitude. However, memory devices based on Cu top electrodes led to a memristive switching with smaller memory window and volatility of programmed states. In addition, memory devices with Cu and Ag top electrodes offer forming-free operation and self-compliance. Moreover, detailed structural and chemical characterization indicated diffusion of Ag and Cu into the Sb_2Te_3 thin films, suggesting that charge trapping is involved in the memristive switching mechanism. Overall, this work shows the high potential of epitaxial layered Sb_2Te_3 thin films for non-volatile memory applications, including neuromorphic computing.

Acknowledgements
The authors would like to thank A. Mill for TEM specimen preparation, P. Hertel for deposition of metal contacts, M. Ehrhardt for laser cutting of shadow masks and A. Prager for XPS measurements. We acknowledge the support by the Free State of Saxony within the project ‘Switching with light’.

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2:00 PM *EL01.04.02

Mitigating Analog Memory Non-Idealities for In-Memory Inference and Learning of DNN Valeria Bragaglia, Syed Ghazi Sarwat, P. V. Jonnalagadda, Benedikt Kersting, J. Luchtenveld, Tommaso Stecconi, Donato F. Falcone, Abu Sebastian and Bert Offrein; IBM Research Europe - Zurich, Switzerland

The rapid improvements in hardware accelerators and the availability of large data sets for training AI models have been pivotal for the progress in Deep Neural Networks (DNNs).
GPUs are an excellent match for Deep Learning (DL) workloads due to the high degree of parallelization. Nonetheless, such accelerators must carefully orchestrate the flow of vast amounts of data between on- or off-chip memories and highly-specialized processing units to perform the matrix manipulations at the core of DL. In in-memory analog computing, matrix manipulations are done on arrays of non-volatile memories (NVMs). These operations, that are inherent in the back-propagation algorithm of training models, can be performed at constant time and in parallel on arrays in which the weights are encoded in the NVM elements. Thus, these computations are performed locally avoiding moving weights from memory to the compute unit and back. This, together with the intrinsic high parallelism, created the recent interest for analog computing for DL [1], with the promise to provide further improvement in compute efficiency.
Several memristive technologies are under study for the implementation of neuromorphic hardware, and they rely on diverse physical mechanisms and materials. However, improvements in the device characteristics remains a necessity for optimal hardware acceleration in both performance precision and energy consumption. Device requirements are also dictated by algorithmic considerations, highlighting the multi-dimensional nature of analog accelerator designing.
Phase Change Memories (PCM) and filamentary-based Oxide Resistive RAM (OxReRAM) are the two most promising NVM candidates in neuromorphic hardware [2,3]. Their conductance change, which is directly mapped into synaptic weights, relies on a phase transition in the material for PCM. Instead, the rupture/formation of oxygen vacancies based conductive paths is responsible for the weight update in filamentary-based OxReRAM. Strength and challenges of the two classes of NVMs will be discussed, as well as the innovative design and material stack concepts that lead to enhanced operational characteristics. A discussion on the ideal class of applications for a more efficient use of PCM- or OxReRAM-based synapses will follow.
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2:30 PM EL01.04.03

Chemical and Structural Characterization of Programmed Ge-Rich GeSbTe Non-Volatile Memory Cells Antonio M. Mio[1], Stefania M. Privitera[1], Giuseppe D'Arrigo[1], Stefano Cecchi[2,3], Marie-Claire Cyrille[4], Nguyet-Phuong Tran[4] and Raffaella Calarco[5]; [1]CNR-IMM Catania HQ, Italy; [2]Paul-Drude-Institut für Festkörperelektronik, Leibniz-Institut im Forschungsverbund Berlin e.V., Germany; [3]Department of Materials Science, University of Milano-Bicocca, Italy; [4]Leti, CEA, University Grenoble Alpes, France; [5]CNR-IMM Roma, Italy

Phase-Change Materials (PCMs), mainly represented by $(GeTe)_x$-$(Sb_2Te_3)_y$ (GST) alloys, are used for high-density data storage in optical media and for solid-state non-volatile memories. Enrichment of GeSbTe alloys with germanium has been suggested as a suitable approach to increase the crystallization temperature and therefore to improve data retention in high-temperature applications of non-volatile phase change memories, such as embedded or

automotive products. However, the tendency of Ge-rich GeSbTe alloys to decompose with the segregation of Ge still requires investigations on the processes involving element diffusion and compositional alterations both in thin films and devices.
The failure mechanism of phase-change memory devices is strongly related with mass transport occurring during device cycling. Mass transport induces phase separation and segregations and indeed these issues has been reported both in heater-based architectures, like vertical mushroom cells, and in self-heating planar architectures, like line cells.
The mass transport behavior observed in literature depends on the architecture and the programming conditions, but some general trends can be recognised. Therefore, one of the main efforts lies in finding compositional and operational condition such that the cell endurance is increased. To this aim, the structural and chemical analysis of devices after forming and cycling could provide an insight into the degradation mechanism.
In this work we report the behavior of non-confined Ge-rich GST mushroom cells in reset and stuck reset states. In these Single Cell Vehicle (SCV) devices, TiN heaters have been fabricated with a diameter ranging from 50 to 100 nm.
SCV devices has been characterized in terms of structural and chemical properties by High-Angle Annular Dark Field (HAADF) Scanning-Transmission Electron Microscopy (S-TEM), Energy X-ray Dispersive Spectroscopy (EDXS) and Electron Energy Loss Spectroscopy (EELS). The SCV devices were previously formed and programmed in the desired reset state and/or cycled up to 10^6 times and electrical characterized. SCV TEM Lamellae have been obtained by Focused Ion Beam.
The present study shows with high spatial resolution how the forming process modifies the initial elemental distribution.
The RESET stucks, occurring after 10^5-10^6 cycles, seem to obey expected failure mechanisms. In this state, voids are formed on top of the heater, preventing a proper current path between heater and top electrode.

2:45 PM BREAK

3:15 PM *EL01.04.04
Ge-Rich GST—The PCM Way to Fit Challenges and Requests of the Embedded Market from Automotive to IoT Massimo Borghi; STMicroelectronics SRL, Italy

The embedded market is trying to find a common platform to support the EV cars revolution with the adoption of more sophisticated ADAS features and widespread demand for chips capable to bring AI at the Edge (IoT). In this scenario, Microcontroller Units (MCU) are pushing the limits for embedded Non Volatile Memories (e-NVM) for what concern size, access time and temperature stability. Phase Change Memory (PCM) is one of the most promising technologies to replace State-of-the-art Floating Gate (FG) memories because it can be integrated in the BackEnd-Of-Line (BEOL), it is compatible with high-k/metal-gate (HKMG) process beyond 40nm and it can afford analog programming and single bit alterability which makes it a promising candidate also for IoT devices with onboard Artificial Intelligence (AI). The convergence of automotive and MCU markets about strong automotive data retention requirements and code integrity maintenance after soldering reflow thermal profile, has fostered the activity for material engineering allowing to develop a Ge-rich chalcogenide alloy (Gerich-GST) able to satisfy both. In the first part of the presentation a review of market trends for memory-enabled solutions with focus on PCM based ones will be given while, in the second part, a technical assessment on the achievements of the 3 years long collaboration within the EU funded project (H2020 - BeforeHand) with the aim to develop novel Ge-rich GST (bulk and heterostructures) alloys with reduced material segregation and programming power will be given.

3:45 PM EL01.04.05
Memristor Behavior in Epitaxial $Cu_{2-x}Se$ Thin Films Becker Sharif, Toyanath Joshi, Anh Nguyen and David Lederman; UCSC, United States

Materials with memristor properties are currently of interest because of their applications in neuromorphic circuitry and resistive switching devices. Memristors are suitable for neuromorphic circuitry due to their low energy consumption, high density, and CMOS compatibility. Additionally, low leakage current and high on-to-off current ratios are essential for efficient devices. Non-stoichiometric copper selenide is a promising material that exhibits the above behavior, where the resistive switching is believed to be attributed to the ionic conductivity of copper ions [1]. We will present the room temperature memory resistive behavior of epitaxially grown $Cu_{2-x}Se$ on Al_2O_3 using Molecular Beam Epitaxy (MBE). The films were characterized using Reflection High Energy Electron Diffraction (RHEED), X-Ray Diffraction (XRD), and Atomic Force Microscopy (AFM). Al interdigitated contacts were used to perform current-voltage (I-V) measurements. The (I-V) measurements showed resistive switching of $Cu_{2-x}Se$ at room temperature with over five orders of magnitude of on-off current ratios.

Rehman at el. Appl. Phys. 50 (2017) 135301 (8pp)

4:00 PM EL01.04.06
Density Functional Simulations of Ag Migration in a Conductive Bridging Random Access Memory Cell and Electron Localization Effects in Recrystallized $Ge_2Sb_2Te_5$ Jaakko Akola[1,2], Konstantinos Konstantinou[2] and Robert O. Jones[3]; [1]Norwegian University of Science and Technology, Norway; [2]Tampere University, Finland; [3]Forschungszentrum Jülich GmbH, Germany

We have performed density functional/molecular dynamics (DF/MD) simulations to investigate the drift of Ag atoms in an amorphous GeS_2 solid-state electrolyte between Ag and Pt electrodes in the presence of a finite electric field [1]. The atomistic model structure represents a conductive bridging random access memory (CBRAM) device, where the electric field induces the formation of conductive filaments across the chalcogenide. Simulations of a 1019-atom structure under an external electrostatic potential of 0.20 eV/Angst. at 480 and 680 K show significant atomic diffusion within 500 ps. Ag migration and the formation of percolating filaments occur in both cases. The electronic structure analysis of selected snapshots shows that dissolved Ag atoms become markedly cationic, which changes when Ag clusters form at the Pt electrode. The electrolyte does not conduct, despite percolating single-atom Ag wire segments. Sulfur becomes anionic during the migration as a result of Ag-S bonding, and the effect is most pronounced near the active (Ag) electrode. The formation of conductive filaments requires a percolating network of Ag clusters to grow from the Pt interface, and the weakest link of this network appers to be at the Ag electrode.

We also presents result for our latest electronic structure analysis of recrystallized $Ge_2Sb_2Te_5$ model systems based on our prior DF/MD simulations [2]. Understanding the relation between the structural disorder in the atomic geometry of the recrystallized state of PCMs and the localized states in the electronic structure is essential for fundamental understanding. Hybrid density-functional theory simulations are employed to ascertain the impact of antisite defects on the spatial localization of the electronic states in the bottom of the conduction band in recrystallized models of $Ge_2Sb_2Te_5$. Te−Te homopolar bonds are the local defective atomic environments mainly responsible for the electron localization of the conduction-band-edge states in the simulated structures, while Sb−Te chains can also induce spatial localization. Unoccupied defect-related electronic states can emerge in the band gap during a crystallization event, while Sb−Sb homopolar bonds have been identified in the defect environment of a deep localized state [3]. These findings are in accordance with the latest results for recrystallized model systems of $Ge_1Sb_2Te_4$ in Ref. [4]

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4:15 PM EL01.04.07

Beyond CMOS Sensory Neuron Devices Based on Vanadium Dioxide for In-Sensory Computing Stefania Carapezzi[1], Aida Todri-Sanial[1,2] and Gabriele Boschetto[1]; [1]LIRMM, University of Montpellier, CNRS, France; [2]Eindhoven University of Technology, Netherlands

The Internet of Things (IoT) is projected to become an hyper-linked system with 30.9 billion of connected devices by 2025. A game-changer step for IoT further evolution will be represented by the development of smart objects that are context- and self-aware, with ability to “self-assemble” in smart units. In this respect, IoT sensory nodes are the key elements to embed ambient-awareness in IoT. Currently, IoT sensory nodes are an ensemble of four basic units, each one dedicated to a specific role: one for sensing, one for processing, the other two for transceiving signals and power supply. The stimuli incoming from the ambient are the inputs of the sensing module, whose output are unorganized data to be fed into processing module. The physical separation between sensing and processing units is the bottleneck for the performance of sensory systems, especially given the present deluge of sensory data that need to be analyzed. Thus, novel approaches are required to enhance the efficiency of IoT sensory nodes.

Recently, the in-sensor computing approach has gained the spot-light from both academic and industrial research, which consists into realizing the integration of sensing and computing functions into a single element. Indeed, this corresponds to mimic the elements of nervous system dedicated to sensory transduction of environmental information, the sensory neurons. In sensory neuron devices the response characteristics becomes not linear, and the thorough understanding of the physical mechanisms which connect the ambient input to the device output is key to control their response characteristics. In the present work, we explore the implementation of a sensory neuron device based on vanadium dioxide (VO_2) volatile memristor. Since the temperature triggers a volatile resistive switching in VO_2, volatile memristors can be fabricated as two-terminal VO_2 devices, where Joule effect is responsible for the resistance change of VO_2 channel. It is possible to fabricate compact and scalable relaxation oscillators [1] by inserting VO_2 volatile memristors into a simple RC circuits, which model the oscillations behavior of biologic neurons. We avail of a dedicated technology computer-aided design (TCAD) approach [2 - 4] to perform 3D electrothermal simulations of VO_2 neuron oscillators. We simulate the modulation behavior of the external temperature over the output of such devices, and thus we unravel the physical mechanism behind the temperature sensing of VO_2 neuron device. The insight we gain from our TCAD simulation is primordial to fully exploit the VO_2 sensory neurons.

Acknowledgments. Authors wish to thank Dr. S. Karg, IBM Research Europe, Zurich, Switzerland, for providing the experimental data used for the calibration of the TCAD model and the useful discussions about the experimental devices. Authors also wish to thank Dr. A. Nejim and Dr. A. Plews, of Silvaco Europe Ltd., Cambridgeshire, United Kingdom, for providing the customized version of PCM model [2] used to simulate the VO_2 material as well as for the useful discussions about the TCAD and mixed mode simulations.

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4:30 PM EL01.04.08

Preliminary Study of Phase-Change Superlattices via Thin-Film Nanocalorimetry Jie Zhao[1], Asir Intisar Khan[2], Mikhail Y. Efremov[3], Zichao Ye[1], Xiangjin Wu[2], H.S. Philip Wong[2], Eric Pop[2,2] and Leslie H. Allen[1]; [1]University of Illinois at Urbana-Champaign, United States; [2]Stanford University, United States; [3]University of Wisconsin—Madison, United States

Phase transitions involving both stable and metastable phases in superlattices (SLs) are the underlying driving forces for the operation of SL-based phase-change memory (PCM) devices. These SL stacks with nanometer-thin sublayers have been proven promising for low-power PCM. Measuring bulk thermodynamic properties is typically done with calorimetry techniques. However, PCM samples are extremely thin (~65 nm), making them inaccessible for most calorimetry methods that require large sample size (>1,000 nm).

Therefore, we use thin-film Nanocalorimetry [1, 2] to probe thermal effects in the as-deposited SLs directly (TiN-capped, all deposited by the same process as functional PCM devices). This unique method allows us to investigate the sample in its natural form of thin-film SL stacks (strain, grain size, and stoichiometry) as in SL-based PCM device. Nanocalorimetry is capable of scanning rates up to 3,000,000 K/s for 1−60 nm thick samples and has quantitatively revealed the Arrhenius crystallization kinetics of 20 nm thick $Ge_2Sb_2Te_5$ in our recent work [3].

Here, we probe the phase transition of 65 nm thick $Sb_2Te_3/Ge_2Sb_2Te_5$ superlattices [4-6] using Nanocalorimetry. Our preliminary measurements quantitatively characterize the heat capacity of the SL samples in a broad temperature range (room temperature - 650 ºC) and reveal several thermal effects that could be classified as glass-to-liquid and melting phase transitions. These thermodynamic properties could provide insights into the low-power switching of the SL-based PCM and thus advancing our understanding of SLs for use in the next generation of energy-efficient data storage devices on rigid and flexible platforms.

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SESSION EL01.05: Poster Session
Session Chairs: Antonio Mio and Stefania Privitera

Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL01.05.02

Study of Chalcogenide Based Ovonic Threshold Switch Device from the Perspective of Thermal Analysis JuHwan Park[1], Myeong Jun Jung[1], Gun Hwan Kim[2], Min Kyu Yang[3], Dustin Kendig[4], Mohammad Shakouri[4] and Byung Joon Choi[1]; [1]Seoul National University of Science and Technology, Korea (the Republic of); [2]Korea Research Institute of Chemical Technology, Korea (the Republic of); [3]Sahmyook University, Korea (the Republic of); [4]Microsanj, United States

Chalcogenide-based ovonic threshold switch (OTS) devices that exhibit volatile resistive switching depending on the external electrical field are being studied as the selector to solve the sneak path current issue. During repetitive switching, joule heating can occur, and such thermal effect may induce degradation of the devices. Also, the operation of the OTS device is not clearly understood, especially at elevated temperatures. To understand the relationship between volatile electronic switching and thermal effects, thermoreflectance (TR) imaging microscopy analysis was conducted.
In this study, we used TR imaging microscopy to observe the thermal image and real temperature during electrical operation using a Microsanj SanjSCOPE™ Transient Thermal Imaging System . A LED light source is injected onto the devices while an electrical bias is applied. After the CMOS camera captures the reflected light, the temperature is evaluated by comparing the change in reflectivity. For this analysis, $GeTe_x$ and Se- doped GeTe (SGT) based OTS devices which show superior threshold switching characteristics were fabricated on a Pt bottom electrode. A TiN metal layer was deposited on a chalcogenide thin film to see the thermal boundary resistance between the metal and chalcogenide-based material. A Au metal layer was deposited on the TiN metal layer as a photothermal transducer layer due to its stability and high thermoreflectance coefficient value. As a result of in situ TR imaging analysis, the temperature during operation and localized volatile resistive switching characteristics were observed, which has not been well characterized before. In addition, time-domain thermoreflectance (TDTR) analysis was also conducted by using Transometer™ (TMX Scientific Inc., US). When a heating pulse is applied to the thin film, thermal decay of thermoreflectance over time is observed while applying the probing pulse continuously. From this analysis, the thermal conductivity and thermal boundary resistance of the film stack can be calculated. Thermal conductivities of $GeTe_x$ films deposited under various conditions were compared to analyze their thermal effects. With multiphysics simulation, we try to understand the elevated temperature and furthermore, its effect on the OTS devices.

5:00 PM EL01.05.03

In-Operando Transmission Electron Microscopy Studies on Diffusion Induced Phenomena at the Dielectric-Electrode Interfaces in Ge_2Te_3-Based Memristor Devices Krishnamurthy Mahalingam[1,2], Austin Shallcross[2], Cynthia Bowers[1], Sabyasachi Ganguli[2], Eunsung Shin[3] and Guru Subramanyam[3]; [1]UES, Inc., United States; [2]U.S. Air Force Research Laboratory, United States; [3]University of Dayton, United States

The memristor is a two-terminal device derived from materials that exhibit resistance switching, wherein the resistance of the material is tunable by an applied electric field. This switching process is reversible, and is also non-volatile, so that the change in resistance is maintained for a long period of time even after the applied field is removed. A wide variety of materials are currently being investigated depending on microstructural mechanisms that triggers the switching process, such as those based on defect migration and phase transformation. Independent of the actual mechanism that drives this switching process, the dielectric-electrode interface plays a significant role in determining device properties and performance. In particular, maintaining interface chemistry and morphology during actual operation is critical to realizing devices with higher switching speed, lower power consumption, and higher endurance. Recent advancements in transmission electron microscopy makes it possible for examining interfacial phenomena in such devices in-operando at high spatial resolution and sensitivity.
In this contribution we perform an in-operando cross-sectional TEM study to investigate microstructural phenomena that control the integrity of the dielectric-electrode interface in Ge_2Te_3-based phase change materials. For the purposes of this study we have examined device structures: Pt/ Ge_2Te_3 (50 nm)/Ti/Pt, grown on (100)-Si substrates. Specifically we employ Z-contrast STEM imaging in combination with X-ray energy dispersive spectroscopy (XEDS) to examine the effect of Ti which is widely used as an adhesion layer prior to the deposition of electrode layer atop the dielectric (Ge_2Te_3) layer. Detailed examination of XEDS results upon electrical biasing clear reveal a deleterious effect of Ti, characterized by in-diffusion of Ti to form a reactive telluride layer and out-diffusion of Ge, resulting in its enrichment at beneath the top Pt electrode. Further studies under systematic electrical biasing and heating conditions reveal that this diffusion process can be significant, leading to progressive degradation of the dielectric-electrode interface. Additional studies aimed at combating this process will be presented. Furthermore, the role of residual surface oxide layer generated during the device fabrication process will also be discussed.

SESSION EL01.06: Nanophotonic Phase Change Devices

Session Chairs: Harish Bhaskaran, Wolfram Pernice and Carlos Ríos
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3001

8:30 AM EL01.06.01

Rapid Discovery, Development, and Integration of Visible-Frequency Materials with Metavalent Bonding Mark Polking[1], Kevin Tibbetts[1], Steven Vitale[1], Juejun Hu[2] and Christopher Roberts[1]; [1]MIT Lincoln Laboratory, United States; [2]Massachusetts Institute of Technology, United States

Materials that exhibit metavalent bonding character have emerged as a promising avenue to dynamically reconfigurable and tunable nanophotonic devices. Conventional materials with metavalent bonding, however, are typically narrow-gap chalcogenides with high free carrier densities, limiting their utility for practical photonic integrated circuits and metamaterials requiring low insertion losses and operation in the visible-NIR frequency band. In this presentation, a new approach to rapid discovery, development, and integration of materials with metavalent bonding character and high optical transparency in the visible-NIR range will be described. This approach begins with a new method for prediction of metavalent bonding character based on consideration of the contributions of individual atomic/ionic species to the overall refractive index. Simple calculations based on this method enable accurate predictions of the refractive indices of crystalline materials lacking metavalent bonding and of the amorphous phases of known phase-change materials. First-principles theory calculations of the electron localization function (ELF), charge density, and Born effective charges for promising materials revealed by the initial screening protocol revealed new families of materials, including binary IV-VI chalcogenides and group III, IV, and V-halide materials, with substantial metavalent bonding character and band gaps as large as 2.6 eV. Preliminary experimental measurements of amorphous and crystalline samples of several of these materials indicate index amorphous-crystalline index contrast values of 0.3-1.1 and low optical losses. This presentation will further describe recent developments in the scalable fabrication of integrated photonic components and metasurfaces using these novel high-frequency metavalent materials at the

200 mm wafer scale. Specifically, selenide-containing phase-change materials such as $Ge_2Sb_2Se_4Te_1$ and Sb_2Se_3 have been integrated with silicon photonic devices such as Mach-Zender interferometers and ring resonators. These allow non-volatile reconfigurability of photonic integrated circuits for practical applications such as switch matrices, optical communications, and photonic quantum computing.

8:45 AM *EL01.06.02
Measuring the Dynamic Thermal Response in Electrically Programmable Phase Change Photonics Nicholas Nobile[1], John R. Erickson[1], Carlos Ríos[2,2], Yifei Zhang[3], Steven Vitale[4], Juejun Hu[3], Feng Xiong[1] and Nathan Youngblood[1]; [1]University of Pittsburgh, United States; [2]University of Maryland, United States; [3]Massachusetts Institute of Technology, United States; [4]Lincoln Laboratory, MIT, United States

Phase-change materials (PCMs)—such as $Ge_2Sb_2Te_5$ (GST), $Ge_2Sb_2Se_4Te_1$ (GSST), Sb_2Se_3, and others—show great potential for next generation reconfigurable photonic circuits, in-memory computing platforms, and tunable metasurfaces. This is made possible by high speed, high contrast, and nonvolatile changes in the refractive index of these materials, making them suitable for applications requiring optical memory or tunability. In the past, the majority of experimental works have demonstrated bistable switching between the amorphous and crystalline states of PCMs using either optical pulses or thermal annealing on a hot plate, which has limited scalability for real-world applications. Thus, integrated approaches are needed which enable electrical switching of areas much larger than the optical wavelength.

Here, we present methods for the design and characterization of foundry-compatible on-chip microheaters for electrically programmable phase-change photonic devices. In the first part of this talk, computational modeling approaches will be applied to various microheater designs (i.e., metallic, resistive, and diode-based silicon microheaters) and insights for optimizing switching speed and energy efficiency will be presented. In the second part of this talk, recent experimental work on optically mapping the dynamic thermal response of these microheaters will be presented and compared with our computational models. Our complementary experimental and computational approach allows us to model and validate the fast heating and cooling dynamics of fabricated devices with diffraction-limited resolution—a crucial step towards optimizing the energy efficiency and operation speed of electrically reconfigurable phase-change photonics.

9:15 AM *EL01.06.03
Integration of Optical Phase Change Materials in On-Chip Silicon Photonic Devices Sharon M. Weiss and Richard Haglund; Vanderbilt Univ, United States

Advances in silicon photonics have contributed to faster data transfer speeds in data centers and other application areas. However, in order to further increase data rates to meet the demand for higher-capacity data communication systems, alternative solutions are needed. A hybrid structure consisting of a silicon photonic backbone and an incorporated optical phase change material (O-PCM) may provide a solution for realizing broadband, low power, small footprint photonic devices capable of achieving record switching speeds. In this presentation, we discuss theoretical and experimental work integrating O-PCMs in silicon photonic devices, including sub-picosecond optical switching using a hybrid silicon-vanadium dioxide waveguide and a lower power, higher extinction ratio optical switch based on a hybrid silicon-vanadium dioxide subwavelength engineered photonic crystal.

9:45 AM BREAK

10:15 AM EL01.06.04
On-Chip Wavelength-Selective and Non-Volatile Reconfigurability in a Single Photonic Element June Sang Lee[1], Nikolaos Farmakidis[1], Samarth Aggarwal[1], Wen Zhou[1], Wolfram Pernice[2] and Harish Bhaskaran[1]; [1]Oxford University, United Kingdom; [2]Universität Heidelberg, Germany

The functionality of photonic circuits relies on their ability to process multiplexed information in wavelength, polarization and phase. While optical signals can carry such multidimensional information, independent modulation of multi-wavelength signals in a single carrier has been challenging. Here, we demonstrate independent and non-volatile modulation of wavelength-multiplexed optical signals within a single photonic element. Our chips rely on the formation of standing wave patterns in a microring resonator which can be individually addressed according to their mode number (i.e. wavelength). By combining this concept with phase-changing nanoantennas, we demonstrate for the first time non-volatile, wavelength-selective modulation. This allows realizing an on-chip, reconfigurable and multi-spectral filter operating within a single element. This novel approach provides a pathway for exploring additional degrees-of-freedom in tunable photonic networks and provides a compact photonic framework for optical storage, routing, and neuromorphic/in-memory computing.

10:30 AM EL01.06.06
Theoretical and Experimental Studies of Metal-based Phase Change Materials toward Optical and Terahertz Applications Kotaro Makino[1], Yuta Saito[1], Shogo Hatayama[1], Masashi Kuwahara[1], Hitoshi kawashima[1] and Paul Fons[1,2]; [1]National Institute of Advanced Industrial Science and Technology (AIST), Japan; [2]Keio University, Japan

Optical applications based on phase change materials (PCMs), that exhibit a significant change in optical properties upon non-volatile amorphous-crystalline phase change, have attracted a lot of attention. The optical response of a material is governed by the complex index of refraction, namely the refractive index (real part) and the extinction coefficient (imaginary part). Recently, Sb_2S_3, Sb_2Se_3 and $Ge_2Sb_2Se_4Te_1$ have been reported to be suitable for low-loss optical phase shifter and plasmonic devices because these materials have a wider band gap [1-3], namely a smaller extinction coefficient than the conventionally used material $Ge_2Sb_2Te_5$ (GST), although GST is still useful for some applications utilizing absorption change and mid-infrared applications [4]. In this sense, PCMs with a wide band gap and a significant change in refractive index upon phase change are highly desirable for efficient optical device applications.
In this work, we focused on the optical properties of PCMs composed of transition metal and chalcogenides such as MnTe and other compounds. We carried out first principles calculations to evaluate the corresponding electronic and optical properties. By using Vienna Ab initio Simulation Package (VASP), we obtained the complex index of refraction for both the crystalline and amorphous phases of PCMs. The amorphous structures were obtained via melt–quench ab initio molecular dynamics simulations (AIMD). We also carried out spectroscopic ellipsometry measurements and terahertz (THz) time-domain spectroscopy for sputter-deposited thin films. It was found that the transition metal-inclusive PCMs are promising for terahertz and 6G telecommunication technology as well as optical applications such as optical switches and program optical resonators.
Part of this presentation is on the result obtained from the commissioned research (03701) by National Institute of Information and Communications Technology (NICT), JAPAN.

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10:45 AM EL01.06.07

Long Live O-PCMs—Understanding Reliability Challenges of Optical-Phase Change Materials Cosmin Popescu[1], Brian Mills[1,2], Louis Martin[1], Luigi Ranno[1], Yifei Zhang[1], Qingyang Du[1,3], Carlos Ríos[4,1], Steven Vitale[5], Christopher Roberts[5], Paul Miller[1,5], Vladimir Liberman[5], Hyun Jung Kim[6], Kiumars Aryana[6], Dennis Callahan[2], Myungkoo Kang[7], Kathleen Richardson[7], Tian Gu[1] and Juejun Hu[1]; [1]Massachusetts Institute of Technology, United States; [2]Charles Stark Draper Laboratory, United States; [3]Zhejiang Lab, China; [4]University of Maryland, United States; [5]Lincoln Laboratory, Massachusetts Institute of Technology, United States; [6]NASA Langley Research Center, United States; [7]University of Central Florida, United States

The ability to reconfigure the optical behavior of a device enables many applications ranging from imaging to sensing and signal control. Such optical devices can be compacted via meta-surfaces, patterned structures with feature sizes below the incident wavelength. Leveraging geometry in addition to material properties and CMOS fabrication techniques has allowed meta-surfaces to operate as lenses, holograms, beam steerers, and more. To incorporate multiple optical functions into one device, various methods of device control have been implemented such as stretching of flexible substrates, tuning the refractive index of the comprising meta-atoms via the electro-optic or the thermo-optic effects, phase transition materials such as VO_2, and more. Chalcogenide glasses used as optical phase change materials, such as $Ge_2Sb_2Te_5$ (GST), have gained increased traction in the optics community for potential use in the NIR and MIR, including the telecom bands. Various chalcogenides such as Sb_2Se_3, Sb_2S_3, $Ge_2Sb_2Se_5$, and $Ge_2Sb_2Se_4Te$ (GSST) have been investigated due to their broad NIR or MIR transparency window and large changes in refractive index. In their amorphous phase, these materials usually display a lower refractive index & low absorption when compared to their crystalline state which displays a higher refractive index and typically larger extinction coefficients. The amorphous-crystalline reversible switching can be done on-chip via fast melt-quenching processes triggered by laser heating or electrical impulses, which rely on a substrate as a heat sink. The potential of PCMs in photonic devices can be limited by intrinsic material limitations as well as by device fabrication issues. To explore the cyclability of GSST, a PCM with large refractive index contrast, on-chip electrothermal switching on a silicon-on-insulator platform has been done to analyze potential failure mechanisms from both a material and device perspective. A brief outline of the instrumentation and phase change contrast analysis is provided. Dewetting of the PCM, delamination of and damage to the PECVD SiN_x protective layer, elemental migration in the PCM, and optical contrast decay have been observed in cycled GSST devices. Guidelines for device performance improvement are proposed and an improved design with greater endurance is shown in this work.

11:00 AM EL01.06.08

Antimony as a Tuneable Element in Integrated Photonics Samarth Aggarwal[1], Tara Milne[1], Nikolaos Farmakidis[1], Johannes Feldmann[1], Xuan Li[1], Yu Shu[1,2], Zengguang Cheng[1,3], Martin Salinga[4], Wolfram Pernice[5,2] and Harish Bhaskaran[1]; [1]University of Oxford, United Kingdom; [2]Kirchhoff-Institute for Physics, Germany; [3]State Key Laboratory of ASIC and System, China; [4]Universität Münster, Germany; [5]University of Münster, Germany

Over past decade there has been a surge in interest for reconfigurable photonic. A number of ways of achieving such reconfigurability have been explored including using heaters exploiting thermo-optic effect , electro-optic devices based on $LiNbO_3$ substrate , charge injection based modulators and phase change materials (PCMs) . Unlike other methods of reconfigurability PCMs like GST and AIST are non-volatile , resulting in low system energy requirements. Besides reconfigurability, phase change materials have also found their application in non-volatile optical switches and for in-memory computing.

Conventional PCMs like GST and AIST are ternary and quaternary alloys with special elemental compositions. Small deviation in elemental composition can result in degradation of device performance. However controlling the composition of alloys is quite challenging and maintaining the composition uniformity over large area has limited the commercial use of conventional phase change materials. Another drawback of using such alloys is of phase segregation. PCMs undergo multiple thermal cycling and this results in elemental segregation at grain boundaries and therefore resulting in variation of alloy composition and hence a degraded device performance. These issues can be circumvented by use of a single element phase change material.

Here we demonstrate the use of elemental antimony as a memory element in integrated photonic[1]. We show a thin film of Sb with thickness under 5 nm can be reversibly switched between amorphous and crystalline phase using femtosecond pulses. We then show a binary memory operation with energy as low as 190 pJ. Further we show multilevel memory operation , similar to conventional PCM like GST , by varying switching pulse energy from 120-230 pJ to achieve intermediate amorphous states. We demonstrate up to 7 memory levels equivalent to 3 bit memory operation. Further using pump probe technique we investigate the switching speed of our antimony based photonic memory. We observe a switching speed of 500 MHz therefore showcasing ultrafast device speed. Next we explore tuneable volatile property of our memory cell. By varying probing and switching energy we study the memory retention time for potential applications ranging from all photonic neurons to leaky integrators for computing.

[1] Samarth Aggarwal, Tara Milne, Nikolaos Farmakidis, Johannes Feldmann, Xuan Li, Yu Shu, Zengguang Cheng, Martin Salinga, Wolfram HP Pernice, and Harish Bhaskaran *Nano Letters* **2022** *22* (9), 3532-3538 DOI: 10.1021/acs.nanolett.1c04286

11:15 AM *EL01.06.09

Phase Change NEMS - A New Paradigm for Phase Change Materials in Nanomechanics Harish Bhaskaran; University of Oxford, United Kingdom

Phase change materials have been widely used in optical discs, electronic memories and more recently in emerging optoelectronic applications such as displays and neuromorphic photonic computing. Yet, in spite of the widespread use of these materials, the change in their mechanical properties had not yet been exploited. In this talk, I shall present recent work on the use of phase change nanowires in mechanical tuning applications - both electronic and photonic, showing that in the unique nanowire configuration, these devices present extraordinary quality factors and tunability.

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SESSION EL01.07: Properties and Applications of Correlated Metal-Insulator Transitions I

Session Chairs: Valeria Bragaglia and Stephan Menzel
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3001

1:30 PM *EL01.07.01

Superlattice Chalcogenides for Low-Power Memory and Neuromorphic Computing Asir Intisar Khan, Xiangjin Wu, Alwin Daus, Sumaiya Wahid and Eric Pop; Stanford University, United States

Phase change memory (PCM) technology could play an important role in future high-density computing systems, including neuromorphic computing. However, PCM based on traditional chalcogenides like $Ge_2Sb_2Te_5$ (GST) requires relatively large power consumption and suffers from resistance drift [1]. This talk will address our recent efforts to tackle these challenges using various types of superlattice PCM (SL-PCM) materials, made of alternating ultrathin (~nm) layered chalcogenides. From a device perspective, we have demonstrated memory with superlattices based both on GeTe/Sb_2Te_3 [2] and GST/Sb_2Te_3 [3,4], showing up to ~10x lower reset current density and 10x lower resistance drift than control GST PCM with the same mushroom cell structure. We uncovered that the quality of the interfaces within the SL plays an important role in the memory behavior [3,4]; in other words, more good-quality interfaces means better thermal and structural confinement, but interfacial intermixing degrades the drift coefficient. Given that thermal confinement plays such an important role in low-power behavior, we also demonstrated SL-PCM with the lowest switching current density to date (~0.1 MA/cm^2) on flexible polyimide substrates, which have ultralow thermal conductivity [5]. Importantly, all our SL-PCM devices show multiple resistance states and scalability with the bottom electrode diameter, offering further promise in ultra-scaled devices.
From a materials perspective, extensive transmission electron microscopy (TEM) revealed van der Waals (vdW)-like interfaces in the superlattices, which facilitate the electro-thermal and structural confinement [2-4]. We found lower cross-plane thermal conductivity and higher electrical anisotropy of the polycrystalline SL stack compared with polycrystalline GST, due to the internal interfaces within the SL [6]. We also explored lateral transport in chalcogenide films and multilayers, measuring good Hall mobilities for GeTe/Sb_2Te_3 superlattices (~18 cm^{2}V^{-1}s^{-1}), 2–3x higher than the other films [7]. These results provide key insights towards new superlattice material design and optimization, and could pave the way to high-density storage and neuromorphic applications using superlattice PCM materials.

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2:00 PM EL01.07.02
Defect Engineering in VO_2 Thin Films via He^+ Irradiation Rebeca M. Gurrola[1], Adelaide Bradicich[1], Ryan M. Schoell[2], Khalid Hattar[2], John M. Cain[2], Tzu-Ming Lu[2], Timothy D. Brown[3], A. A. Talin[3], Matt Pharr[1] and Patrick Shamberger[1]; [1]Texas A&M University, United States; [2]Sandia National Laboratories-NM, United States; [3]Sandia National Laboratories-CA, United States

Vanadium dioxide is a desirable material for neuromorphic computing applications due to its nonlinear electrical transport properties. These are the result of a metal-insulator transition (MIT) that can be accompanied by up to a four orders of magnitude change in electrical conductivity. At ~68°C, the MIT is coupled with a structural phase transition (SPT) as VO_2 transforms from an insulting monoclinic phase to a metallic rutile phase. In order to utilize VO_2 as a dynamically controllable material, it is critical to understand how to control 1) the electrical conductivities of two phases, and 2) aspects of the structural transition itself, including the extent of phase coexistence. Previous research has attempted to alter the MIT by use of chemical dopants that either decrease the MIT transition temperature, such as W and Mo, or increase the transition temperature, such as Ge [1-2]. Irradiation has also been used to modify MIT behavior, primarily by creating vacancy and interstitial defects that in turn alter the phase transition behavior [3-4]. Finally, the use of different substrates to grow highly oriented VO_2, notably Al_2O_3 and TiO_2 single crystal substrates, has been shown to shift the transition temperature as low as 35°C and as high as 80°C due to the resulting anisotropic compression/tension on the c-axis of VO_2 [5-6]. However, less research has focused on the intersection of strain and defects caused by irradiation.
The goal of this research is to establish the effect of defects caused by irradiation on the MIT behavior and electrical transport in VO_2 thin films. Polycrystalline VO_2 thin films were grown on SiO_2(100nm)/Si, while epitaxial VO_2 was grown on Al_2O_3 (0001). Photolithography was used to make both 4-terminal and 2-terminal devices at unique crystallographic directions [10-10] for sapphire, due to the six-fold symmetry. To study device switching performance, a range of device widths and lengths were used ranging from 1 to 60 um and 1 to 25 um. These films were irradiated with He+ ions under two distinct energy regimes(10 keV, and 2 MeV), and fluences ranging from 5E13 to 5E16 cm^{-2}. We will describe the conjunction of coupled strain and irradiation defects on the electrical conductivities of the two phases of VO_2, as well as the hysteresis, width of phase transition, and temperature of transition. In this study, VO_2 is shown to be fairly resistant to irradiation and can also be used for rad-hard material applications. This research furthers the exploration of the limits of the metal-insulator transition in VO_2 via nanoscale material manipulation for neuromorphic applications.

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2:15 PM EL01.07.03
Physics of Resistive Switching in $LaCoO_3$ Revealed by X-Ray Absorption Spectromicroscopy Mahnaz Islam[1], Christopher Perez[2,1], Rajashree Bhattacharya[3,4], Sumaiya Wahid[1], Timothy D. Brown[2], Matthew Marcus[5], Hendrik Ohldag[5], Vincent Gambin[3], Suhas Kumar[2] and Eric Pop[1]; [1]Stanford University, United States; [2]Sandia National Laboratories, United States; [3]Northrop Grumman Corporation, United States; [4]University of California, Los Angeles, United States; [5]Lawrence Berkeley National Laboratory, United States

Insulator-metal-transition (IMT) oxides exhibiting volatile resistance switching upon electrical excitation are intensely studied for applications as selectors in nonvolatile memory, radio-frequency switches, electrostatic discharge clamps, etc. [1, 2]. Popular IMT oxides such as VO_2 and NbO_2 exhibit an abrupt reduction in resistance, driven by a Mott transition, when their temperature exceeds a threshold value. This threshold temperature is too low for VO_2 (~340 K) and too high for NbO_2 (~1100 K) to be suitable for commercial electronics. When localized Joule heating is used to drive the IMT by applying a current, the abrupt change in resistance also leads to large dynamical current and local temperature overshoots, causing device damage. Such limitations inspire the need for IMT materials beyond Mott insulators for use in commercial electronics.
In this work, we study $LaCoO_3$ (LCO), which undergoes a gradual thermally-driven IMT between 350-650 K, induced by an electron-spin-state transition, thus offering favorable on-chip operating temperatures [3, 4]. Crystalline 49-106 nm thick LCO films were epitaxially grown on (100) $LaAlO_3$ substrates at 973 K by DC sputtering of metal La and Co targets. Two-terminal lateral devices with LCO channels of lengths 2-8 μm and widths 4-15 μm with Pd (20 nm)/Au (80 nm) electrodes were lithographically defined. We find that, despite the gradual thermally-driven IMT, LCO exhibits a sharp and abrupt

electrically-driven volatile resistive switching upon increasing voltage bias, enabled by the non-linearity in its resistance-temperature property. Upon increasing current bias, we also find a region of current-controlled negative differential resistance (NDR), underlying the voltage-driven resistive switching characteristics.

We perform *in-situ* scanning transmission X-ray microscopy (STXM) at the oxygen K edge on two-terminal LCO devices under increasing bias, to study the evolution in the X-ray absorption features arising from an electrically-driven IMT. For this study, polycrystalline LCO deposited on thin SiN_x membranes was biased with Pd electrodes at increasing current levels, chosen to measure spectra below, within, and above the start of the NDR, as identified from the *I-V* measurements. We observe creation of t_{2g} states within the bandgap, evident by the gradual shift in spectral intensity from 529.6 (unoccupied e_g states) to 528.7 eV (unoccupied t_{2g} states), with increasing bias levels that were large enough to put the device in the NDR region. Spectra measured for low bias levels below the NDR region did not show such changes and were identical to spectra without applied bias. For comparison, we also perform STXM on ambient-temperature-controlled LCO thin films, which exhibit identical spectral changes compared to bias-driven measurements. These changes are consistent with a distinct low to high electron-spin-state transition in the Co^{3+} ion, as reported for a thermally-driven IMT in bulk LCO [4].

In summary, we show an electrically-driven abrupt transition in LCO utilizing the non-linearity in its resistance-temperature behavior. We measure volatile spectral changes during volatile electrical switching in LCO, consistent with thermally-driven low to high spin-state transition in the Co^{3+} ion. Our work introduces LCO as a suitable on-chip and energy-efficient electrical switching material.

This work was supported in part by the Stanford Graduate Fellowship (M.I., S.W.), the Stanford SystemX Alliance and by Lab. directed R&D at Sandia Labs under DE-NA0003525.

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2:30 PM BREAK

SESSION EL01.08: Properties and Applications of Correlated Metal-Insulator Transitions II
Session Chairs: Valeria Bragaglia and Stephan Menzel
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3001

3:30 PM EL01.08.03
Epitaxial VO_2 on Si 100 via TiN Buffer Layer for CMOS Applications Rama Satya S. Ventrapragada, Arvind S. Rajnarayan, Yeswanth Pattipati, Sandeep Vura and Sushobhan Avasthi; Indian Institute of Science, India

Vanadium oxide (VO_2) exhibits an insulator-to-metal (IMT) transition at 68 °C from a low-temperature insulating phase ($P2_1/c$) to a high-temperature metallic phase ($P4_2/mnm$). The optical or electrical excitation can trigger the IMT resulting in an abrupt change in resistance ($x10^4$) of VO_2. Due to IMT, VO_2 is used in bolometers, electro-optic modulators, and infrared photodetectors [1]. VO_2 films are grown on single crystalline substrates like Al_2O_3, which severely limits its applications. Integrating epitaxial VO_2 films on Si (100) (complementary metal-oxide-semiconductor) platform enables integrated electro-optic devices and temperature sensors. Moreover, preserving the symmetry of the substrate in some form would pave the way for integrating further oxides epitaxially on top of the VO_2 film. Yun et al.[2] had seen superior performance of UV detector by integrating ZnO on VO_2. The formation of amorphous SiO_2 at the VO_2/Si interface limits its heteroepitaxial integration on Si (100). An epitaxial TiN interlayer layer deposited by reactive pulsed laser deposition (RPLD) [3] is introduced between Si and VO_2 to overcome the same. This work focuses on the growth, crystallography, and IMT characteristics of VO_2/TiN/Si.

Epitaxial VO_2 films on TiN buffered Si is achieved through pulsed laser deposition (PLD) using a V_2O_5 target in oxygen ambient. The deposition pressure is finely tuned to find the narrow growth window for the VO_2 phase [4]. Dual-stage growth is employed, in which an initial few layers (2-5 nm) of deposition at low pressure is followed by high-pressure deposition. The VO_2 film growth is monitored in situ using reflection high energy electron diffraction (RHEED) and shows clear diffraction spots confirming the epitaxial growth of VO_2 on TiN/Si. The VO_2 films grow on TiN/Si in a 3D growth mode in which islands of films nucleate and merge to form continuous films. The high-resolution X-ray diffraction (HRXRD) pattern shows only VO_2 (011) and (022) peaks which indicate the films are phase pure with (011) orientation in the out-of-plane. The symmetric rocking curve FWHM is 1.8°, which reveals the mosaic nature of the films in the out-of-plane direction. For (200) VO_2 Bragg condition, 8-Bragg reflections were seen, vs. (111) TiN 4-Bragg reflections in the merged pole figure of TiN(111) and VO_2(200), suggesting the presence of in-plane rotation variants [5]. Temperature-dependent XRD and electrical measurements were done to confirm IMT behavior. A comprehensive study on the epitaxial orientation relationship between these variants investigated by X-ray diffraction and electron microscopy (HREM and SAED) and IMT characteristics will be discussed at the conference.

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3:45 PM EL01.08.04
Phase Change Materials from the Thermal Point of View Nele Harnack, Pengyan Wen, Olivier Maher, Siegfried Karg and Bernd Gotsmann; IBM Research Europe - Zurich, Switzerland

Materials with a structural phase transition are interesting as emerging devices for neuromorphic and in-memory computing. Most prominent are non-volatile phase-change memory devices (PCMs) based on chalcogenides that utilize a transition between amorphous and crystalline states. Persistent states with different resistance are set by controlling the relation between heat generation and dissipation. In contrast, materials with an insulator-to-metal transition (IMT) exhibit a structural phase change upon heating but return to the original state when cooling back to room temperature. This behaviour can be exploited for oscillators rather than memories. As an example, VO_2 transitions from a monoclinic to a rutile crystalline structure accompanied by a resistance change of up to 5 orders of magnitude.

Processes in these materials are inherently tied to temperature changes and thermal transport. In PCMs, the (re)crystallization is driven by Joule heating to a certain temperature and subsequent (slow) cooling, leading to a stark change in resistance. In VO_2, the IMT can be induced by temperature rise due to self-heating in the highly resistive state, which is highly non-uniform due to inhomogeneities of the material. The complex interplay between resistive heating, heat spreading, and the thermal phase-transition correlated with a strong change of resistance makes investigation challenging. Current filaments that form are similar to resistive oxide memories.

Thermal imaging can elucidate the thermal processes in resistance switching devices. A valuable characterization technique for this task is Scanning Thermal Microscopy (SThM) due to its high spatial and temperature resolution. Moreover, it can image original devices in-operando and give quantitative values in a non-destructive, non-interfering manner. The SThM method determines the local temperature by measuring the heat flow between the device and an AFM-like cantilever with an integrated heating and sensing element [1]. We have developed and advanced the SThM method for devices with non-linear and volatile characteristics and applied it to various applications.
For example, we were able to quantify local temperature distributions caused by heat-dissipating current filaments at sub-10 nm resolution in VO_2 and resistive RAM devices in different voltage-dependent states. It was found that the form and position of the current filament in a lateral, polycrystalline VO_2 device varies when the voltage is changed to switch between insulating and metallic state. This explains the undesirable varying oscillator characteristics during operation and suggests the development of new device designs. The temperature of vertical resistive RAM elements was imaged through the top electrode, revealing the position of a current filament which stays stable during cycling and does not change when switching between high and low resistive state. The dimension of the filament and the heat spreading radius can be estimated from the thermal image, which can be utilized to determine the minimum device size and the maximum packing density of those memories.
In conclusion, the thermal imaging method developed here can be used to map the temperature distribution in a variety of devices during their operation, including those showing volatile and non-volatile switching. The interpretation of the resulting temperature maps can reveal thermal processes and guide design decisions and fabrication processes.

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4:00 PM EL01.08.05
The Time Scale of Metal-Insulator Transitions by Electrostatic Gating in a Solid-State Three-Terminal VO_2 Device Satoshi Hamasuna, Satya Prakash Pati and Takeaki Yajima; Kyushu University, Japan

Vanadium dioxide (VO_2) exhibits a metal-insulator transition (MIT) above room temperature and the electrical resistivity of VO_2 abruptly changes by three orders of magnitude. At room temperature, this transition can be easily triggered by Joule heating, and therefore, various VO_2-based applications have been proposed including analog crossbar switches, oscillator networks, and neuromorphic computing [1]. The transition is induced not only by temperature change but also by electron doping, and its static characteristics have been studied in detail over many years [2]. On the other hand, its transient characteristics are not yet fully understood. The major challenge is the difficulty to control fast and precisely the temperature that causes the transition at the transition temperature (T_{MIT}). Although the transient characteristics were partially elucidated in laser-induced transition [3] and Joule heat-induced transition [4], the high nonequilibrium nature of laser-induced electronic excitation or the thermal runaway in conductive filaments makes the situation more complicated. Our research group has recently developed a solid-state electrostatic gating device that causes MIT by electron accumulation via high-permittivity titanium dioxide (TiO_2) gate dielectric [5,6]. Although the modulation is relatively small, this device has the potential to control the MIT with high speed and precision, being ideal for investigating the transient characteristics. In this study, we exploited this solid-state gating device to systematically investigate the transient characteristics of the MIT in the VO_2 channel. We found that the transition occurs in the time scale of several ten milliseconds, and this time scale is exponentially shortened by increasing the gate voltage. When the influence of the gate voltage is converted to the equivalent temperature effect, we found the transition speed is accelerated by three orders of magnitude per 1 K. These results provide the underlying physics for the high-speed operations of VO_2-based devices and enable further applications of this material to neuromorphic and other functionalities.
Epitaxial VO_2 films (7 nm) were grown on the Nb (0.05 wt.%) doped TiO_2 substrate and were patterned by photolithography. The fabricated device is a three-terminal device consisting of the substrate as the gate electrode, VO_2 film as the channel (35 μm × 50 μm), and the depletion layer formed inside the doped TiO_2 substrate as the gate insulation layer [5]. The VO_2 channel of the device showed an abrupt resistance change around 309 K. Next, the drain voltage of the three-terminal device was fixed at 0.1 V, a pulse voltage was applied to the gate terminal at the temperature slightly below T_{MIT}, and the time variation of the source current was measured. The measurement results showed that the transition was induced by the applied gate voltage and the speed of the transition can be enhanced up to three orders of magnitude by changing the gate voltage from 1 V to 5 V. When the electron accumulation effect due to gate voltage converted to the equivalent temperature effect, the speed of the transition can be enhanced up to three orders of magnitude per 1 K. The origin of this high-speed transition is attributed to the collective nature of the domain growth during MIT. These results provide the underlying physics for the high-speed operations of VO_2-based devices and enable further applications of this material to neuromorphic and other functionalities. [1] B. Y. ZHOU *et al*., PROCEEDINGS OF THE IEEE 103, 8, August 2015 [2] K. Shibuya *et al*., *Appl. Phys*. *Lett*. **96**, 022102 (2010) [3] A Cavalleri *et al*., Physical Rev. B 70 1161102 (2004) [4] J Valle *et al.*, Nature **569**, 388-392 (2019) [5] T. Yajima *et al*., *Nature Commun*. **6**, 10104 (2015) [6] T. Yajima et al., Adv. Elec. Mater. 8, 2100842 (2021)

SESSION EL01.09: Virtual Session
Session Chairs: Stefania Privitera and Carlos Ríos
Wednesday Morning, April 26, 2023
EL01-virtual

8:00 AM EL01.09.01
Phase-Change Memristive Materials for Physically Unclonable Anticounterfeiting Devices Shao Xiang Go[1], Qiang Wang[1], Kian Guan Lim[1], Tae Hoon Lee[2], Natasa Bajalovic[1] and Desmond K. Loke[1]; [1]Singapore University of Technology and Design, Singapore; [2]University of Cambridge, United Kingdom

Anticounterfeiting devices driven by physical unclonable functions (PUFs), as one of the emerging tools against counterfeiting, are easy to create but challenging to replicate due to intrinsic randomness. Phase-change memristive materials show large degree of randomness suitable for high performance and down-scalable PUF devices. Herein, we demonstrate the utilization of high-degree-of-randomness amorphous (A) state variations concomitant with different operating conditions via thermal fluctuation phenomena, together with a hybrid framework for in memory computing and next generation security primitive, i.e., A PUF, for attaining secure key generation and device authentication. Rapid crystallization process enables large-size key reconfigurability in A-PUF, while in-memory computing empowers a strong eXclusiveOR (XOR-) and-repeat A PUF construction to avoid machine learning attacks. Near ideal uniformity and uniqueness without additional initial writing overheads in weak memristive A-PUF is achieved. These PUF devices could provide a potential system to realize unbreakable anticounterfeiting.

8:05 AM *EL01.09.02
Atomic-Scale Characterizations of Phase Transitions in Ge-Sb-Te Alloys Wei Zhang; Xi'an Jiaotong University, China

Tailoring the degree of structural disorder in Ge-Sb-Te alloys is important for the development of non-volatile phase-change memory and neuro-inspired computing. In this talk, I will present the atomic-level details of the multi-fold structural transitions, including crystallization, amorphization, vacancy ordering/disordering induced crystal-crystal transitions, in Ge-Sb-Te alloys by in situ high-resolution transmission electron microscopy experiments and ab initio density functional theory calculations. The impact of atomic ordering on altering the electronic and optical properties of Ge-Sb-Te alloys will be discussed in detail, which is relevant to practical applications. At last, I will also discuss the challenges and progress on atomistic modelling of Ge-Sb-Te alloys at the device scale. References: [1] T.-T. Jiang, X.-D. Wang, J.-J. Wang, H.-Y. Zhang, L. Lu, C. Jia, M. Wuttig, R. Mazzarello, W. Zhang*, E. Ma, In situ characterization of vacancy ordering in Ge-Sb-Te phase-change memory alloys, Fundamental Research DOI: 10.1016/j.fmre.2022.09.010 (2022). [2] Y. Xu, Y.-X. Zhou, X. Wang, W. Zhang*, E. Ma, V.L. Deringer, R. Mazzarello*, Adv. Mater. 34 (2022) 2109139. [3] Y.-X. Zhou, W. Zhang*, E. Ma, V. L. Deringer*, Unlocking device-scale atomistic modelling of phase-change memory materials, arxiv: 2207.14228 (2022)

8:35 AM EL01.09.03
Reversible Optical Switch of Sb2S3 Thin Films for Tunable Nanophotonic Applications Capucine Laprais[1,2], Lotfi Berguiga[1,3], Nicolas Baboux[1,3], Guillaume Saint Girons[1,2] and Sébastien Cueff[1,2]; [1]Institut des nanotechnologie de Lyon, France; [2]Ecole Centrale Lyon, France; [3]INSA Lyon, France

Phase change materials (PCM) have emerged as a promising solution for developing active nanophotonic devices. The reversible and significant change in the optical properties of their amorphous and crystalline state can enable multi-functionality and reconfigurability of the devices. Additionally, PCM exhibit a rapid (ns) and non-volatile phase transition between their amorphous and crystalline state allowing for low energy consumption [1]. Low loss PCM specifically have been a subject of increasing interest in the photonic community as their extinction coefficient nearly vanishes in the near infrared for both phases. Sb_2S_3 is one of this emerging PCM presenting exciting properties: above 780 nm it has no absorption in neither phase while its refractive index contrast remains significant ($\Delta n=1$) [2]. This makes Sb_2S_3 interesting for novel tunable nanophotonic applications in the visible and near infrared regime. However, this material is not well known yet when it comes to its switching properties, chemical stability, endurance, etc. There are also some integration issues to address, especially to control the phase switching mechanisms at the device level [3].

In this work, we use optical switching to induce the phase transition in Sb_2S_3: by properly choosing the laser pulse duration and energy it is possible to locally crystallise or amorphise the PCM. We show that we can reversibly switch Sb_2S_3 thin films from the crystalline to the amorphous phase using a pulsed laser. With a laser fluency lower than the ones reported in the literature [4][5], we successfully switched different thin films thicknesses of Sb_2S_3 deposited by ebeam evaporation on various substrates. We could also achieve partial amorphisation in the depth of the PCM, which is promising for multi-states switching. Here, we discuss the physical mechanisms behind the laser-induced change of phase using multi-physics considerations to draw conclusions on potential optimizations of the reversible phase switching of Sb_2S_3. This should lead to a full control of the multi-level optical switch of Sb_2S_3, and show promise in using this material for rewriting optical devices multiple times, encoding multi state information in the depth of the PCM, designing holograms,...

We acknowledge funding from the French National Research Agency (ANR) under the project MetaOnDemand (ANR-20-CE24-0013).

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8:50 AM EL01.09.04
Multistate phase transition and polymorph stability through interface engineering in vanadium dioxide system Ujjwal Chitnis[1], Sooraj Kumar[1], Syed A. Bukhari[2], Ram K. Ghosh[3] and Ankur Goswami[1]; [1]Indian Institute of Technology, Delhi, India; [2]National Research Council of Canada, Canada; [3]Indraprastha Institute of Information Technology, Delhi, India

Transition metal oxide systems are notably known for their phase transition behaviour, of which vanadium dioxide (VO_2) has gained prominence due to its reversible metal-insulator transition (MIT) at critical temperature (T_c) of 340 K by change in its electrical, optical, structural and thermal properties. The structural transition, occurs from the initial monoclinic (M1) polymorph to the final rutile (R), through a metastable monoclinic (M2) polymorph. Both M1 and R have caught the most attention due to their easy synthesis and MIT behaviour but other metastable polymorphs like VO_2 (A), VO_2 (B), VO_2 (T), VO_2 (P), etc, also exists, which are challenging to stabilize around room temperature ranges. Achieving reduction in T_c with multiple polymorphs near room temperature will facilitate application of VO_2 in resistive switching, reconfigurable memory, frequency controlled and neuromorphic devices[1-3]. As the devices are subjected to heating during any operation, it can potentially lead to thermal throttling, noise signals, and energy losses in any electrical system, leading to reduction in the device efficiency and limiting the application of VO_2 in low power devices and computing units. To overcome this challenge, unique out-of-plane device architecture along with interface engineering can contribute to modification of structural and electronic properties by reducing the transition temperature much closer to room temperature. Through this work, focus on highlighting the effect of titanium dioxide (TiO_2) interface in modifying the microstructural and electrical properties of VO_2 system is presented. Thin films gown by pulsed laser deposition (PLD)[4] are investigated for device application due to uniform surface morphology[5]. Reduction in T_c due to interface misfit strain and modified carrier behaviour is observed. Electrical measurement across the TiO_2 interface uncovers stable multistage phase transition which is then confirmed using spectroscopy techniques that indicate presence of polymorphs and phases like M1, R, M2, T and V_2O_3, etc in the system. Surface topological measurement using KPFM indicates interface driven work function change which possibly leads to stabilization of metastable polymorphs like M2, T and other phases. Further, DFT calculations were performed incorporating misfit strain which reveals a decrease in Tc, much closer to the room temperature value. Thus, through selecting a suitable device architecture and interface engineering, VO_2 devices can be tuned to achieve higher efficiency for applications in reconfigurable memory, computation units and multistate devices.

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9:05 AM EL01.09.05
Improving VO_2 Granular Films' CMOS Compatibility to Perform Oscillation-Based Computing Olivier Maher, Nele Harnack, Roy Bernini, Bernd Gotsmann and Siegfried Karg; IBM Zurich, Switzerland

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The growing interest in polycrystalline phase-change materials to develop brain-inspired learning and novel computing approaches makes VO_2 a first-choice material, with its ability to switch from a high to a low resistive state around room temperature (68°C). Natural oscillations triggered by running a current through this material are offering the means to fabricate electronic oscillators that once coupled, create an oscillating neural network (ONN), best suited to compute pattern recognition tasks and solve optimization problems [1, 2, 3]. This type of network shows the promise of energy-efficient computing by processing data locally while avoiding issues related to the different frequency operations from the memory access to the processor's calculation times [1, 3, 4]. Improving CMOS compatibility with pristine material quality and a highly reliable fabrication process to produce uniform devices is paramount for industrial purposes [5, 6].
The integration of VO_2 layers on a Si-based platform typically results in polycrystalline films presenting granular structures with a rugged surface topology [5]. This introduces undesired variability among our electrical oscillators that needs to be reduced to a minimum before their integration in a compound circuit, such as our ONN [6]. To minimize device-to-device variations, VO_2-based oscillators in planar and crossbar configurations have been fabricated. The devices excel in high-frequency operation and power efficiency.
A 50 nm thick Vanadium oxide film is deposited by a water-based ALD reaction on a $Si/SiO_2/HfO_2$ substrate for CMOS compatibility. A post-annealing step is required to turn the amorphous film into a crystalline VO_2 layer. We use two different annealing techniques which vary in steepness of temperature ramps and oxygen pressure to obtain reproducible behavior in our devices. The impact of the different annealing methods on the grain size, the surface roughness, the electric behavior, and the quality of the resulting VO_2 film are studied through Raman Spectroscopy, Atomic Force Microscopy (AFM), and by measuring the resistance of the film as a function of temperature. The devices are then placed in a circuit to measure the resulting natural oscillations before being coupled with one another. The power efficiency and the oscillation frequency could be significantly improved by device scaling and optimizations.
Our network of VO_2-based oscillators shows the promise of an attractive and scalable computing unit for hardware accelerators [3, 4], thanks to its high-performance switching properties and CMOS compatibility.
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9:20 AM EL01.09.06
High Temperature Phase Change Materials Nacer Ibaroudene, Md. Khirul Anam and Ethan Ahn; The University of Texas at San Antonio, United States

Chalcogenide thin films that exhibit a reversible transition between crystalline and amorphous phases has been the important material platform for data storage and emerging neuromorphic computing applications. For the past decades, a wide variety of phase change alloys, including GST ($Ge_2Sb_2Te_5$) – the most commonly used for phase change memory, have been studied in a general effort of increasing the speed performance or energy efficiency of modern electronics and computing hardware. However, the (semiconductor) chip shortage is still one of the biggest challenges in the nation, and in particular, a high temperature application domain has strong demands for novel scientific and engineering approaches to develop materials of the highest reliability and stability. For example, the use of high temperature electronics (operating at above 125 °C) continues to grow in an automotive industry, and thus, heat-resistive metals, plastics, and semiconductors need to be further researched and developed. Phase change materials are identified as an essential semiconducting component of high temperature electronics for data storage, sensing, and energy harvesting and conversion.

Here in this work, we performed a systematic study on phase change materials for far-reaching applications in the high temperature domain. It has been understood that GeSb possesses the high potential to become the next-generation platform for high temperature electronics due to its relatively high crystallization temperature (T_C). We synthesized 50 nm-thick $Ge_{14}Sb_{86}$ thin films by using the RF sputtering technique, and carefully measured the resistivity vs. temperature characteristics. It is found that T_C of our $Ge_{14}Sb_{86}$ thin film reaches the value as high as 230 °C, which is in good agreement with the literature. This is best attributed to the growth-driven crystallization kinetics of GeSb (i.e., crystallization tends to start occurring at the crystalline-amorphous interfaces). However, it still remains unanswered if GeSb can satisfy the multiple requirements of contemporary high temperature electronics because a holistic study that further investigates GeSb beyond its high T_C is still missing. For example, GeSb is known for relatively slow (SET) switching speed, and the topic of enhancing the switching speed of GeSb while still affording the high T_C remains unexplored. Therefore, our work is expected to greatly advance the field by exploring the performance of GeSb in multiple aspects, including the crystallization temperature, crystallization (SET switching) speed, data retention, and reliability.

It is highlighted that our experimental approach is based around the idea that doping is key to best engineer the phase change materials and find the optimal balance among properties desired for high temperature applications. In this work, we fabricated a wide variety of phase change materials such as (undoped) GeSb, Ti-doped GeSb, and Al-doped GeSb, and found that Al-doped GeSb achieves the T_C value of greater than 230 °C, excellent data retention (10-year data retention @ around 140 °C), and switching speed of a few tens of nanoseconds at a moderate amount of current applied. We're currently investigating the effect of other dopants as well, such as Hf and Ta, while performing comparative studies and analyses with reference samples that consist of undoped or doped conventional GST thin films. Therefore, our study features a holistic approach to investigate both phase change materials of GST and GeSb that are either undoped or doped by various transition metal elements in terms of high temperature application-specific performance criteria.

SYMPOSIUM

April 10 - April 25, 2023

Symposium Organizers
Robert Hoye, Imperial College London
Maria Antonietta Loi, University of Groningen
Xuedan Ma, Argonne National Laboratory
Wanyi Nie, Los Alamos National Laboratory

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* Invited Paper
\+ Distinguished Invited

SESSION EL02.01: Interface I
Session Chairs: Wanyi Nie and Joshua Stein
Monday Afternoon, April 10, 2023
Moscone West, Level 3, Room 3002

1:30 PM *EL02.01.01
Development of Robust Perovskite Solar Cells Using Interfacial Materials Lee Yih Wang[1], Hsin-Hsiang Huang[1], Hsinhan Tsai[2,3], Rathinam Raja[1], King-Fu Lin[1], Wanyi Nie[2] and Sergei Tretiak[2]; [1]National Taiwan University, Taiwan; [2]Los Alamos National Laboratory, United States; [3]University of California, Berkeley, United States

The power conversion efficiency (PCE) of perovskite solar cells (PSCs) has risen rapidly from 3.8% to a certified 25.7%. However, their relatively short operational lifetime remains a critical hurdle for commercialization. Herein, we present two simple ways to enhance the environmental stability of PSCs. In the first approach, a tiny amount (0.01 wt%) of exfoliated montmorillonite (*ex*MMT) was incorporated into the perovskite precursor solution and these *ex*MMT nanoplates were able to self-organize into an ultra-dense top layer with a thickness of around 50 nm and strongly bonded to the perovskite crystalline grains through cationic exchange with organic cations during the spin-drying process. Such self-assembled layer acted as an effective protection shell that retarded the penetration of gases and moisture into the perovskite during environmental aging, achieving extremely stable photovoltaic cells against moisture, thermal and photo stresses. The thus prepared unencapsulated devices exhibited exceptionally steady PCE, which showed negligible degradation after 4680 h of storage in 50% relative humidity and room temperature. In the second route, a fluorine-containing fullerene adduct (5F-PCBP) was introduced to replace PCBM as an electron-transporting layer (ETL) to establish PSCs that delivered an excellent PCE of 21.27%. The fluorinated ETL not only increased the surface hydrophobicity but also filled the surface iodine vacancy and immobilized the ion migration, thus protecting the solar devices against harsh environment. As a result, The CsFAMA perovskite solar devices with 5F-PCBP ETL without physical encapsulation exhibited a T_{80} over 1920 hours under industrial relevant conditions i.e., relative humidity of 85% and heat stress at 85°C.

2:00 PM *EL02.01.02
Heterointerface and Intragrain Microstructures of Perovskite Semiconductors Yuanyuan Zhou; Hong Kong Baptist University, China

Heterointerface and intragrain microstructures can be key factors influencing performance of perovskite semiconductors, which have been less studied. In my talk, I will discuss our recent advances on the high-resolution characterization and novel tailoring of these microstructures, advancing our fundamental understanding of microscopic structure-property-performance relationship in perovskites. Specifically, I will first illustrate several unique structural designs of perovskite heterointerfaces (interpenetrating, elastic, or de-doped) which mitigate the major issues of perovskite solar cells in different device setting. Then, I will discuss on leveraging a novel scanning transmission electron microscopy methodology to unravel performance-limiting intragrain interfaces in perovskite solar cells.

2:30 PM EL02.01.03
Engineering the Wettability Problem of SAMs Hole Transport Layers for Highly Efficient Sn/Pb- Perovskite Solar Cells Matteo Pitaro[1], Javier S. Alonso[1], Jane Kardula[1], Lorenzo Di Mario[1], karolina Tran[1], Malin B. Johansson[2], Erik Johansson[2], Ryan Chiechi[3] and Maria Antonietta Loi[1]; [1]University of Groningen, Netherlands; [2]Uppsala University, Sweden; [3]NC State university, United States

Mixed tin-lead perovskite materials are the most promising option to reduce Pb content in hybrid perovskite solar cells (HPSC) and to tune the band gap towards the near infrared. Recently, self-assembled monolayer of (2-(9H-carbazol-9-yl)ethyl)phosphonic acid (2PACz) have been reported as alternative candidates to poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT: PSS) as hole transporting material (HTL).[1] However, the adoption of 2PACz as HTL opens challenges for the deposition of the perovskite active layer in a reproducible manner, due to the poor wettability of the perovskite precursor solution on carbazole group. Here we demonstrate that by depositing an additional interlayer, which exposes polar groups, between the carbazole-based monolayers and the perovskite active layer the wettability problem can be solved, opening to the use of carbazole-based molecules HTL for large area devices.
We implemented Br-2PACz molecules as HTL, and as interlayer we synthetized 9H-Carbazole-9-butane-1-ammonium iodide ($4NH_3CzI$). We expect that the two carbazole groups, one from Br-2PACz and the other from $4NH_3CzI$ will interact through a π-π stacking giving rise to a surface of exposed ammonium groups, which drastically improves the wettability for the $Cs_{0.25}FA_{0.75}Sn_{0.5}Pb_{0.5}I_3$ precursor solution.
Solar cells with Br-2PACz and $4NH_3CzI$ acting as HTL showed an efficiency of 19.45% for 0.04 cm^2 active area devices (while 19.25% was obtained without the interlayer. The interesting result is the improved reproducibility of the double-layer HTL compared to Br-2PACz. In fact, the Br-2PACz- based solar cells present an average value on 20 devices of 9.65 ± 9.62% with several not working solar cells due to a poor substrate coverage for the perovskite layer. On the contrary, the solar cells with the double-layer HTL present an average PCE of 18.98 ± 0.28%.
While this is a record efficiency for this perovskite composition, the most important result is the in the area scaling of the efficiency. Devices of 0.8 cm^2 area fabricated with the two-layer HTL showed an efficiency of 12.5%, while the ones using only Br-2PACz where not working. Finally, the two-layer HTL has also a strong effect on the stability under continuous 1.5 AM solar illumination. Devices maintain 80% of the initial efficiency after 365 hours respect to the 230 hours reached by the Br-2PACz-only.

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2:45 PM EL02.01.04
2D/3D Heterostructures with Conjugated Organic Cations for Stable and Efficient Perovskite Solar Cells Jiaonan Sun and Ke Ma; Purdue University, United States

Surface passivation is proven an effective way to enhance the efficiency and stability of perovskite solar cells (PSCs). However, a key challenge faced by most of the passivation strategies is reducing the interface charge recombination without imposing energy barriers to charge extraction. Herein, a series of novel semiconducting organic ammonium cations were designed as interface modifiers between the light-harvesting perovskite film and the hole transporting layer. We show that the conjugated cations can directly extract holes from perovskite efficiently. Together with delicate energy level tuning and stabilized interface in devices, we demonstrate a FAPbI3 based triple cation perovskite solar cell with an excellent power conversion efficiency of 23.64%, and the suppressed ion migration and halide phase segregation, which lead to a long-term thermal stability over 2000 hours and light stability over 500 hours. Our strategy provides a new practical method of interface engineering in perovskite solar cells towards improved efficiency and stability.

3:00 PM BREAK

SESSION EL02.02: Harsh Environments
Session Chairs: Hsinhan Tsai and Lee Yih Wang
Monday Afternoon, April 10, 2023
Moscone West, Level 3, Room 3002

3:30 PM EL02.02.02
Halide Perovskite Direct X-Ray Detector with an Extremely Low Dark Current via Interfacial Engineering Ganbaatar Tumen-Ulzii, Oliver Moseley, Tiarnan Doherty, Miguel Anaya and Samuel D. Stranks; University of Cambridge, United Kingdom

X-ray detection technology has been developed and frequently used for medical imaging diagnostics, security inspection and scientific research areas. In a scintillator-type detector, a semiconducting material is excited by a probing X-ray and emits ultraviolet-visible (UV-Vis) light into a photodetector, which in-turn outputs an electrical signal and, ultimately, forms an image. However, this technology suffers from strong self-absorption and afterglow emission leading to a blurred image.[1]
In contrast, X-ray direct detectors which convert X-ray photons into electric charges have a superior resolution than scintillators and are more efficient since they don't suffer from optical losses. However, current commercial solutions (e.g. amorphous Se) are not suitable for high-energy X-ray applications such as computed tomography (CT) for cancer detection because of their low atomic number (Z). Recent innovations based on Cadmium Telluride (CdTe) or Cadmium Zinc Telluride (CZT) semiconductors with high Z are promising for high-energy CT relevant X-rays. However substantial challenges in the fabrication and deployment of the active layer material have limited their widespread adoption. For instance, high-quality CdTe crystals take 3 months of high-temperature growth to fabricate at a cost in excess of \$1500 per cm^3.
Recently, halide perovskite (PVK) materials have emerged as promising materials for direct X-ray detection, already demonstrating excellent mobility-lifetime products (μτ) comparable to CZT and CdTe, detector-grade bulk resistivity, and high stopping power at high-energy X-rays.[2] To date, high sensitivity up to 10^6 μC Gy_{air} cm^{-2} and a very impressive lowest detectable dose rate (LoD) of <10 nGy s^{-1} have been achieved.[3] However, the dark current is still large >1 nA cm^{-2} which is one of the main obstacles to commercialising PVK X-ray direct detection technology. One of the origins of the large dark current is related to the interface defects at the PVK material and charge transport layers in the device stack.

In this talk, we present a high-performing, direct X-ray detector with a device structure based on an alloyed perovskite single crystals synthesized via a state-of-the-art inverse temperature crystallisation (ITC) method. We introduce the use of a fluoride-based buffer layer to attain control over the device's dark current to reach an impressive low dark current of ~10 pA cm^{-2}. This value establishes a new record, 10x lower than conventional CZT and CdTe direct detectors. Furthermore, the detector showed a clear X-ray-induced current and the LoD of 167 nGy s^{-1}. This study will open a new direction for PVK X-ray detectors with extremely low dark current towards integration with application-specific integrated circuit (ASIC) chips/backplanes for multi-pixel detection.

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3:45 PM EL02.02.03
Implications of Dynamic vs. Static 2D/3D Halide Perovskite Interfaces on Solar Cell Stability Alan Kaplan, Xiaoming Zhao, Quinn C. Burlingame and Lynn Loo; Princeton University, United States

Employing a 2D perovskite or ammonium-halide salt passivation layer is a promising method to improve the stability and efficiency of halide perovskite solar cells (PSC). Recent work has revealed that the initial structure of this passivation layer may evolve during PSC aging, depending on the identity of the halide salt employed. Our work has indicated that the nature of the organic ligands that form the 2D perovskite passivation layer can also impact the operation stability of the resulting solar cells. Specific to this investigation, we have examined the structural evolution of several 2D/3D perovskite interfaces comprising different organic ligands using ex-situ photoluminescence and x-ray diffraction measurements. We found the 2D/3D perovskite interface to be "dynamic" when mono-functional ammonium ligands, i.e., butylammonium and 4-fluorophenethylammonium, are used to form the 2D perovskite layers atop the 3D perovskite, as the structure of the 2D perovskite layers evolve substantially during aging. Replacing the mono-functional ammonium ligands with a bifunctional diammonium ligand, i.e., 1,4-butanediamine, instead results in a "static" interface in which the structure of the 2D perovskite layer remains stable during aging. Given the chemical difference in the organic ligands, we ascribe the difference in stability of these 2D/3D perovskite interfaces to the extent of binding the organic ligands have with their adjacent inorganic layers within the 2D perovskites, with a greater extent of binding enhancing the structural stability of the interface.

4:00 PM EL02.02.04
Rational Design of Photoelectrochemical Perovskite-BiVO$_4$ Tandem Devices for Scalable Solar Fuel Production Virgil Andrei[1,1], Geani M. Ucoski[1], Robert Jagt[1], Chanon Pornrungroj[1], Demetra S. Achilleos[1], Katarzyna Sokol[1], Judith MacManus-Driscoll[1], Robert Hoye[2], Richard Friend[1] and Erwin Reisner[1]; [1]University of Cambridge, United Kingdom; [2]Imperial College London, United Kingdom

Metal halide perovskites have emerged as promising alternatives to commonly employed light absorbers for solar fuel synthesis, enabling unassisted photoelectrochemical (PEC) water splitting[1,3] and CO_2 reduction to syngas.[2,4] While the bare perovskite light absorber is rapidly degraded by moisture, recent developments in the device structure have led to substantial advances in the device stability. Here, we give an overview of the latest progress in perovskite PEC devices, introducing design principles to improve their performance and reliability. For this purpose, we will discuss the role of charge selective layers in increasing the device photocurrent and photovoltage, by fine-tuning the band alignment and enabling efficient charge separation. A further beneficial effect of hydrophobicity is revealed by comparing devices with different hole transport layers (HTLs).[1,3] On the manufacturing side, we will provide new insights into how appropriate encapsulation techniques can extend the device lifetime to a few days under operation in aqueous media.[1,2] To this end, we replace low melting alloys with graphite epoxy paste as a conductive, hydrophobic and low-cost encapsulant.[3,5] The combined advantages of these approaches are demonstrated in a perovskite-BiVO$_4$ tandem device archiving selective unassisted CO_2 reduction to syngas.[4] These design principles are successfully applied to an underexplored BiOI light absorber, increasing the photocathode stability towards hydrogen evolution from minutes to months.[6] Finally, we take a glance at the next steps required for scalable solar fuels production, showcasing our latest progress in terms of device manufacturing. A suitable choice of materials can decrease the device cost tenfold and expand the device functionality.[7] Such materials are compatible with large-scale, automated fabrication processes, which present the most potential towards future real-world applications.[8]

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4:15 PM EL02.02.05
Photoelectrochemical Water-Splitting Device Based on a Halide Perovskite Solar Cell Protected by a Single Crystal TiO$_2$ Choongman Moon, Jaehyuk Koh and Byungha Shin; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Photoelectrochemical (PEC) water splitting is a renewable way to produce hydrogen by introducing electrocatalysts on the surface of photovoltaic materials. Compared to a system electrically connecting separate photovoltaic and electrochemical devices, PEC has a simpler structure because it can remove peripheral components (e.g. Ag metal grid or power electronics) and it may lead to a significant reduction in system cost and efficiency loss. However, one of the greatest challenges in PEC is that light-absorbing materials are in contact with (or in the vicinity of) electrolytes, and it would cause severe damage to the light-absorbing materials. This issue becomes more serious when it comes to a halide perovskite light absorber. The halide perovskite solar cell is an emerging photovoltaic material with great potential, however, because of its instability when in contact with water or oxygen, PEC devices forming a solid-liquid junction between halide perovskites and electrolytes have been showing poor stabilities. A typical approach to protect a PEC device is depositing a protection layer with a tens or hundreds nanometer thickness over the light-absorbing materials, however, a protection layer completely impermeable to an electrolyte has not been demonstrated yet. Furthermore, processing for protection layer deposition often requires a high temperature, which is not applicable to thermally vulnerable halide perovskite materials. For these reasons, PEC devices based on halide perovskites have been showing

only several hours of device lifetime.
In this study, we improve the stability of a perovskite PEC device by transferring a single crystal TiO_2 wafer (1cmX1cm) onto a halide perovskite cell. In order to form an ohmic contact on a TiO_2 wafer, indium tin oxide (ITO) was deposited on one side, while the other side was decorated with Pt for catalyzing hydrogen evolution reaction. The TiO_2 wafer was transferred onto a halide perovskite solar cell by bridging the perovskite cell and ITO contact with a transparent conductive adhesive, which is prepared by embedding Ag particles into paraffin. The PEC device showed an open circuit potential of ~1.1 V and short-circuit current density of ~14 mA/cm^2, and was able to operate for ~2 days without degradation in current density.

SESSION EL02.03: Interface II
Session Chairs: Robert Hoye and Kai Zhu
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3002

10:30 AM *EL02.03.01
Understanding and Realising Stable Perovskite Optoelectronic Device Operation Samuel D. Stranks; University of Cambridge, United Kingdom

The efficiency of halide perovskite optoelectronic devices including solar cells and LEDs continue to rise, yet operational stability remains a challenge. Here, I will outline recent developments towards understanding and realising stable perovskite device operation in both solar cell and LED platforms on different length scales. I will show a variety of multimodal operando microscopy measurements to understand device degradation, realising generalised understanding of instability pathways. I will show how material and contact optimisation and passivation leads to greatly increased device stability, opening up pathways to realise long-term stability.

11:00 AM *EL02.03.02
Chalcogenide Molecule-Based Interface Passivation for Enhancing the Stability of Perovskite Solar Cells Lydia H. Wong; Nanyang Technological University, Singapore

Over the last decade, perovskite solar cell (PSC) has emerged as very promising future-generation solar cell technology with a power conversion efficiency (PCE) of over 25%. However, the long-term stability of PSC still remains a barrier to its commercialization. For improving the stability of the PSC different classes of defect passivators have been investigated [1-3]. Among them, Lewis base-based passivators have been shown to be particularly effective owing to their ability to passivate various Pb^{2+} and Pb^0 related defects. Nonetheless, there is a lack of clear understanding regarding the defect passivation mechanism of these Lewis bases, resultantly, the predictability of the passivation strength of different Lewis base molecules is poor. This creates a challenge in selecting the superior passivator molecules among the plethora of options that are available.
In this talk, I will speak about our group's effort to understand the comparative interface passivation strength among different chalcogenide-based defect passivators. In our recent work, we use three different organic passivators (of similar structure) decorated with different chalcogenide atoms, (O, S, and Se) to study their effect on the stability of the devices. We observe that the sulfide and selenide passivated devices show superior stability compared to both un-passivated and oxide-passivated ones. This excellent stability with the sulfide and selenide passivators is most likely due to their strong interaction with the Pb cation, which can be explained using the hard-soft-acid-base principle. By taking the idea forward, we have used Al-doped CuS (Al-CuS) as sulfur-based inorganic hole transport layers (HTL) in inverted architecture PSC [1]. Al-CuS HTL-based devices show superior stability compared to NiO HTL-based control devices. After 650 hours of storage (at 30% RH, 20 °C), sulfide HTL-based devices retain more than 60% of their initial stability. In contrast, their oxide counterparts retain less than 40% of their original value in the same timeframe.

References:
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[2] M Rai, L.H. Wong* et al, Advanced Energy Materials, 2021, 2102276.
[3] S Lie, LH Wong, L Etgar*, ACS Applied Materials & Interfaces, (2022) 14 (9), 11339-11349.

11:30 AM EL02.03.03
Chelation with Polydentate Ligands for Effective Passivation of Pb-related Defects Towards Stable and Efficient Perovskite Solar Cells Seongheon Kim[1], Seong Ho Cho[1], Kiwan Jeong[2], Jieun Lee[1], Yonghoon Jung[1], Mansoo Choi[1,2] and Yunseog Lee[1]; [1]Seoul National University, Korea (the Republic of); [2]Global Frontier Center for Multiscale Energy Systems, Korea (the Republic of)

Organic-inorganic hybrid perovskite based solar cells (PSC) have shown tremendous progress in photovoltaic performance demonstrating a record power conversion efficiency (PCE) over 25%. However, attaining long-term stability under operation conditions is still challenging issue for commercialization. The key factor to achieve long-term stability as well as high PCE is to synthesize high-quality perovskite thin-films which can be represented by a lower defect density. In particular, Pb-related defects such as Pb clusters and uncoordinated Pb^{2+} ions are reported to accelerate the degradation of the devices. To mitigate the defect-induced degradation, various passivation strategies have been employed, mostly by introducing additional passivation layers between perovskite and charge transport layer. Among them, surface passivation methods utilizing materials with functional groups that can donate electrons on the defect site have shown significantly improved passivation effect. Therefore, chelation with polydentate ligands with the electron-donating functional groups can be employed for more effective passivation.
In this study, we investigate a novel strategy that can further enhance the chelation-driven defect passivation effect of perovskite thin-films. Chelating ligands possess stronger affinity to metal ions compared to conventional monodentate ligands which would be more advantageous to passivate Pb-related defects. Thus, we introduce various carboxylic acid based chelating agents with different numbers of functional groups during the synthesis process of the perovskite thin-films. We show that the number of functional groups that forms chelating bond is more significant, in this case, carboxyl group. Citric acid (CA), which contains three carboxyl group and one hydroxyl group, demonstrated the highest film quality regarding Pb-related defect passivation. Nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy are carried out to investigate the chelating bond between CA and Pb. Furthermore, we discover that the chelation at the nucleation and crystallization steps are highly effective for defect passivation. Finally, we demonstrate the CA chelation during the crystallization process results in higher performances of PSCs as well as the device stability.

11:45 AM EL02.03.04
Chemical Vapor Deposition of Cuprous Iodide as a Hole Transport Material for Perovskite Photovoltaics Eliza Spear[1], Luke Davis[2] and Roy Gordon[1]; [1]Harvard University, United States; [2]Tufts University, United States

A typical perovskite solar cell (PSC) requires both an electron and a hole transport material (ETM and HTM, respectively). The commonly employed organic HTMs are a significant source of instability in PSCs: the organic HTMs themselves have high resistivities, on the order of 10^5 Ohm cm, and require dopants, which can migrate and wreak havoc throughout the cell [1, 2]. Inorganic HTMs have the potential to improve both device stability and performance due to their own inherent stability and higher conductivity, which eliminates the need for dopants.

Inorganic HTMs, which include NiO_x, VO_x, copper delafossites, and cuprous iodide, are relatively underexplored, which motivates the development of new inorganic HTMs and techniques for depositing device-quality films of those HTMs. In considering deposition techniques for inorganic HTM candidates, vapor methods such as chemical vapor deposition (CVD) and atomic layer deposition (ALD) could enable rapid scaling and conformal coatings even on textured substrates [3, 4]. This makes them especially attractive for application in tandem silicon/perovskite devices where a perovskite cell is deposited directly atop a textured crystalline silicon cell [4, 5].

The optically transparent p-type semiconductor cuprous iodide (CuI) is a promising HTM candidate, with a band gap ~3.1 eV, low resistivity (~10^{-2} Ohm cm), and high hole concentration and mobility (~10^{19} cm^{-3} and ~1-10 $cm^2V^{-1}s^{-1}$, respectively) [6]. PSCs employing CuI as the HTM have achieved up to 17.6% photoconversion efficiency [7], but while CuI crystallite arrays have been obtained by CVD [8], CVD of continuous CuI thin films has only been accessed through a two-step vapor conversion process, requiring initial deposition of a copper chalcogen followed by vapor-phase conversion to the halide [6].

We have recently developed a CVD technique capable of direct deposition of continuous films of CuI at temperatures as low as 50 °C [9]. X-ray diffraction and Rutherford backscatter spectrometry confirm deposition of stoichiometric zincblende CuI. Progress in depositing continuous CuI films on substrates relevant to both n-i-p and p-i-n PSC device configurations will be discussed.

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SESSION EL02.04: Roundtable: SETO-American Made Solar Perovskite Prize Programming

Session Chairs: Xuedan Ma and Wanyi Nie
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3002

1:30 PM *EL02.04.01
Opportunities and Challenges for Perovskite PV R&D—A Perspective from US DOE SETO Timothy Siegler; Solar Energy Technologies Office, U.S. Department of Energy, United States

Halide perovskite photovoltaics is an emerging photovoltaic technology. They have recently achieved power conversion efficiencies (PCEs) of over 25% in 0.1 cm^2 small-area solar cells and over 32% in 1 cm^2 hybrid silicon tandems. While small area performance continues to push forward, demonstration of larger area performance is required if perovskite PV will contribute to aggressive domestic solar manufacturing and deployment goals required to meet the United States' current decarbonization targets. The U.S. Department of Energy Solar Energy Technologies Office (SETO) has a history of funding perovskite PV technology focused on increasing scale and demonstrating durability in large area modules. In this talk, SETO will discuss their perspectives on halide perovskite PV. This presentation will highlight some of the future opportunities of this technology, as well as the ongoing challenges required to advance this technology in the areas of efficiency at scale, durability, manufacturing and process control, and bankability.

2:15 PM *EL02.04.02
American-Made Challenges Perovskite Startup Prize Countdown Celebration Timothy Siegler; Solar Energy Technologies Office, U.S. Department of Energy, United States

The American-Made Challenges (AMC) Perovskite Startup Prize is a $3 million prize competition designed to accelerate the growth of the U.S. perovskite industry and to support the rapid development of solar cells and modules that use perovskite materials. This competition has two stages: "Countdown" and "Liftoff." In the initial Countdown stage, new startup entities incorporated after September 24, 2020, competed for a $200,000 prize. Winners of the Countdown prize were eligible to advance and compete for the $500,000 Liftoff prize. The submission deadline for the final Countdown competition was March 23, 2023. To celebrate the end of the Countdown Contest, the U.S. Department of Energy Solar Energy Technologies Office (SETO) will highlight and celebrate winners of the Countdown Contest. After a short introduction, Countdown Contest winners from previous cycles (Beyond Silicon, Verde Technologies, SoFab Inks, and MujiElectric) will participate in a pitch showcase where each winner will have 5 minutes to highlight their technologies and companies. This will be followed by a networking meet-and-greet between the startup companies, conference attendees, and SETO.

3:00 PM BREAK

3:30 PM *EL02.04.03
US Perovskite Industry Roundtable—Challenges and Opportunities for the Academic Community Timothy Siegler; Solar Energy Technologies Office, U.S. Department of Energy, United States

While halide perovskite PV has made significant progress in laboratory research, much less than 1 MW of perovskite PV installations have been commissioned globally. In this roundtable discussion, SETO and members of the US solar industry involved in perovskite research and development (R&D) will sit down and discuss the challenges of effectively translating this lab progress with perovskites to large-scale deployment. We will discuss how academic researchers can partner with the perovskite PV industry to aid in scale-up processes and will highlight which research questions are most interesting for industry R&D efforts. Further, we will discuss the tools and skills students need to be able to perform innovative, relevant solar R&D in the halide perovskite PV industry and will talk about strategies students may use to best position themselves for their post-graduate careers.

SESSION EL02.05: Novel Structure I
Session Chairs: Robert Hoye and Samuel Stranks
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3002

8:15 AM *EL02.05.01
External Stimuli, Timescales and the Structure of 2D and 3D Perovskites Mercouri G. Kanatzidis; Northwestern University, United States

Understanding and tailoring the physical behavior of halide perovskites under external stimuli is critical for designing efficient optoelectronic devices. We found that continuous light illumination leads to a contraction in the out-of-plane direction in two-dimensional hybrid perovskites, which is reversible and strongly dependent on the specific superlattice packing. Constant light illumination causes the accumulation of positive charges in the terminal iodine atoms, thereby enhancing the bonding character of inter-slab I-I interactions across the organic barrier and activating out-of-plane contraction. This results in a threefold increase in carrier mobility and conductivity, consistent with an increase in the electronic band dispersion predicted by first-principles calculations. Flux-dependent space-charge-limited current measurement reveals that light-induced interlayer contraction activates interlayer charge transport. The enhanced charge transport boosts the photovoltaic efficiency of two-dimensional perovskite solar cells by increasing the fill factor and open-circuit voltage. The dynamic behavior of MAPbI$_3$, under optical stimulation using X-ray diffraction, also revealed unexpected phenomena. We identified several nonequilibrium structures and phenomena that have not been shown in studies where the structure is measured in equilibrium. Using ultrafast X-ray diffraction techniques, we identified and characterized the dynamic, photo-excited structures of MAPbI$_3$. We observed anisotropic distortions and rates of change along specific directions of the lattice as the material transitioned from the starting phase to a higher-symmetry, metastable excited structure over 1 ns following photoexcitation. The dynamics of these nonequilibrium structures demonstrate the flexible lattice response of metal halide perovskites, which facilitates favorable properties and provides further insight to enable new device architectures.

8:45 AM EL02.05.03
High-Efficiency and Durable MA and Br Free Phase-Pure Dion Jacobson 2D Lead Halide Perovskites for Perovskite-Perovskite Tandems Ayush Agrawal, Jin Hou, Siraj Sidhik and Aditya D. Mohite; Rice University, United States

Three-dimensional (3D) metal halide perovskite solar cells have displayed tremendous progress in photo conversion efficiencies in the last decade. The tunable bandgaps enable mixed halide perovskite compositions to be used as the wide bandgap (WB) sub-cell in perovskite-perovskite tandems. However, halide segregation and ion migration under photo-illumination create bandgap instability that limits the long-term durability of these wideband gap sub-cells. 2D halide perovskites, on the other hand, have demonstrated better durability against moisture and photo-illumination due to their large organic cations but still lag in efficiency due to >2eV band gaps and charge extraction barriers. The methylammonium (MA$^+$) cation is also hygroscopic and can limit the long-term moisture stability of the perovskite. Here, we synthesize formamidinium (FA$^+$) based 2D Dion Jacobson (DJ) perovskite solar cells with a diammonium 3-(aminomethyl)piperidinium (3AMP$_{2+}$) organic spacer cation. Optical absorption on FA 2D DJ reveals a band gap of 1.7-1.8eV for (3AMP)-FA$_2$Pb$_3$I$_{10}$ (n=3), which is ideally suited for building bottom cells for perovskite-perovskite and perovskite/Si tandems. Films fabricated using the phase-selective memory seeds process preserved the phase purity of the (3AMP)-FA$_2$Pb$_3$I$_{10}$ 2D perovskite and yielded solar cells with a PCE of 17% with a Voc approaching 1.2 V. More importantly, FA 2D DJ perovskite solar cells demonstrate commercially viable durability against temperature, moisture, and maximum power point (MPP) tracking. These properties make FA 2D DJ perovskites promising candidates for wide bandgap subcells in perovskite-perovskite tandems.

9:00 AM BREAK

SESSION EL02.06: Novel Structure II
Session Chairs: Robert Hoye and Shijing Sun
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3002

10:00 AM *EL02.06.01
Chemical Design for Metal Halide Perovskites Nanostructures Loredana Protesescu; Nanomaterials Chemistry/Zernike Institute for Advanced Materials/RUG, Netherlands

Metal halides perovskites with nanoscale geometries have revolutionized the field of solution-processed photovoltaics and light-emitting devices due to their strong absorption and exceptional photoluminescence properties combined with a remarkable tolerance to structural defects. However, the further development of these materials to practical commercialization is hindered by their toxic components like lead and their inherent structural lability. Moreover, we still have little understanding of their crystallographic structures, chemical and physical interactions, and surface chemistry at a fundamental level.
The chemical design of metal halide perovskites proved to be the key to addressing those issues. Our recent findings confirm that a direct transition of the synthetic approach at nanoscale from Pb to Sn halide perovskites is not feasible. For Sn-based perovskites nanostructures, the structural dynamics between 3D cuboids and 2D Ruddlesden-Popper nanosheets colloids are highly dependent on the synthetic strategy. The presence of both species has a direct impact on the optoelectronic properties. Moreover, heterostructures containing halide perovskites nanocrystals are the next step towards obtaining accessible materials for industry. With the help of polymers or metal-organic frameworks, we can access air stable materials or ultra-small quantum dots.

10:30 AM *EL02.06.02
Improving the Stability of Halide Perovskite by Building Perovskite Hetero-structures Hsinhan Tsai; University of California, Berkeley, United States

Halide perovskites are outstanding semiconductors for high performance opto-electronics, the drawback is their material instability in humid environment, and the poor device operational stability under external stress like electrical fields or illumination. In this talk, I will present two types of hetero-structure that can stabilize the material. In the first part, I will discuss a bilayer heterostructure to stabilize the interface. We grow a fluorinated small molecule on the perovskite thin film to increase the surface energy. This hetero-structure suppresses the voltage induced ion diffusion. As a result, we demonstrate a radiation detector that can operate under high electrical field stress. In the second part, I will present how we stabilized the perovskite nanocrystals embedded in metal-organic frameworks (MOFs). Here we assembled perovskite nanocrystals in MOF matrix that can enhance the material stability and inhibit crystal merging problems. Finally, I will discuss the device performance using these strategies in optoelectronics applications such as light-emitting diodes, X-ray detector and photovoltaics.

Reference:
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[3] Tsai et al. Advanced Materials 34 (13), 2106498 (2022).

11:00 AM EL02.06.03
Quantum-Dot-in-Matrix Stabilizes Metal Halide Perovskite Solid by Deterministic Strain Engineering Yuan Liu[1,2], Tong Zhu[2], Luke Grater[2] and Edward H. Sargent[1,2]; [1]Northwestern University, United States; [2]University of Toronto, Canada

Phase transitions, segregation, and decomposition of MHPs occur with the presence of humidity, light, heat, oxygen, and electrical fields. With these factors, perovskite-based devices suffer steady performance losses. Strain engineering is proven to improve the stability of perovskite materials[1,2]. Here, we propose to stabilize perovskite solid using perovskite quantum dot (QD) implants. The strain is created due to the manipulated lattice misalignment between the QD and matrix lattices.
Prior QD-in-matrix solid studies using PbS QDs show enhanced stability of $CsPbI_3$ perovskite but failed to exploit optical properties of the perovskite matrix[3,4]. This prevents the use of covalent quantum dots as implants and limits the universality of this material platform.
Our method is universal and practical because perovskite QDs are versatile as they can be compositionally engineered to meet bandgap and lattice parameter requirements. Given the range of lattice parameters and composition of the QD, this method estimates their capability towards stabilizing the matrix of choice before diving into lengthy synthesis.
We examined mixed halide perovskite, α-$CsPbI_3$ and α-$FAPbI_3$ and found that the compressive strain introduced by QD implants enhanced the stability of the optically desired phases. For solar cell application, perovskite QD ensures a type-I band alignment where the QD features a larger bandgap, and therefore allows efficient extraction of the electron-hole pairs from the matrix perovskite. Solar cells using QD-in-mixed halide perovskite matrix solid show an open circuit voltage of 1.35 V, a power conversion efficiency of 20 %, and operation stability of over 200 hrs. This fills the gap between the configuration of QD-in-matrix and utilization of matrix perovskite for photovoltaic application, compared to prior QD-in-matrix methods.

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11:15 AM EL02.06.04
Perovskite Quantum Dots for High-Efficiency Solar Cells and Beyond Lianzhou Wang; University of Queensland, Australia

Halide perovskite solar cells have witnessed great successes recently while their instability is a big hurdle for practical application. Herein we discuss our recent progress in addressing the stability of perovskite solar cells, including introduction of capping layers to improve the stability against moisture and heat, and perovskite size engineering to suppress phase segregation. In particular, quantum dots (QDs) have the advantages of quantum confinement effect, defect-tolerant nature, and processability for flexible devices. We discuss a new surface ligand engineering strategy in designing new hybrid perovskite QDs with controllable compositions and sizes The QDs have been used as building blocks in quantum dot solar cells delivering a certified world-record efficiency of 16.6% with excellent long-term operation stability. By using QDs as light absorbing materials, the QD based photocatalysts also exhibited good stable performance in photocatalytic hydrogen production. The integration of perovskite solar cells and rechargeable batteries have led to a single module type rechargeable solar batteries with an overall storable solar energy conversion efficiency of >12%. The composite of perovskite quantum dots with metal organic frameworks (MOFs) resulted in ultrastable photoluminescent property of >10000h.

11:30 AM EL02.06.05
Zwitterions in 3D Perovskites: Organosulfide-Halide Perovskites Jiayi Li[1], Zhihengyu Chen[2], Santanu Saha[3], James Utterback[4], Michael Aubrey[1], Rongfeng Yuan[4], Hannah L. Weaver[4], Naomi S. Ginsberg[4], Karena Chapman[2], Marina Filip[3] and Hemamala Karunadasa[1]; [1]Stanford University, United States; [2]Stony Brook University, United States; [3]University of Oxford, United Kingdom; [4]University of California, Berkeley, United States

Lead halide perovskites are extensively studied in solar-cell applications, achieving high power-conversion efficiencies. However, weak metal-halide bonds may be responsible for their moisture/thermal instability, hindering large-scale implementation. In this work, we propose to introduce sulfide into the halide perovskite lattice and demonstrate a synthetic strategy to do so by using organosulfides under mild conditions. We show that a zwitterionic organosulfide (L), can serve as both the X site and A site in the ABX_3 halide perovskites, yielding the first examples of 3D organosulfide-halide perovskites: $LPbX_2$ (X = Cl or Br). The structures are determined by single-crystal X-ray diffraction and pair distribution function analysis. Notably, the band structures of $LPbX_2$ capture the direct bandgaps and dispersive bands of $APbX_3$ perovskites. The sulfur orbitals compose the top of the valence band in $LPbX_2$, affording unusually small direct bandgaps of 2.31 eV and 2.16 eV for X = Cl and Br, respectively, falling in the ideal range for the top absorber in a perovskite-based tandem solar cell. Measurements of the carrier dynamics in $LPbCl_2$ suggest carrier trapping, possibly due to defects or lattice distortions. The highly desirable bandgaps, band dispersion, and improved stability of the organosulfide perovskites demonstrated here motivate the continued expansion and exploration of this new family of materials. Our strategy of combining the A and X sites with zwitterions may offer more members in this family of mixed-anion 3D hybrid perovskites.

SESSION EL02.07: Device Fabrication I
Session Chairs: Xuedan Ma and Lakshminarayana Polavarapu
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3002

1:30 PM *EL02.07.02
From Composition to Composite Design—Chemical Tricks that Stabilize Halide Perovskites Shijing Sun; Toyota Research Institute, United States

Despite the outstanding optoelectronic properties of hybrid organic-inorganic perovskites (HOIPs), prototypical halide perovskites, such as methylammonium lead iodide ($MAPbI_3$, MA = CH_3NH_3), suffer from poor environmental stability. From ionic substitutions at an atomic level to post-synthesis treatment at a microscopic level, there has been intensive research in the community of materials chemistry to increase the structural and chemical stability of $MAPbI_3$. However, obstacles exist efficiently navigating this large and complex materials design space. A question that often gets asked is: how far can we extend the stability lifetime of a perovskite photoactive material, without lowering its optoelectronic performance?

In this talk, I will demonstrate three distinct approaches to delay the onset of HOIP degradation and discuss their relative advantages and disadvantages in perovskite electronics applications. I will start by discussing how stability changes non-linearly as a result of composition engineering in a combinatorial space, where the MA ions in $MAPbI_3$ are partially replaced by less volatile cations such as Cs and formamidinium.[1] Without modifications on the $MAPbI_3$ lattice, I will then move to capping methods, where a capping layer serves the dual function of forming a protective layer against oxygen and water, as well as improving the interface passivation.[2] I will then share our most recent findings in additive engineering, where porous organic cage molecules were introduced for the first time in perovskite films, forming perovskite-cage composites that show remarkable resistances to high humidity and temperature.[3] I will end my talk by briefly mentioning the role of machine learning in helping guide the experimental exploration of materials design and optimization in our projects.

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2:00 PM EL02.07.03
Robot-Assisted Study on the Crystallization Pathway of FAPbI3 in Air Simon M. Arnold[1,2], Edward Barnard[1], Stephen Whitelam[1], Carolin M. Sutter-Fella[1] and Christoph J. Brabec[2]; [1]Lawrence Berkeley National Laboratory, United States; [2]Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Organic-inorganic halide perovskites allowed for the most rapid increase in power conversion efficiency of single junction solar cells ever seen from any photovoltaic technology. For some time now, it has become a major goal for the community to fabricate and stabilize pure α-FAPbI3 due to its - compared to other perovskites - superior photovoltaic properties, such as small bandgap, long carrier lifetime and low defect state density. Unfortunately, the photoactive cubic α-phase is only metastable at room temperature and transforms into the photoinactive hexagonal δ-phase over time. Recent efficiency improvements of α-FAPbI3-based perovskite solar cells have been enabled by insights and application of compositional, intermediate phase and dimensionality engineering, all enhancing the phase purity and stability of α-FAPbI3.

In this talk, I will report on the investigation of the mutually influencing effects of precursor composition, thin film synthesis conditions, and annealing profile, on the crystallization process of FAPbI3 in a sequential two-step spin coating process in air. Thereby, we first screened the high-dimensional parameter space using a robotic spin coating platform for automated thin film synthesis, annealing and in-line optical characterization (UV/vis, photoluminescence). We paired the platform with external X-ray diffraction measurements and neural networks which are trained on the time-dependent annealing process to optimize the synthesis protocol for crystal quality and optical properties in a closed-loop.
In a second step we used multimodal in-situ characterization techniques (GIWAXS, UV/vis, absorption) for certain composition/process conditions and annealing profiles to better understand the effects of described parameters on the crystal phase formation and phase stability of FAPbI3. These insights may help to develop a robust and reproducible synthesis protocol for high quality and stable α-FAPbI3 in air, which further propels the commercialization of perovskite solar cells.

2:15 PM BREAK

SESSION EL02.08: Theory
Session Chairs: Robert Hoye and Maria Antonietta Loi
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3002

3:30 PM *EL02.08.01
Topological Transport and Charge-Spin Conversion in Lead Halide Perovskites Alessio Filippetti; University di Cagliari and CNR-IOM, Italy

Spin-orbitronics has been recently rising tremendous excitement in the route towards a novel nanoelectronics with superior performances in terms of low energy consumption, operational speed, and information storage density. At the core, there is the idea of exploiting the spin-orbit coupling to implement new functionalities controlled and manipulated by electric, magnetic, strain, thermal, or radiative fields. A remarkable example is charge-spin (or the reversed spin-charge) conversion, which can foster visionary applications such as spin-diffusive transistors and electrically controlled magnetic memories.

Lead-halide perovskites appear as promising spin-orbitronic materials, featuring a set of key properties instrumental to the aim, first and foremost a strong SOC at the band gap extrema, together with good electron mobility, tendency to develop electric polarization, flexibility of structural and chemical design, easy integration in 2D heterostructures and devices, low-cost processing.

In this talk we review the fundamental electronic properties of LHP's, with particular emphasis on the detailed description of the band edges where SOC is displayed in spectacular form in terms of Rashba spin splitting and chiral spin texturing. Our analysis reveals a topological band transformation from low-density, genus-1 to high-density, genus-0 Fermi surfaces. The implications of this transition on the transport properties are discussed on the basis of a

Bloch-Boltzmann theoretical approach. Also, a model is developed to describe Rashba-Edelstein charge-spin conversion in both 3D and 2D lead-halide prototypes. Our results furnish a strong assessment to the remarkable potential of LHP's in the spin-orbitronic playground.

4:00 PM *EL02.08.02
Modeling of Charge Dynamics in Low-Dimensional Halide Perovskites Sergei Tretiak; Los Alamos National Laboratory, United States

Hybrid organic−inorganic perovskites (HOPs) have demonstrated an extraordinary potential for clean sustainable energy technologies and low-cost optoelectronic devices. For example, crystalline two-dimensional (2D) layered perovskites demonstrate exceptional properties for light emission and x-ray detection. The photophysics of 2D materials is defined by an interplay of strongly bound excitons and lower-energy states associated with the edges of the perovskite layers. Using molecular dynamics with time-domain density functional theory methods at room temperature, we compare the dominant non-radiative electron-hole recombination and dephasing processes in several low-dimensional lead halide perovskite materials. Our study demonstrates that performance limiting nonradiative carrier recombination processes greatly depends on the electron–phonon interactions induced by structural fluctuations and instantaneous charge localization in these materials. Overall, our results provide insights towards the material design principles for 2D perovskites to strategically tune their optoelectronic properties.

4:30 PM EL02.08.03
Predicting Thermodynamic and Phonon Transport Properties of 13,205 Single Perovskite Structures—Toward Stable Perovskite Electronics Ming Hu; University of South Carolina, United States

Although first-principles based anharmonic lattice dynamics method coupled with the phonon Boltzmann transport equation has been developed to obtain the phonon properties including lattice thermal conductivity at highest accuracy ever, the costly and time-consuming nature of the required interatomic force constants calculations renders high-throughput infeasible when facing tens of thousands of new materials. Here, a high-dimensional multi-element deep neural network is trained, dubbed Elemental Spatial Density Neural Network Force Field (Elemental-SDNNFF), achieving a competitive force root mean square error and a speed-up of 3 orders of magnitude in comparison to first-principles. The effectiveness and precision of the Elemental-SDNNFF approach is demonstrated on a set of >100,000 inorganic crystalline structures spanning 63 elements in the periodic table by prediction of complete phonon properties such as phonon dispersions and lattice thermal conductivity. We then use our trained neural network model to predict and screen full phonon properties of 13,205 perovskite structures. Due to the inherent structural feature of dynamical disorder, the perovskite structures have shown diverse thermodynamic and phonon transport properties. Thermodynamic stability of all 13,205 perovskite structures is predicted by screening negative frequencies in the Brillouin zone. Four-phonon scattering and two-channel thermal transport are also analyzed and screened. The underlying mechanism is analyzed in deep at the electronic level. This study demonstrated that our algorithm is very powerful for predicting phonon properties of large-scale inorganic crystals and is also promising for accelerating high-throughput search of novel phononic materials for emerging applications.

SESSION EL02.09: Poster Session I

Session Chairs: Xuedan Ma and Wanyi Nie
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL02.09.01
Determinatnion of the Exciton Binding Energy in Quasi- Low Dimensional Perovskite Namhee Kwon[1,2], Kitae Kim[2,1], Wonsik Kim[1], Yeonjin Yi[2] and Soohyung Park[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of)

In recent years, the two-dimensional (2D) perovskites has been considered as promising optoelectronic materials for their interesting optical and electronic properties. Particularly, 2D perovskites has been reported to have exotic excitonic behaviors represented by large exciton binding energy that is hardly been observed in neither three-dimensional perovskites such as $MAPbI_3$ or $FAPbI_3$ nor other semiconductors. Since the exciton binding energies of perovskites are directly related with quantum yields and power conversion efficiency of light emitting didoes and solar cells, respectively, it is important to understand them to utilize 2D perovskite as devices successfully. However, characteristic charge and dielectric confinement effects originated from their innate multiple quantum well structure make it hard to determine their exciton binding energy, remaining the reported values controversial.
Herein, we demonstrate the exciton binding energies of 2D perovskites with general formula $(C_nH_{2n+1}NH_3)_2PbI_4$ where n stands for the number of carbon atoms in the organic cation. Each investigated perovskite was fabricated by using different type of organic cations which are ethylamine (EA), Propylamine(PA), Butylamine(BA), Amylamine(AA), Hexylamine(HA), Octylamine(OA) and Dodecylamine(DA) in order from the shortest to the longest. The information on valence band and conduction band was respectively collected via ultraviolet photoelectron spectroscopy (UPS) and inverse photoelectron spectroscopy (IPES). From them we were able to precisely measure the electrical bandgaps of each 2D perovskite. With help of the density functional theory (DFT) calculations, each 2D perovskites were followed for further analysis. As a results, the exciton binding energies were calculated by comparing the electrical bandgap with optical bandgap measured by absorption and photoluminescence spectrum. We figured out that the dielectric constant became smaller as the number of carbon atoms in the organic cations decreases and therefore modifies the exciton binding energy. EA_2PbI_4, the perovskite with the shortest organic cation exhibited the smallest exciton binding energy, on the other hand, it was confirmed that the perovskite with the longest organic spacer, DA_2PbI_4 showed the highest exciton binding energy. We believe that our findings will provide essential information on 2D perovskite band structures and understandings for the development of optoelectronic devices with 2D perovskite in the future.

5:00 PM EL02.09.02
Wide-Bandgap Perovskite Solar Cells for Multi-Junction Photovoltaics Simone V. Laar, Kunal Datta, Martijn M. Wienk and Rene A. Janssen; University of Technology Eindhoven, Netherlands

The ability to easily tune the bandgap (E_g) of perovskite semiconductors makes them excellent candidates for multi-junction applications. By combining narrow-bandgap lead-tin perovskites (E_g ~ 1.2 eV), iodide-based mid-bandgap perovskites (E_g = 1.4 – 1.5 eV), and mixed-halide wide-bandgap perovskites (E_g ~ 2.0 eV), high efficiency triple-junction devices can be developed[1]. High quality wide-bandgap perovskites are a primary bottleneck in the development of these devices. Specifically, the deposition of smooth, mixed-halide perovskite layers is a key challenge. High open-circuit voltage (V_{oc}) losses in such devices are also detrimental to their efficacy in multi-junction solar cells[2]. Another important hurdle in developing multi-junction devices is the poor photostability of wide-bandgap perovskites as a result of light-induced halide segregation, which impairs their operational stability[3].

This work investigates the organic-inorganic $FA_xMA_{1-x}Pb(Br_yI_{1-y})_3$ (FA: formamidinium, MA: methylammonium, Br: bromide, I: iodide) and fully-inorganic $CsPb(I_{1-y}Br_y)_3$ perovskites for triple-junction photovoltaics. Several aspects such as phase purity, morphology, photostability and photovoltaic performance are examined through *in-situ* and *ex-situ* characterization tools.

First, $FA_{1-x}MA_xPb(I_{1-y}Br_y)_3$ perovskite films with different MA and Br contents are prepared using a one-step antisolvent-based process to approach $E_g \sim$ 2.0 eV. We observe that the composition strongly affects surface morphology; the films with high Br content demonstrate surface wrinkling, with features as high as 1 – 2 µm and widths around 5 – 10 µm. The wrinkling correlates to a preferential vertical crystal orientation, as observed by grazing incidence wide-angle X-ray scattering. However, the presence of wrinkles increases surface roughness that impedes the use of such layers in solution-processed multi-junction solar cells.

In contrast, a sequential interdiffusion method to prepare $FA_xMA_{1-x}Pb(Br_yI_{1-y})_3$ is found to yield unwrinkled films with $E_g \sim$ 2.0 eV[4]. However, we find that such films show the presence of de-mixed I-rich and Br-rich phases that lead to low-energy photoluminescence (PL) emissions. Under continuous irradiation, using *in-situ* PL spectroscopy, we find that ion migration further exacerbates the formation of I-rich and Br-rich domains. Upon subsequent storage in the dark, entropy-driven halide remixing causes the PL emission to blue-shift to ~ 2.0 eV, indicating the formation of a homogeneous mixed-halide phase. Thereafter, the process of halide segregation and remixing can be cycled by light-dark exposure in these materials. When used in *p-i-n* solar cells, the efficiency of 2.0 eV organic-inorganic mixed-halide cells decreases as a result of light-induced halide segregation, dominated by a loss in J_{sc}, while the V_{oc} is hardly affected. Nevertheless, the high efficiency (> 10%) of the solar cell is undermined by its limited photostability, making it less ideal for multi-junction use[5].

Finally, fully-inorganic *p-i-n* $CsPb(I_{0.67}Br_{0.33})_3$ (E_g = 1.9 eV) solar cells are prepared, yielding an efficiency of over 9%. A high-energy PL peak (maximum at ~ 1.9 eV) confirms the I-Br homogeneity of the film. Furthermore, under prolonged illumination the PL peak displays only a marginal red-shift, indicating superior stability compared to organic-inorganic counterparts. Similarly, $CsPb(I_{0.67}Br_{0.33})_3$ solar cells demonstrate negligible performance degradation under operational conditions, emphasizing their photostability.

This work demonstrates key elements in the processing and compositional engineering of wide-bandgap perovskites to develop triple-junction-compatible materials. The results highlight the high performance and stability of inorganic mixed-halide perovskite solar cells.

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2. *J. Mater. Chem. A* **2017**, *5*, 11401
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5:00 PM EL02.09.04

Dimension-Controlled SnO_2 Nanostructures for High Performance Flexible Perovskite Solar Small-Modules (900cm^2) Da Seul Lee, Ki Woong Kim, You-Hyun Seo, Myung Hyun Ann, Jaehoon Chung, Gabkyung Seo, Nam Joong Jeon, Jangwoon Seo and Seong Sik Shin; Korea Research Institute of Chemical Technology, Korea (the Republic of)

In the past decade, organic-inorganic hybrid metal halide perovskites have attracted much attention as potential photovoltaic (PV) materials owing to their attractive advantages such as high absorption coefficients, tunable bandgaps, long carrier diffusion length, low cost, flexibility, and low processing temperature. In particular, owing to low crystallization temperature (<150 ^{o}C), perovskites can be applied to a polymer substrate. This would make it possible to develop flexible perovskite solar cells (PSCs) that could open the door to low-cost mass production through roll-to-roll processes in the near future. In addition, the development of flexible PSCs has shown great potential in the field of wearable power supplies and integration with architectures in the future. However, despite the rapid development of low-temperature-processed PSCs, the power conversion efficiencies of flexible PSCs using polymer substrates are still inferior owing to the limitation of the electron transport layer (ETL) using colloidal nanoparticles (NP). Furthermore, ensuring both the efficiency and stability of flexible PSCs remains a considerable challenge for their commercialization.
In this study, we found for the first time that these solar cells suffer from a trade-off relationship between efficiency and stability due to the off-balance between surface coverage and the charge-transporting property of electrodes fabricated from a conventionally used colloidal Tin(IV) oxide (SnO_2) nanoparticles (NP). To resolve this trade-off, we designed a new electrode by controlling the dimensionality of the NPs. The development of multidimensional (MD) electrodes enables a PCE of 22.0% (0.094 cm^2) on a flexible substrate. When applied to the large area module, flexible modules show a PCE loss of nearly 10% by module size from mini-module to small-module (Type of Module is divided into mini-module (< 200cm^2), sub-module (200-800cm^2) and small-module (800-6500 cm^2) depending on the size of modules). Moreover, when the MD electrode is applied to the flexible sub-module (400cm^2) and small-module (900cm^2), the PCEs of MD electrode f-PSMs are 17.3% (active areas: 364cm^2) and 17.7% (active areas: 837cm^2). These results are the highest PCE reported to date. Furthermore, PSCs and the f-PSM based on the MD electrode retain 86% and 80% after 500h and 300h under continuous operation conditions, respectively. We believe that our strategy provides a new way to realize highly efficient and stable flexible perovskite photovoltaics.

5:00 PM EL02.09.05

Combinatorial Synthesis Process—A New Library Excepted Halide Perovskite-Based Materials of Photovoltaic Devices SangMyeong Lee, Won Bin Kim, Jae Myeong Lee, Hee Jung Kim, Oh Young Gong, Geon Woo Yoon and Hyun Suk Jung; Sungkyunkwan University, Korea (the Republic of)

Halide perovskites (HPs) has been conceived as next generation photovoltaic devices; this is due to their tunable band gap, excellent absorption properties, and excellent carrier mobility. However, some compositions of HPs are discarded until new applications are discovered due to limitations in their photovoltaic properties. Herein, this study reports a new library of HPs including HPs with ambiguous properties by using a combinatorial synthesis process. Firstly, the basic optoelectronic properties of synthesized HPs were measured and classified according to composition by using combinatorial synthesis process. Then, the study of band structure, band gap, hole effective mass, and electron effect mass via first-principles simulations explains the basic optoelectronic properties of synthesized HPs. Additionally, the library was formed that can be used as a variety of photovoltaic devices by controlling the crystalline phase of HPs. This paper suggests the new possibilities of HPs with ambiguous properties for photovoltaic devices.

5:00 PM EL02.09.06

Efficient and Stable Perovskite Solar Cell with Safe-to-Use Zhen Li and Zonglong Zhu; City University of Hong Kong, Hong Kong

Presently, over 85% of the world's energy is provided by non-renewable fossil fuels with concealed consequences on health and the environment. Developing and engineering novel materials and devices to provide efficient and sustainable energy is imperative. Metal halide perovskite solar cells (PSCs) have attracted enormous attention from academic and industrial communities due to their great promise of addressing the scalability challenges for affordable clean energy.

Power conversion efficiencies (PCEs) as high as 25.7% have been realized for single-junction conventional (n-i-p) PSCs, comparable to state-of-the-art crystalline-silicon solar cells. Inverted (p-i-n) devices have exhibited greater stability and lifetimes because of their un-doped hole-transporting layers (HTLs) and the formation of highly crystalline perovskite films, while their PCE still lag the conventional devices. Interfacial engineering to mitigate the interface recombination in the heterojunctions between perovskites and charge-transporting layers was considered as one of the promising strategies to further improve the photovoltaic performance and long-term stability of PSCs. Another concern occurs from the toxic element lead (Pb), a significant portion of the active layer in the most efficient PSCs. The potential risk of lead leaking due to damage by natural factors becomes the biggest challenge in entering the market.

To understand the impacts of the interface on perovskite, we systematically study interfacial engineering with respect to molecule design. We have developed a ferrocene-based organometallic interface material ($FcTc_2$), the functional groups assembled in the side arms of the ferrocene unit can provide chemical solid Pb-O binding between perovskite and molecule, effectively reducing surface trap states. Moreover, the electron-rich and electron-delocalized ferrocene units can accelerate interfacial electron transfer. These synergetic effects of $FcTc_2$ contribute to a record PCE of inverted PSCs and superior device operational stability, leading to a PCE of 25.0% (with certified 24.3%) and maintaining> 98% of its initial efficiency after continuously operating at the maximum power point for 1500 hours under simulated AM1.5 illumination. It is noteworthy that the $FcTc_2$-based device exhibited satisfactory durability under damp heat environment, which meet the IEC61215:2016 qualification (*Science* 2022, 376, 416-420).

For the lead leakage prevention in PSCs, we designed and synthesized novel lead trapping materials. Cation exchange resin (CER) and sulfonated graphene aerogels (S-GA) were first assembled in rigid and flexible perovskite PV encapsulation structures. The extremely low-cost CER with a sulphonic acid group (SO^{3-}) in Na^+ form possesses efficient adsorption capability of Pb^{2+}. More than 90% of the Pb^{2+} from the degraded perovskite PV solar modules (PSMs) could be captured under simulated severe weather conditions. The lead leaching of perovskite solar modules could meet the requirement of the US Resource Conservation and Recovery Act Regulation (RCRA) (*Nano Energy* 2022, 93, 106853). The large specific area of sulfonated graphene aerogels and their high binding energy with Pb^{2+} give them superior lead adsorption capacity in an aqueous solution. The encapsulant can capture over 99% of Pb^{2+} from the degraded flexible PSMs under different simulated conditions (scratching, bending, and thermal circling) to reduce the lead leakage to ≈10 ppb (*Adv. Energy Mater.* 2022, 12, 2103236). We also designed the thiol-functionalized 2D conjugated MOF as an electron extraction layer at the perovskite/cathode interface for electron extraction and Pb leakage prevention (*Nat. Nanotech.* 2020, *15*, 934). These works pave the way for the real-life application of perovskite photovoltaic technology.

5:00 PM EL02.09.07

$FAPbI_3$-based Thin Single Crystal Perovskite for Efficient, Stable Perovskite Solar Cell Muhammad N. Lintangpradipto and Osman M. Bakr; King Abdullah University of Science and Technology, Saudi Arabia

Perovskite solar cells (PSCs) have been rising in the last decade with solvent, compositional, and interface engineering methods to improve film crystallinity, optimize light absorption wavelength, inhibit intrinsic defect and passivate surface charge accumulation sites, reaching device efficiency of 25.7%. However, the lackluster stability performance remains lingering due to a large number of perovskite defects existing on the surface and grain boundaries inducing ion migration and interface degradation from moisture, oxygen, and other constituent ions thus limiting the operational stability of PSCs. Countless works have reported enhancing PSCs stability by using stable transport layer and metal contact especially passivating perovskite defect and grains boundaries to stop the degradation process from its root. Nevertheless, the source of the degradation remains as the intrinsic defect and grains boundary are always present in the polycrystalline film.

Single crystal as free-grain perovskite is an appropriate candidate for stable perovskite solar cells with defect density a few magnitude orders lower than polycrystalline film. Recent works on inverse temperature crystallization (ITC) demonstrated the fabrication of thin single crystal perovskite that is proportional to the solar cell application. 22.8% PCE has been achieved by employing formamidinium (FA) cation to $MAPbI_3$-based perovskite solar cells. However, as the advantages of $FAPbI_3$-based perovskite is obvious with a narrower band gap, superior crystal quality, and higher thermal stability, the move to $FAPbI_3$-based perovskite is inevitable. Nevertheless, synthesizing $FAPbI_3$ pure alpha-phase is challenging with non-perovskite delta-phase as stable form at room temperature and limitation of precursor volume on space confined ITC method.

Here in this study, we demonstrated the growth of thin single crystal $FAPbI_3$-based perovskite with cesium incorporation for stable alpha-phase PSCs. We confirmed the presence of cesium in the crystal with EDX SEM following the stoichiometric reaction. We performed a double 85 test to observe the crystal under harsh conditions. The alpha-phase $FAPbI_3$-based single perovskite is stable more than two-fold than its polycrystalline counterpart and the current best single crystal PSC $MA_xFA_yPbI_3$ under relative humidity 85%, and temperature 85°C test conditions. With a bandgap closing to ~1.47 eV, we show the possibility of an exceeding 23% efficiency device owing to the high current density reaching 27.8 mA/cm^2 enabling thin single crystal perovskite closer to the highest efficiency p-i-n polycrystalline perovskite devices to date. We also performed MPPT tracking to observe device operational stability under light irradiation in an inert atmosphere.

5:00 PM EL02.09.09

Carbazole Based Self-Assembly Monolayers for Highly Efficient Sn/Pb- Based Perovskite Solar Cells Matteo Pitaro[1,2], Javier S. Alonso[1], Lorenzo Di Mario[1], karolina Tran[1], Malin B. Johansson[2], Erik Johansson[2] and Maria Antonietta Loi[1]; [1]University of Groningen, Netherlands; [2]Uppsala University, Sweden

Highly performing mixed tin-lead perovskite materials are among the most promising options as an alternative active layer in perovskite solar cells to reduce Pb content. Moreover, these compounds open the possibility of fabricating full perovskite tandem devices, owing to their reduced band gap. The most efficient single junction mixed Sn/Pb perovskite solar cells have been fabricated using methylammonium cations (MA^+), and a p-i-n structure where poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT: PSS) is implemented as hole transport layer (HTL).[1] The record devices were reported to show limited stability, this can be attributed to two major reasons: i) MA^+ cations easily desorb at high temperature (85 C°) from the perovskite surface, introducing MA vacancies; ii) PEDOT: PSS, due to its hygroscopic and acid nature, reacts with the perovskite active layer, affecting the long-term stability.

In this work we employed a MA^+ free perovskite composition, namely, $Cs_{0.25}FA_{0.75}Sn_{0.5}Pb_{0.5}I_3$ and 2-(9H-carbazol-9-yl) ethyl) phosphonic acid (2-PACz), and [2-(3, 6-dibromo-9H-carbazol-9-yl) ethyl] phosphonic acid (Br-2PACz) as hole transport layers, with the aim of replacing PEDOT: PSS. Moreover, the fact that 2PACz and Br-2PACz can form a monolayer may allow reducing parasitic recombination.

$Cs_{0.25}FA_{0.75}Sn_{0.5}Pb_{0.5}I_3$ deposited on SAMs showed absence of pinholes, higher crystallinity (XRD), and larger grain size (SEM) when compared with the layers of PEDOT: PSS.

The fabricated solar cells using PEDOT: PSS as HTL exhibited a champion device efficiency of 16.33%, while devices fabricated on 2PACz and Br-2PACz showed an improved efficiency of 18.44% and 19.57%, respectively. The 19.57% efficiency is the record for the aforementioned perovskite composition.

It furthermore interesting to note that encapsulated Br-2PACz based solar cells retained 80% of the initial efficiency after 230 hours under continuous working condition, while device fabricated on PEDOT: PSS maintained 79% only for 72 hours. In addition, the shelf-life test in N_2 atmosphere showed much more stable devices when using Br-2PACz, with 89% of the initial efficiency after 42 days, when compared to PEDOT: PSS based devices, which solely preserve the 71% of the initial PCE. Moreover, the Br-2PACz-based device retained the 80% of the initial efficiency after 138 days in N_2 atmosphere.

[1] S. Hu, K. Otsuka, R. Murdey, T. Nakamura, M. A. Truong, T. Yamada, T. Handa, K. Matsuda, K. Nakano, A. Sato, K. Marumoto, K. Tajima, Y. Kanemitsu, A. Wakamiya, *Energy Environ. Sci.* **2022**, 15, 2096-2107.

5:00 PM EL02.09.10

Tetraalkylammonium Halide-Based One-Pot Ligand Engineering of Organic–Inorganic Hybrid Perovskite Nanocrystals for Enhanced Long-Term Stability and Controlled Photoluminescence Han-Jung Ryu and Jae-Seung Lee; Korea University, Korea (the Republic of)

Organic–inorganic hybrid perovskite nanocrystals have attracted scientific attention owing to their efficient and controlled photoluminescence, which is highly advantageous for optoelectronic applications. However, the limited long-term stability of organic–inorganic hybrid perovskite nanoparticles (OIHP NPs) has significantly hindered their practical and reliable application. Despite several synthetic strategies and encapsulation methods to stabilize OIHP NPs, complicated multi-step procedures are often required. In this study, we introduce a one-pot ligand engineering method for stabilizing and controlling the optical properties of OIHP NPs using tetraalkylammonium (TAA) halides with various molecular structures at different concentrations. Our one-pot ligand engineering substantially enhanced the stability of the OIHP NPs without post-synthetic processes. Moreover, in certain cases, approximately 90% of the initial photoluminescence intensity was preserved even after a month under ambient conditions. To determine the role of ligand engineering in stabilizing the OIHP NPs, the surface binding properties of the TAA ligands were thoroughly analyzed using Raman spectroscopy. Specifically, the permanent positive charge of the TAA cations and consequent effective electrostatic interactions with the surfaces of the OIHP NPs are pivotal for preserving the initial photoluminescence properties. Our investigation is beneficial for developing OIHP nanocrystals with improved stability and optical tunability for various optoelectronic applications, such as light-emitting devices, photosensitizers, photodetectors, photocatalysis, and solar cells.

5:00 PM EL02.09.11

Temperature-Controlled Slot-Die Coating for Antisolvent-Free-Processed Efficient and Stable Inverted Perovskite Solar Cells You-Hyun Seo[1,2], Nam Joong Jeon[1] and Seok-In Na[2]; [1]Korea Research Institute of Chemical Technology, Korea (the Republic of); [2]Jeonbuk National University, Korea (the Republic of)

The perovskite solar cells (PSCs) have continued to show their potential as a next-generation power source, achieving record power conversion efficiency (PCE) of over 25% due to their excellent optoelectronic characteristics. However, despite the impressive advances in the PCE to date, most high-performance PSCs are still fabricated with laboratory-scale production (i.e., a spin-coating process associated with anti-solvent dripping), which limits the path to large-area and mass production for commercialization of PSCs. To overcome these issues, it is important to develop high-quality perovskite films in scalable fabrications without spin-coating and/or anti-solvent steps and shift from laboratory scale to industrial scale that guarantees to upscale high-efficiency PSCs.
In this work, for the purpose of practical and scalable fabrication in PSCs, the temperature-controlled slot-die coating method is presented. This concept is further extended to control the solution temperature by using a thermistor-connected slot-die head that releases a hot solution onto a hot substrate. By careful cross-checking the bed and head temperature with coating speeds and its effect on the device performance, it was found that the introduction of the hot head can significantly influence the perovskite film morphology, and a PCE of 17.05 % could be realized at optimized-processing condition (head: 75 °C, bed: 150 °C, coating speed: 3 mm s-1) without spin-coating steps and anti-solvent dripping, which is a higher value than that of the device (12.61 %) without hot head condition. Systematic investigation of device characteristics, film morphologies, and carrier dynamics to reveal the origin of the enhanced PCE shows that the use of the hot-head produces a highly-oriented pinhole-free perovskite morphology with larger and thicker film, which results in enhanced light-harvesting capability, efficient charge carrier transport, and suppressed carrier recombination, leading to the remarkable enhancement in device performance. In addition to the device performance, optimized film condition can also show significant retardation of the decomposition of perovskite films, which lead to long-operation time in the ambient air and thermal condition. Finally, the optimized hot slot-die coating condition is directly utilized to fabricate the scaled device, showing a very close efficiency for spin coating-based PSCs without further modification. As a result, considering the compatibility of slot-die coating that is highly suitable for roll-to-roll (R2R) and sheet-to-sheet line production, hot slot-die coating approaches can provide a simple and useful way to manufacture perovskite films to achieve highly efficient and reliable PSC for industrial purpose

5:00 PM EL02.09.12

High Stable Perovskite Solar Cells using Ionic-liquid Addition and Cesium Halides Intercalation Technology Md. Shahiduzzaman, Munkhtuul Gantumur, Feng Yue, M. Nakano, Makoto Karakawa, Jean M. Nunzi and Tetsuya Taima; Kanazawa University, Japan

The rapid development of perovskite solar cells with a certified power conversion efficiency (PCE) of 25.7% is already at the level of commercialization. Still, long-term operational stability has become a major concern owing perovskite's intrinsically soft ionic crystal structures. Very recently, we used the ionic liquid (IL) aided-CH3NH3PbI3 (MAPbI3) perovskite nanoparticles (NPs) as a seeded-growth approach to fabricate high moisture-stable perovskite solar cells with a PCE of around 20%.1 It retained above 80% of its initial output even after 6000 hours of storage at ambiance with relative humidity (RH) range of 30−40% (non-encapsulated).
In the first half, I will talk about the nanoscale investigation of with and without IL-based perovskites. In this study, we investigated the nanoscale degradation mechanisms of why the higher stability was achieved by high-speed atomic force microscopy (AFM). We found that IL-aided MAPbI3 NPs form in the grain boundary of the CsFAMA perovskite crystal domains. This implies that the embedding of IL-aided MAPbI3 NPs in the CsFAMA perovskite crystal domain showed increased hydrophobicity (water contact angle of 72.3°) than pristine CsFAMA (water contact angle of 54.1°) by repelling moisture and preventing drop water infiltration under humid conditions.
In the second half, I will talk about cesium halides (CsX: CsCl, CsBr, CsI) intercalation technology for efficient and stable PSCs. Previously, we intercalated vacuum deposited cesium iodide (CsI) into solution processed host MAPbI3 perovskite framework and achieved a PCE of 18.43% and remained above 80% of their initial output after 6000 h storage in open air (non-encapsulated) for the first time.2 In this study, we introduced vacuum deposited CsX (CsCl, CsBr and CsI) thin layers into solution processed host MAPbI3 perovskite film from the up, down or both layers to promote precise intercalation, resulted in high-quality perovskite film for high stable PSCs. The use of CsX layer greatly altered the MAPbI3 morphology to produce large grain sizes, as a result of the precise intercalation of the CsX molecules into the host MAPbI3. We tested thermal stability at 85 °C on hot plate at RH range of 50−60% for more than 30 hours, Cs-containing perovskite films showed higher stability (no color changed, retained black) than pristine MAPbI3 film (color changed and degraded). The light-soaking of devices prepared with CsCl, CsBr and CsI intercalation remained 76.9%, 77.2% and 71.2%, respectively, of their initial PCEs, while the pristine MAPbI3 device showed only 4.3% of its initial PCE after 120 minutes of continuous light illumination (1 sun). More importantly, a similar trend with the CsCl, CsBr, and CsI-based PSCs were observed for the moisture stability for 3000 h storage at ambient with a RH range of 50–60% (non-encapsulated). This ILs and CsX intercalation technology will enable a significant improvement in the device operational stability.
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5:00 PM EL02.09.13
Bulky Organic Cations with Large Steric Hinderance Inhibit Structural Degradation and Enhance Open Circuit Voltage in Perovskite Solar Cells
Sakshi Sharma, Carlo Andrea Riccardo Perini and Juan Pablo Correa Baena; Georgia Institute of Technology, United States

Despite the growth in power conversion efficiencies of lead halide perovskite solar cells to over 25% in recent years, interfaces at the active layer/charge transport layers prove to be a key factor in limiting charge extraction. Organic ammonium cations such as PEA$^+$ commonly used for passivation of interfacial defects can cause reconstruction of the cubic perovskite phase upon thermal exposure, affecting charge extraction and long-term device performance. Here, we have explored molecules with extended π-conjugation length in the form of ammonium halide salts such as 2-([2,2'-bithiophen]-5-yl)ethan-1-aminium iodide (2TI), 2-(3‴,4′-dimethyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)ethan-1-ammonium iodide (4TmI) to explore the structural changes and defect passivation induced at the perovskite/Hole Transport Layer interface. Our XPS studies suggest lowering of Iodine and undercoordinated lead defects on perovskite films with passivation. However, lattice distortion is triggered by formation of low dimensional Ruddlesden Popper phase as 2TI penetrates the bulk on thermal treatment. On the other hand, large steric hinderance in 4TmI inhibits octahedral tilting in the inorganic $[PbX_6]^{4-}$ layer by preventing the ammonium head from replacing the A site cations in the perovskite lattice. The limitation on the reconstruction of the interface along with defect passivation translates to enhanced charge extraction and reduced nonradiative charge recombination. These mechanisms will be confirmed by GIWAXS and Photoluminescence measurements. Differences in layer uniformity and grain morphology for varying steric sizes of the cations are highlighted in SEM images. Using conjugated 2TI and 4TmI molecules acting as a shielding layer over the perovskite film, we have fabricated solar cells showing highest open circuit voltage of 1.09 with over 20% efficiency.

5:00 PM EL02.09.14
Chlorine Incorporation in 1.8 eV Wide Bandgap Perovskite Solar Cells to Enhance Efficiency and Photostability Severin Siegrist, Victor A. Marrugat, Ayodhya N. Tiwari and Fan Fu; Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Monolithic all-perovskite tandem solar cells show the potential of high efficiency at low manufacturing cost. In the 2-terminal device configuration, the current matching condition requires an optical bandgap of 1.8 eV for the wide bandgap top cell, to optimally pair with the 1.25 eV narrow bandgap bottom cell in the stack. To develop 1.8 eV bandgap perovskite, 40 mol% of Br is generally alloyed with I in the perovskite. However, solar cells with such high Br fractions in perovskite absorber suffer from low open-circuit voltages and exhibit poor photostability. Adding Cl to form triple halide (I, Br, Cl) perovskite compositions is a promising approach to obtain 1.67 eV perovskite materials without using high Br fractions.
In this contribution, we present our results on Cl incorporation to achieve 1.8 eV wide bandgap perovskite compositions with much lower Br fractions. We investigate Cl-containing precursors with respect to their effectivity to incorporate Cl into the perovskite lattice. Furthermore, we probe the limits of Cl incorporation for given Br fractions and perform steady-state and time-resolved photoluminescence measurements to check the photostability of the triple-halide perovskite films as well as the charge carrier lifetimes. Additionally, we investigate the uniformity and spatial distribution of Cl in the perovskite film by XPS and ToF-SIMS depth profiling. Finally, we implement the most promising films in solar cells to evaluate the PV performance as well as the thermal and the light-soaking stability.

5:00 PM EL02.09.15
Electrical Analysis of Mobile Ion Reaction According to the Applied Voltage for Lead Halide Perovskite Solar Devices JaeGwan Sin[1], Gisung Kim[1], Mijoung Kim[1], Moonhoe Kim[1], Geon Park[1], Jaeho Kim[1], Jinpyo Hong[2] and JungYup Yang[1]; [1]Kunsan National University, Korea (the Republic of); [2]Hanyang University, Korea (the Republic of)

Lead halide perovskite has significantly improved efficiency and stability over the past decade. This has been achieved by various passivation and surface treatment, such as understanding the trap density and interface of the perovskite thin film. For trap density analysis, dark current-voltage curve is typically used by various fitting formulas of space charge limited current (SCLC). In addition, it is possible to extract charge carrier, depletion region, built in potential (V_{bi}), and trap density inside the device measured by capacitance-voltage (C-V) curve. However, perovskite still has limitations in exactly device analysis due to its unusual electrical behavior. Especially, mobile halogen elements cause perturbation with peripheral carriers by continuous electric fields. Since the general electrical measurement methods applied to the device by continuous voltage, it is difficult to exclude the effect of mobile halogen ions. Here, we have investigated the dark current-voltage and capacitance-voltage characteristics using pulsed voltage for more accurate analysis of perovskite solar device. The use of pulsed voltage could be measured by limiting the movement of halogen elements and changing the inside of the perovskite film from an abnormal state to a normal state. In the case of methyl-ammonium lead tri-iodide ($MAPbI_3$), migration of halogen ions was suppressed, and reproducible V_{bi} was observed even after multiple measurements. The calculated trap density from the low temperature C-V curve was obtained as $5x10^{16}$ cm^{-3}, which is equivalent to the value extracted from the SCLC curve measured by pulse voltage.

5:00 PM EL02.09.19
Unraveling the Advantages of 3-Terminal Perovskite/Silicon Tandem Solar Cells Seyma Topcu[1], Michael Saliba[1,2] and Stephanie Essig[1]; [1]Institute for Photovoltaics (ipv), University of Stuttgart, Germany; [2]Institute for Energy and Climate Research (IEK-5), Forschungszentrum Jülich, Germany

Perovskite/silicon tandem solar cells are of increasing interest due to their high power conversion efficiencies (PCE) of over 30% and low fabrication costs. However, the stability of the perovskite cells cannot compete with the superior lifetime of silicon (Si) photovoltaics (> 20 years), which threatens their commercialization. So far, most record perovskite/silicon tandem cells have been monolithically integrated and feature 2-terminal (2T) configuration. Hence the sub-cells are connected in series and the highest efficiencies can only be achieved if the perovskite top and Si bottom cells generate the same photocurrent. While the current matching can be well controlled by optimizing the bandgap of the top cell, a faster degradation of the perovskite top cell compared to the silicon bottom cell may cause a severe current mismatch during ageing. This current mismatch dramatically deteriorated the tandem efficiency to values lower than single-junction devices. To pinpoint this stability disparity and its consequences we have performed a thermal degradation study in a dry atmosphere. To overcome this limitation of 2T perovskite/Si tandem cells, we employ a 3-terminal (3T) tandem architecture which does not require current matching. Consequently, the long-term performance of 3T perovskite/Si cells will surpass the one of 2T devices.
Here we show the first implementations of 3T tandem cells with *nip* and *pin* triple-cation perovskite top cells deposited on laser processed Interdigitated Back Contacted Silicon solar cells (Si IBC) with 1 cm^2 cell area. Our studies include current-voltage (I-V) and External Quantum Efficiency (EQE) analysis of the 3T tandem cells before and after ageing. Furthermore, Scanning Electron Microscope (SEM) imaging is used to check the conformal coating of the textured Si solar cells.

5:00 PM EL02.09.20

Pb-Sn Halide Perovskites for Photovoltaics—Understanding Carrier Extraction with a Doped Active Layer Antonella Treglia[1,2], Francesco Ambrosio[2,3], Giulia Folpini[2], E Laine Wong[2], Filippo De Angelis[4], Isabella Poli[2] and Annamaria Petrozza[2]; [1]Politecnico di Milano, Italy; [2]Istituto Italiano di Tecnologia, Italy; [3]Istituto CNR di Scienze e Tecnologie Chimiche "Giulio Natta" (CNR- SCITEC), Italy; [4]University of Perugia, Italy

The possibility of extending the absorption of lead based metal halide perovskites (LHPs) to the near-infrared region by partially substituting Pb with Sn has attracted great attention for the possible applications in tandem devices[1] and single junction solar-cells[2]. In addition to the nonlinear reduction of the band gap, the gradual substitution of lead with tin also changes significantly the photophysical properties of the material.[3,4] Despite the optoelectronic quality of tin halide perovskites (THPs) being inherently comparable to LHP[5], device efficiency and stability are still limited.[6,7]
With a combination of steady-state, time-resolved and pump-probe spectroscopy techniques we address the interplay of radiative and non-radiative processes occurring in tin-halide perovskites $FA_{0.85}Cs_{0.15}Sn_xI_3$. Recombination dynamics are explored as a result of electronic and chemical doping, oxidation and density of surface to bulk trap states. Carrier dynamics simulations and density functional theory calculations of defects are adopted to understand experimental results and identify the dominant processes occurring in different regimes of photoexcitation. We demonstrate that when the material is highly doped Auger recombination plays a fundamental role in limiting performances even at low photoexcitation density.[8,9]
We also investigate the fundamental optoelectronic properties of THPs when integrated in a device. The currently used architecture of lead-based solar cells, where an intrinsic absorber is sandwiched between two organic extraction layers (pin), is intrinsically not suitable for THPs as it would result in a p-p-n structure (as long as the THP remains intrinsically p doped). The short carrier lifetimes deriving from the intrinsic p-doping and the upshifted valence and conduction bands result in a reduced extraction capability. The bulk-free carrier dynamics in the presence of extraction layers are probed with transient absorption spectroscopy from the fs to time scales. We find changes in the extraction of electrons and holes in different temporal regimes and identify the presence of long-lived trap states. This information is correlated with spatial and time-resolved photoelectron spectroscopy (tr-PEEM)[10,11] at the interface of THPs with an evaporated extraction layer. The band alignment, surface trap distribution and charge transfer are probed for mixed $FA_{0.85}Cs_{0.15}Pb_{1-x}Sn_xI_3$: as the lead-based perovskite is alloyed with tin, its doping density, valence band position and bandgap can be gradually tuned, resulting in a modified energetic landscape of photogenerated carriers affecting carrier extraction.

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5:00 PM EL02.09.21

Fabrication of Hybrid Low-Dimensional Perovskite Solar Cells by Combing Scalable Doctor Blade Coating and Methylamine Post Treatment
Tung-Yu Hung and Chih-Liang Wang; National Chung Hsing University, Taiwan

Three-dimensional (3D) metal-halide perovskites have been paid much attention for use in solar cells due to the high absorption coefficient, great ambipolar charge mobility, long carrier diffusion length, and low exciton binding energy. However, the poor stability of 3D perovskite from the hydrophilic nature limits the practical application. In this regard, the hybrid low-dimensional perovskites are developed by combing the doctor blade coating and methylamine post-treatment process. A series of different hybrid low-dimensional perovskites are facilely made by the addition of phenethylammonium iodide (PEAI) in the doctor blade coating solution of $MAPbI_3$ perovskite based on the hot-casting approach. The result shows that the addition of PEAI can form a low-dimensional perovskite layer on top of the 3D $MAPbI_3$ perovskite film right after the doctor blade coating, which improves the perovskite stability but lowers the device performance due to the large bandgap and poor charge transportation. To find a compromise between the device stability and performance, the methylamine post-treatment process is employed on such a hybrid low-dimensional perovskite. The SEM, XRD, Raman microscopy, Kelvin probe force microscopy (KPFM), and UV-Vis are carried out to understand the morphology, crystallization, contact potential difference and optical property of the hybrid low-dimensional perovskites before and after the methylamine post treatment. More details related to the perovskite device stability and performance, affected by the amount of added PEAI and methylamine post treatment, will be mentioned in the presentation.

5:00 PM EL02.09.22

Photo De-Mixing in Mixed Halide Perovskites—the Role of Dimensionality Ya-Ru Wang[1], Alessandro Senocrate[1], Marko Mladenović[2], Algirdas Ducinskas[2], Gee Yeong Kim[1], Ursula Roethlisberger[2], Jovana V. Milic[2], Davide Moia[1], Michael Grätzel[2] and Joachim Maier[1]; [1]Max Planck Institute for Solid State Research, Germany; [2]EPFL, Switzerland

Photo induced phase separation observed in mixed halide perovskites(Photo de-mixing) has opened important questions on the thermodynamics of energetically pumped systems. In addition, the improved phase stability observed experimentally in low dimensional perovskites under light[1] compared with classic 3D hybrid perovskites, raises questions on the influence of dimensionality on the defect chemistry and the phase properties of these mixtures.

Here, we investigate the dependence of the phase behavior of mixed halide perovskites with different dimensionality under light. We consider thin films of 3D, 2D and nanocrystalline (size ~10 nm) mixed halide perovskites and we probe the changes in absorption properties and conductivities when the films are exposed to light. We find that nanocrystalline films show no de-mixing in contrast to 2D and 3D under similar illumination intensities, consistent with previous observations[2] and with the role of interfacial energy in the formation of de-mixed phases.[3]We then consider Dion-Jacobson mixtures based on $(PDMA)Pb(Br_{0.5}I_{0.5})_4$ (PDMA: 1,4-phenylenedimethanammonium spacer) as a model system for evaluating thermodynamic properties of photo de-mixing, given their superior stability compared to 3D films. We demonstrate that 2D mixed halide perovskites undergo photo de-mixing with direct transformation from the pristine phase to the de-mixed phases. Almost complete re-mixing of these phases occurs when the sample is left in the dark, showing that the process is reversible in terms of optical and structural properties. We further conduct temperature-dependent absorption measurements under light to extract the photo de-mixed compositions and to map the photo-miscibility-gap with three different methods.[4] We finally compare the kinetics and thermodynamics of photo de-mixing in 2D and 3D systems.

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5:00 PM EL02.09.23
Mechanism Study of High Efficiency Perovskite Solar Cells Based on Planar or Mesoporous Metal-Doped TiO_2 Electron Extraction Layer Yin-Hsuan Chang, Shih-Hsuan Chen, Ching-Mei Ho, Shun-Hsiang Chan, Ying-Han Liao and Ming-Chung Wu; Chang Gung University, Taiwan

Organic-inorganic halide perovskite solar cells (PSCs) is considered as one of the renewable energy sources. Over the last decade, the power conversion efficiency (PCE) of PSCs has rapidly promoted from 3.8% to 25.7%. The charge collection and defect states in a device are the most significant issues hindering the progress of PCE. On the other hand, hysteresis phenomenon in n-i-p PSCs, namely mismatch current density at different scanning directions, is one main issue that needs to deal with. Note that several factors that result in the hysteresis phenomenon. First, the imbalance between electron and hole flux in a device, attributed to lower electron mobility of TiO_2 can lead to severe hysteresis. Secondly, shallow trap states close to the conduction band increasing the charge recombination. As a result, carrier pathway between the perovskite active layer and the electron extraction layer (EEL) and smooth contact interface with the perovskite active layer play critical roles in charge transportation. Previous studies have investigated metal doped TiO_2 as EEL, such as Mg, W, Co, Zn, Ag, and Sn, in depth. With the suitable dopant, it could tune the band alignment between the EEL and perovskite active layer. That contributes to improve charge transportation in a device. Typically, the inferior contact between planar EEL and perovskite layer and low conductivity of pristine planar TiO_2 EEL deteriorate the hysteresis phenomenon in a perovskite solar cell. Therefore, mesoporous structure TiO_2 being intimate contact between perovskite layer allow perovskite to infiltrate into mesoporous microstructure and to provide large contact area for electron transportation. Also, the intimate contact can reduce the defect density between an interface. As mentioned above, we believed that developing metal doped meso-TiO_2 EEL is promising for improving electron properties and passivating defects. In this study, we adopted three metals (Ag, Zn, Sn) as dopants into the planar or mesoporous TiO_2 to compare the difference between planar and mesoporous EEL. In the planar PSCs series, a promising Sn-doped TiO_2 PSC showed an average PCE of 14.4%. In the mesoporous PSCs series, the device with optimized 1.0 mol% Sn-doped meso-TiO_2 achieved an average PCE of 19.51%. Further characterization revealed that the absorption edge of Sn-doped TiO_2 red shifted along with the increased doping concentration. Also, the defect density in EEL can be passivated by Sn doping. The upper shift of the conduction band and valance band edge made the energy level alignment in devices much more appropriate. That facilitates electron injection into the EEL with minor recombination. Finally, the champion device with 1.0 mol% Sn-doped meso-TiO_2 EEL delivered a PCE of 20.55%, a high fill factor (*FF*) of 81.72%, and a minor hysteresis index of 0.03.

5:00 PM EL02.09.24
Demystifying Voltage-Induced Halide Segregation in Mixed-Halide Perovskite Devices Zhaojian Xu[1], Ross Kerner[2], Steven Harvey[2], Kai Zhu[2], Joseph J. Berry[2,3,4] and Barry P. Rand[1,5]; [1]Princeton University, United States; [2]National Renewable Energy Laboratory, United States; [3]Renewable and Sustainable Energy Institute, University of Colorado Boulder, United States; [4]University of Colorado Boulder, United States; [5]Andlinger Center for Energy and the Environment, Princeton University, United States

Mixed-halide perovskites, owing to straightforward bandgap tuning through halide stoichiometry variation, have been considered in many optoelectronic devices. However, unwanted halide segregation under operational conditions, including light illumination and voltage bias, restrict practical applications. While light-induced halide segregation has been heavily studied, voltage-induced halide segregation still lacks in-depth investigation and the mechanism behind remains unclear. Herein, we systematically study the impact of voltage bias on mixed bromide/iodide perovskite devices across the full range of bromide/iodide ratios by conducting a series of long-time voltage biasing tests, and observe three voltage thresholds for an optically stable, mixed-halide perovskite composition with a low bromide ratio, and assign them, in order of increasing voltage, as the hole transport material doping threshold, halide segregation threshold, and degradation threshold, respectively. These empirical threshold voltages are minimally affected by composition until very Br-rich compositions, revealing the dominant role of iodide/triiodide/iodine electrochemistry in voltage-induced halide separation in mixed-halide perovskite devices. Furthermore, voltage-induced halide redistribution is directly visualized by cross-sectional scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM–EDX). By changing the metal electrodes (Au and Ag) and testing different voltage polarities (forward and reverse bias), we demonstrate the mechanism of voltage-induced halide segregation: iodide oxidation at the anode initiates unbalanced bromide, iodide, and oxidized iodine mass transport fluxes, resulting in vertical halide redistribution. The suppression of halide segregation by Ag anode indicates that halide perovskite devices operate as solid-state electrochemical cells when threshold voltages are exceeded, and the species/reaction with the lowest oxidation potential and the species/reaction with the lowest reduction potential in the metal halide device dictate the stability behavior under voltage bias.

5:00 PM EL02.09.27
Stabilizing the Surface of Metal Halide Perovskite Nanocrystals for Grafting Functional Charge Carrier Acceptors and Polymer Matrixes Aaron S. Malinoski[1,2], Hua Fu[1] and Chen Wang[1,2]; [1]Queens College, City University of New York, United States; [2]The Graduate Center, The City University of New York, United States

Protecting the vulnerable surface of perovskite nanocrystals (PNCs) while creating facile charge carrier migration pathways across the ligand interface is a dilemma that is confronted by researchers in many scenarios of applications. Previous work from our group demonstrated that the overabundant synthetic ligands required for passivating the PNC's dynamic surface in the colloidal phase were a major obstacle to establishing strong electronic coupling between the perovskite core and external molecular acceptors. We therefore devised a strategy where we first reconstruct the surface ligand layer of PNCs using small molecule zwitterion ligands (ZLs), and we then investigate various surface functionalization methods. By carefully selecting the binding affinity of the initial reconstructing ZLs, we not only successfully stabilize the PNC surface in solution with a low ligand loading, but we also facilitate quantitative grafting of various functional structures via bidentate coordination anchoring motifs. Functional species that can be tightly anchored to the PNC surface using this strategy include molecular charge carrier, organic semiconductors, and precursors that can carry out photopolymerization reactions. We illustrate the surface functionalization process step by step using NMR and steady-state optical spectroscopy. The rapid migration of photogenerated electrons and holes between the PNC and the grafted functional molecules is observed with time-resolved photoluminescence and transient absorption spectroscopy, confirming that the functionalization strategy can establish strong electronic coupling. The molecular charge carrier acceptors grafted on the PNC surface do not create surface trap states but can serve as routes for extracting the excitonic energy. By inducing the photopolymerization of precursors anchored in the PNC ligand shell, we generate a polymer matrix that tightly wraps the PNC core to enhance their stability. We monitor the dynamics of charge carriers shuffling through the polymer layer using time-resolved optical spectroscopy and adjust the polymerization condition to achieve balanced protection and charge transport mobility.

5:00 PM EL02.09.28
Understanding Structural Differences in Completely Dry-Processed $MAPbI_3$ Thin Films by Detailed Analyses of Temperature-Dependent Optical Spectroscopy Christina Witt, Konstantin Schötz, Meike Kuhn, Nico Leupold, Simon Biberger, Philipp Ramming, Anna Kohler, Ralf Moos, Eva M Herzig and Fabian Panzer; University of Bayreuth, Germany

In recent years, halide perovskites have attracted much attention due to remarkable increase in associated solar cell efficiencies, which were achieved by processing high quality thin films. Here, even small differences in film morphology seem to be relevant for optimized optoelectronic functionality and stability. However, a detailed understanding of how small morphological differences in perovskite films affect related structural and optoelectronic properties has not yet been fully developed.
Here, we investigate the influence of small morphology differences induced in $MAPbI_3$ thin films by (hot-)pressing, characterized by small increase in crystallographic orientation and grain size, on the structural properties phase transition, defects and energetic disorder. To this end, we perform detailed analyses of temperature-dependent absorption and PL measurements between 300 K and 5 K. We use $MAPbI_3$ thin films prepared by a completely dry processing approach, comprising film formation based on mechanochemically synthesized $MAPbI_3$ powder via powder aerosol deposition method [1,2], followed by (hot-)pressing. The latter has emerged as an attractive method for manufacturing and post-treatment of perovskite films [3,4]. Detailed temperature-dependent absorption and PL analyses reveal lower strain, decreased defect density and less energetic disorder in films with higher out-of-plane orientation and grain size. To resolve even small differences in static energetic disorder, suitable, powerful analysis methods of the Urbach energy are presented.
Our results demonstrate the importance of considering even small morphology differences in halide perovskite films regarding related structural and optoelectronic film properties. The gained knowledge will facilitate identifying structural differences in halide perovskites to further optimize their functionality and stability.

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5:00 PM EL02.09.29
Perovskite/Graphene Sandwiches—Halide Perovskite Heterostructures with Blocked Anion Diffusion Matthew Hautzinger, Steven Harvey, Matthew C. Beard, Joseph Luther and Jeffrey Blackburn; National Renewable Energy Laboratory, United States

Halide perovskites exhibit notoriously fast anion diffusion. This intrinsic material property has hindered advancements in the growth of halide perovskite heterostructures $APbX_3/APbX'_3$ (where X and X' are different halide species), as the halides quickly diffuse across the heterojunction forming an alloy. This inability to grow heterostructures severely limits the utility of halide perovskites as semiconductors, as they are not at parity with the complex heterostructures accessible with traditional semiconducting materials. Here we present the growth of such halide perovskite heterostructures by depositing single layer graphene in between two perovskite layers, $CsPbBr_3$ and $CsPbI_3$. The heterostructure shown, $CsPbBr_3$/Graphene/$CsPbI_3$, shows no anion diffusion after being stored in ambient conditions over long periods of time. In contrast, $CsPbBr_3/CsPbI_3$ deposited sequentially rapidly form alloys of $CsPb(Br_{3-x}I_x)$. A suite of characterizations convincingly demonstrate that the heterojunction formed is sharp and no apparent halide diffusion occurs. DFT calculations, UPS, and TA spectroscopy show there is a type I band alignment between the perovskites in this system and that the graphene has little effect on the interactions of the two perovskite materials. Furthermore, the deposition process for integrating graphene with halide perovskites is extremely facile and does not require expensive laboratory equipment. As such, we believe this can enable numerous advances in halide perovskite research, across many research groups, including more advanced heterostructure architectures, graphene enhanced perovskite device stability, and fundamental studies on halide perovskite/2D materials research.

5:00 PM EL02.09.30
Effect of Light Soaking on the Charge Extraction and Recombination Dynamics of Perovskite Solar Cells Abasi Abudulimu[1,2], Agustin M. Ontoria[2], Zhaoning Song[1], Iwan zimmerm[3], Jose Santos[2], Juan Cabanillas[2], Nijiati Aimaiti[2], Manoj Rajakaruna[1], You Li[1], Lei Chen[1], Sheng Fu[1], Adam Phillips[1], Michael J. Heben[1], Mohammad K. Nazeeruddin[3], Nazario M. Leon[4,2], Yanfa Yan[1] and Randy Ellingson[1]; [1]University of Toledo, United States; [2]Imdea Nanociencia, Spain; [3]EPFL VALAIS, Switzerland; [4]Universidad Complutense de Madrid, Spain

Through a decade of intensive research and development, over 25% of power conversion efficiency has been achieved in perovskite solar cells, placing it in direct competition with silicon-based solar cells. Further improvement toward theoretical limits relies on a better understanding of the charge dynamics in the device under operational conditions. Charge carrier recombination and extraction rates are key parameters that directly define the device performance. However, there are notable variations among the values reported for the device made with the same material and device stacks. Here, we study the charge extraction and recombination dynamics in perovskite solar cells based on the most common compositions, including prototypical methylammonium lead iodide ($MAPI_3$), formamidinium (FA)-cesium lead iodide ($FA_{0.95}Cs_{0.05}PbI_3$), triple-cation lead halide ($[(FAPbI_3)_{0.87}(MAPbBr_3)_{0.13}]_{0.92}[CsPbI_3]_{0.08}$), and mixed tin-lead iodide ($FA_{0.7}MA_{0.3}Sn_{0.5}Pb_{0.5}I_3$) perovskites via transient photovoltage and photocurrent (TPV/TPC) techniques under various illumination intensities and light soaking conditions. We also investigated the effect of a hole transporting layer (Spiro-OMeTAD derivative referred to as HTM3) on $MAPI_3$-based devices under the same experimental conditions. We found that the TPV and TPC traces vary significantly with light soaking in terms of TPV/TPC amplitudes and lifetimes of the fast and slow components, depending on both perovskite and HTM. On the triple-cation lead halide perovskite-based device, the effect occurs on the TPC, while on the $MAPI_3$-based device with HTM3, it appears on the TPV. Careful analysis of the data, including the reproduction of short-circuit current densities and open-circuit voltages of each device measured at various light intensities using the parameters extracted from TPV/TPC, revealed that the variation in TPV/TPC of the light-soaked devices relates to the changes in perovskite composition and perovskite-HTM interface.

5:00 PM EL02.09.31
Top-Down Approach Using Laser Ablation to Achieve High-Performance Semitransparent Perovskite Solar Cells Mayank Kedia[1,2], Monika Rai[1] and Michael Saliba[1,2]; [1]University of Stuttgart, Germany; [2]Forschungszentrum Jülich GmbH, Germany

Semitransparent perovskite solar cells (ST-PSCs) act as promising candidates for building-integrated photovoltaics (BIPVs) as windows and facades. An optimum balance between the power conversion efficiency and transparency in the visible range is required to satisfy these requirements. Amongst many ways to increase the transmittance of halide perovskite thin films, decreasing the absorber thickness by spin coating with the diluted solution is the most

common way. However, these ultrathin films are discontinuous and have often pin-holes due to low concentrations of precursor ink. Thus, achieving a uniform and continuous ultrathin film with reliable scalability is of pressing need.
Here, we employ a top-down approach where a pulsed UV laser is used to etch a thick pre-crystallized film till the desired transparency is achieved without any structural damage. A regressive decrease in the perovskite film thickness from ~500 nm up to ~100 nm is achieved by controlling the laser fluence and exposure time. To obtain an average visible transmittance (AVT) of >22%, the perovskite film is laser ablated to ~ 250 nm. The developed semitransparent devices without any additives have shown a high PCE of > 14%. Additionally, a remarkable PCE of >11 % is achieved for a ~ 100 nm thick perovskite solar cell with ~ 30 % AVT. The results highlight an innovative fabrication method of laser thinning together with patterning to improve high-efficiency semitransparent PSCs while maintaining their transparency.

5:00 PM EL02.09.32
Structural and Electronic Studies on the All-Inorganic $CsPb(I_{1-x}Br_x)_3$ Perovskite in Terms of Light Soaking, Interfacial Layers and Crystallization Kinetics for Efficient and Stable Solar Cells Xiao Wu and Xinhui Lu; The Chinese University of Hong Kong, Hong Kong

Organic-inorganic hybrid perovskites have shown promising applications in optoelectronic devices. However, the volatile nature of organic cations such as methylammonium (MA^+) and formamidinium (FA^+), imposes intrinsic thermal stability issues. To this concern, inorganic $CsPbX_3$ ($X=I^-$ or Br^-) perovskites have attracted rising interest in recent years, owing to their excellent thermal stability and suitable bandgap for tandem applications with narrow-bandgap solar cells such as crystal silicon and CIGS. However, on one hand, the efficiencies of inorganic perovskite solar cells (PSCs) are still lagging behind the hybrid counterparts, demanding fundamental studies on the crystallization mechanisms for high-quality films and the interfacial modifications for efficient charge collection. On the other hand, operational stability under light illumination has always been a concern for solar cells, especially for the halide perovskites with easily mobile halide ions. **Here, we will first present a remarkable light soaking (LS) induced performance enhancement of $CsPb(I_{1-x}Br_x)_3$ PSCs.**[1] **We clarified the impact of light and radiative heating on the crystal structure via in situ grazing-incidence wide-angle X-ray scattering measurements (GIWAXS)** and elucidated the common LS phenomenon in $CsPb(I_{1-x}Br_x)_3$ with various Br/I ratio, which is related to ion migration. Also, we proposed an effective means to suppress the LS effect for obtaining more stable and efficient $CsPb(I_{1-x}Br_x)_3$ PSCs. **Second, we report an efficient low-temperature processed ZnO electron transporting layer engineered by incorporating PbX_2 ($X=I^-$, Cl^- and $CH3COO^-$).**[2] This method could tune the oxygen vacancies in ZnO, promote the growth of the perovskite layer with improved morphology and orientational order, and form a favorable energy level alignment with the perovskite layer, thus facilitating charge extraction and suppressing charge recombination. **Finally, we elucidate the phase transition mechanism of inorganic $CsPb(I_{1-x}Br_x)_3$ from precursor state to perovskite film via GIWAXS measurement and DFT calculations.** It was discovered the phase transition was not a simple conversion from the room-temperature stabilized yellow δ-phase to the high-temperature stabilized black phase. Instead, a multistage phase transition of the γ-δ-γ regime was found throughout the annealing process, resulting in poor film quality. To address this issue, we proposed a method to suppress the transition to δ-phase during heating and achieved efficient (20.1%) and stable $CsPb(I_{1-x}Br_x)_3$ solar cells.

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5:00 PM EL02.09.34
Efficient Perovskite Solar Cells via Improved Carrier Management Jason J. Yoo[1], GabKyung Seo[1], Matthew Chua[2], Tae Gwan Park[3], Yongli Lu[2], Fabian Rotermund[3], Chan Su Moon[1], Nam Joong Jeon[1], Juan Pablo Correa Baena[4], Vladimir Bulovic[2], Seong Sik Shin[1], Moungi G. Bawendi[2] and Jangwoon Seo[1]; [1]Korea Research Institute of Chemical Technology, Korea (the Republic of); [2]Massachusetts Institute of Technology, United States; [3]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [4]Georgia Institute of Technology, United States

Metal halide perovskite solar cells (PSCs) are an emerging photovoltaic technology with the potential to disrupt the mature silicon solar cell market. Great improvements in device performance over the past few years, thanks to the development of fabrication protocols, chemical compositions and phase stabilization methods, have made PSCs one of the most efficient and low-cost solution-processable photovoltaic technologies. However, the light-harvesting performance of these devices is still limited by excessive charge carrier recombination. Despite much effort, the performance of the best-performing PSCs is capped by relatively low fill factors and high open-circuit voltage deficits (the radiative open-circuit voltage limit minus the high open-circuit voltage). Improvements in charge carrier management, which is closely tied to the fill factor and the open-circuit voltage, thus provide a path towards increasing the device performance of PSCs, and reaching their theoretical efficiency limit. Here we report a holistic approach to improving the performance of PSCs through enhanced charge carrier management. First, we develop an electron transport layer with an ideal film coverage, thickness and composition by tuning the chemical bath deposition of tin dioxide (SnO_2). Second, we decouple the passivation strategy between the bulk and the interface, leading to improved properties, while minimizing the bandgap penalty. In forward bias, our devices exhibit an electroluminescence external quantum efficiency of up to 17.2 per cent and an electroluminescence energy conversion efficiency of up to 21.6 per cent. As solar cells, they achieve a certified power conversion efficiency of 25.2 per cent, corresponding to 80.5 per cent of the thermodynamic limit of its bandgap.

5:00 PM EL02.09.36
Vacuum Deposition of Thermally Stable Perovskite Solar Cells Qimu Yuan[1], Kilian Lohmann[1], Robert Oliver[1], Alexandra Ramadan[1,2], Siyu Yan[1], James Ball[1], Greyson Christoforo[1], Nakita K. Noel[1], Henry Snaith[1], Laura Herz[1] and Michael Johnston[1]; [1]University of Oxford, United Kingdom; [2]University of Sheffield, United Kingdom

Vacuum deposition is a solvent-free method which has proven suitable for growing thin films of metal-halide perovskites (MHPs) [1] and charge-transport layers. Vacuum-based methods offer a diverse array of advantages, including precise control of layer thickness, excellent uniformity and homogeneity of the formed thin film, choice over a wide range of materials and compositions, and the flexibility to grow multi-layer structures and larger-scale modules without the need to rely on complex choices of “orthogonal solvents”. In particular, we have elucidated a multi-source co-evaporation process of formamidinium-caesium (FACs)-based perovskite thin films. Excellent device performance was obtained when such vapour-deposited perovskite intrinsic layer was incorporated into an “inverted” p-i-n solar cell architecture, owing to reduced defect density and improved charge-carrier lifetimes [2].

However, most reports of high-efficiency solar cells based on vacuum-deposited MHP films often utilise solution-processed hole transport layers (HTLs) such as PTAA or Spiro-OMeTAD. Not only are these HTLs relatively expensive, and the additional solution-processing step complicates the overall fabrication process, but also more critically, materials such as Spiro-OMeTAD are prone to degradation under different environmental stressors of temperature and humidity, and thus curtailing the operational lifetime of these devices.

We investigated organometallic copper phthalocyanine (CuPc) and zinc phthalocyanine (ZnPc) as alternative, low cost, and durable HTLs in all-vacuum-deposited solvent-free $[CH(NH_2)_2]_{0.83}Cs_{0.17}PbI_3$ ($FACsPbI_3$) perovskite solar cells. We reveal that the vacuum-deposited CuPc HTL demonstrated improved compatibility in a photovoltaic device with p-i-n configuration, in comparison with ZnPc. Furthermore, we thoroughly examined the long-term stability of these all-vacuum-processed devices under a range of testing conditions. Importantly, unencapsulated devices as large as 1 cm^2 exhibited outstanding thermal durability, demonstrating no observable degradation in efficiency after more than 5000 hours in storage and 3700 hours under 85 °C heat-stressing in N_2 atmosphere [3].

In addition, we uncover the striking differences in the sticking, adhesion, and nucleation of the organic perovskite precursor, formamidinium iodide (FAI), to various HTLs. We highlight the impact of varying sticking characteristics to the stoichiometry of co-evaporated perovskite films and the importance of optimising growth parameters specific to individual charge transport layer if FAI is to be used as a precursor in co-evaporated perovskites [3].

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5:00 PM EL02.09.37
Engineered Negative Pressure in Nanoscaffolded $CsPbI_3$ Imparts Thermodynamic Stability and Optical Tunability to the Perovskite Phase Arkita Chakrabarti and Aaron Fafarman; Drexel University, United States

Strain at heterointerfaces in functional composite materials is inevitable and has in 2D geometries been intentionally engineered to improve superconductivity, ferromagnetism, and phase stability. As an example, tensile strain generated due to the mismatch in thermal expansion coefficients between thin-film $CsPbI_3$ and its substrate (so called substrate-clamping) has been shown to impart metastability of the otherwise unstable perovskite phase at room temperature. However, such substrate-induced stress is biaxial, resulting in an opposing strain in the third, orthogonal axis. Herein, we extend such engineered interfacial strain to all three dimensions to approximate the condition of 'negative pressure,' i.e., 3D tensile stress. Using a generalizable approach, we show negative pressure stabilizes the symmetric, low density, cubic perovskite phase of $CsPbI_3$, which is a promising absorber material for photovoltaic devices. In this work, we crystallized $CsPbI_3$ in the perovskite phase inside rigid oxide scaffolds at elevated temperatures and quenched them. Given the extremely low modulus of $CsPbI_3$, when it is synthesized within a rigid, ordered metal-oxide nanoscaffold at high temperature and then rapidly quenched, a tensile interfacial stress is generated. The three-dimensional tensile strain generated by this thermally induced stress differs from its biaxial counterpart in that it can thermodynamically favor high symmetry crystal phases i.e., the functional perovskite phase. We used X-ray diffraction and high-resolution transmission electron microscopy to identify the phase and estimate lattice expansion as a function of thermal excursions imposed on the $CsPbI_3$-scaffold composite. Furthermore, photoluminescence studies showed bandgap tunability as a consequence of negative pressure. Such an experimental materialization of 3D-interfacial stress or "negative pressure" to access the thermodynamically forbidden phases and tune optoelectronic properties of a perovskite material has been demonstrated for the first time in this work.

5:00 PM EL02.09.38
Stability Enhancement of Ambient Fabricated Perovskite Film Using Ionic Liquid Dopant Supawinee Chaosukho[1], Sorrawit Meeklinhom[2], Sasiphapa Rodbuntum[2], Nuttaya Sukgorn[2], Anusit Kaewprajak[2], Pisist Kumnorkaew[2] and Paiboon Sreearunothai[1]; [1]Sirindhorn International Institute of Technology, Thammasat University, Thailand; [2]National Science and Technology Development Agency, Thailand

The stability of the perovskite film is a crucial factor that challenges the commercialization of Perovskite solar cells (PSCs). It can be affected by factors such as moisture, oxygen, light, and temperature. Another critical factor in the fabrication of PSCs is the ability to deposit the perovskite film in ambient conditions rather than in an inert atmosphere (N_2). To address these issues, this study aims to improve the stability of the perovskite film by adding ionic liquid, such as 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) and 1,3-dimethyl-3-imidazolium hexafluorophosphate ($DMIMPF_6$), to the perovskite precursor using a two-step deposition method in ambient air. The degradation of the perovskite film was observed under high relative humidity (around 70-80% RH) without encapsulation.
Results from UV-visible spectroscopy showed that the best stable perovskite film with the $BMIMBF_4$ ionic liquid additive achieved 144 hours of α phase perovskite film without changing absorbance and also prolonged the perovskite structure for over 240 hours before being entirely degraded into the undesirable δ phase. $DMIMPF_6$ also showed potential for longer stability than the control film without an ionic liquid additive and could be doped into both the PbI_2 layer (step one) and the FAI/MAI layer (step two). Adding ionic liquids also improved the hydrophobicity of the perovskite film. X-ray diffraction results showed that the film with an ionic liquid dopant could suppress residual PbI_2 compared to the one without an ionic liquid. Overall, this study presents promising results for the large-scale fabrication of stable PSCs.

SESSION EL02.10: Device Fabrication II
Session Chairs: Maria Antonietta Loi and Peter Muller-Buschbaum
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3002

8:15 AM *EL02.10.01
Approaches to Enhancing Efficiency of Tin Based Perovskite Solar Cells Shuzi Hayase; University of Electro-Communications, Japan

Tin based perovskite solar cells (Tin perovskite solar cells (Sn PVK PV) and Tin-Lead alloyed perovskite solar cells SnPb PVK PV) have attracted attention for Pb free PVK PV and narrow band gap PVK PV working as the bottom cells of PVK/PVK tandem solar cells, respectively. At the beginning of the research, these Tin PVK PV efficiencies were low, compared with those of the Pb PVK PVs, because of the presence of the high carrier trap density associated with various lattice defects including the grain boundary and carriers due to the formation of Sn4+ (self-doping)(1). We have reported that the formation of Sn4+ was suppressed by the addition of small amount of GeI2 (2) and the grain boundaries defects were decreased by ethylenediamine passivation (3). In addition, the ethylene diamine passivation made the Fermi level of the Sn-PVK surface shallower, which causes the band bending near the grain boundary. Because of the band-bending, electron injection from the Sn-PVK layer to n-type layer (fullerene) was accelerated by around 10 times and the charge injection of the holes (from Sn-PVK to hole transporting layer (HTL)) and that of the electrons (from Sn-PVK to electron transporting layer (ETL)) were balanced. By combining these defect suppression engineering, the efficiency of Sn-PVK PV with inverted structure was enhanced to 13.2%

(4). PEDOT-PSS is commonly employed for the HTL of the Sn-PVK PV. From the viewpoint of the stability, inorganic HTLs have advantage over organic HTLs. We found that SnOx (x=1.7-1.8, 10 nm thickness) prepared by plasma-oxidized Sn metal layer is worked for the HTL of the Sn-PVK PV. In addition, the electron injections from the Sn-PVK to fullerene is accelerated by inserting ultrathin plasma-oxidized Sn metal layer (1 nm thickness). These heterointerface engineering enhanced the efficiency of the Sn-PVK PV to 14.1%(5). These defect suppression methods were effective for enhancing the SnPb-PVK PV with narrow bandgap (around 1.2 eV). By introducing mixed monolayer HTL which probably increases the efficiency of the SnPb-PVK PV was enhanced from 23.3%(6).

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8:45 AM *EL02.10.02
Structure and Mechanism of Crystallization in 3D and 2D Sn-Based and Mixed Sn-Pb Perovskites Giuseppe Portale; University of Groningen, Netherlands

Three dimensional (3D) perovskite materials with an ABX_3 structure (where A is either an organic or an inorganic cation, B is a divalent metal cation, and X is a halide anion) have demonstrated superb properties as light absorbers in photovoltaic devices. Lead (Pb) based hybrid perovskite solar cells (HPSCs) have achieved an impressive power conversion efficiency (PCE) up to a certified 25.5%.[1] Despite these outstanding achievements, the toxicity of lead causes concerns for the health and the environment. Therefore, attention has recently turned towards lead free HPSCs with the idea of replacing lead by less toxic metals. Among the various alternatives to lead, tin (Sn) has great potential as the Sn based hybrid perovskites display excellent optical and electrical properties such as high absorption coefficients, small exciton binding energies, and high charge carrier mobilities.[2] However, much less is known about Sn-based perovskites, especially about their crystallization mechanism from solution.
Another important aspect is the stability of the perovskite systems when exposed to light and to environmental conditions different than inert atmpsphere. An efficient way to improve HPSCs' stability, is to use the so-called miced dimensional systems, where an amount of 2D perovskite material is added to the 3D perovskite.
For instance, the addition of different amounts of low-dimensional PEA_2SnI_4 perovskite to $FASnI_3$ to form a 2D/3D composed system increases the stability against humidity and improves the performances to a value of PCE as high as 9.0 %.[3] Recently, the efficiency of Sn HPSCs is increased to 14%.[4] Similar approaches were also used to improve the properties of mixed Sn Pb systems.
Key of the reported performance and stability improvement is the formation and distribution of highly aligned structure that occurs during the perovskite solution deposition.
In this contribution, I will report our findings in understanding the formation mechanism during spin coating of this aligned structure in some of these mixed 2D/3D systems. In particular, our approach is to use in-depth structural analysis by ex-situ and in-situ gracing incidence wide angle X-ray scattering (GIWAXS). The ex-situ analysis is performed in a depth resolved manner in our laboratory, while the in-situ data are gathered using a custom-made spin coating device interfaced with 3rd generation synchrotrons.[5]
Our structural findings reveal that the vertical distribution of the 2D phase is crucial to the HPSC performances and stability, but most importantly, the presence of the long cations from the 2D precursor material alters the crystallization pathways during drying, promoting surface nucleation that drives guided crystallization of 3D-like crystals with preferred orientation.

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9:15 AM EL02.10.03
Improving Efficiency and Stability of Wide-Bandgap Perovskite Solar Cells Through $PEABF_4$ Passivation Layer Jaehyuk Koh, Daehan Kim and Byungha Shin; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

In order to realize perovskite-based tandem solar cells that can overcome the theoretical efficiency of a single junction solar cell, active research efforts are being conducted on wide-bandgap (WBG) perovskite solar cells (bandgap ~ 1.7 eV). However, WBG perovskite solar cells still lag behind the current state-of-the-art single junction solar cells based on regular bandgap (1.5 – 1.6 eV) perovskite in both efficiency and stability, mainly due to halide segregation and incomplete passivation of grain boundaries and interfaces which act as a recombination center. To overcome these issues, a passivation strategy using two-dimensional (2D) perovskite, which preferential forms at grain boundaries and interfaces, has been used and shown to suppress halide segregation and passivate defects at the internal and external surfaces. In this study, double passivation strategy were proposed where grain boundaries of WBG perovskite, $(FA_{0.65}MA_{0.2}Cs_{0.15})Pb(I_{0.8}Br_{0.2})_3$, are passivated with 2D layers formed by PEAI and PEASCN while electron transporting layer (ETL)/perovskite interface is passivated by $PEABF_4$. Steady-state and time-resolved photoluminescence confirmed that the introduction of $PEABF_4$ reduced non-radiative recombination, and space-charge-limited current measurement for electron-only device revealed a reduce trap density compared to a reference without the $PEABF_4$ passivation. With our comprehensive passivation approach, we have achieved a very high V_{OC} of 1.21 V along with the champion efficiency of 19.5%. We have also demonstrated a shelf lifetime stability of 1400 hours and 240 hours under N_2 atmosphere and ambient air (RH: 30~40%), respectively.

9:30 AM BREAK

SESSION EL02.11: Mechanism and Characterizations I
Session Chairs: Maria Antonietta Loi and Sergei Tretiak
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3002

10:00 AM *EL02.11.01
Ultrafast Dynamics in 2D and Mixed 2D/3D Hybrid Metal Halide Perovskites Rebecca L. Milot; University of Warwick, United Kingdom

Two-dimensional hybrid metal halide perovskites have been investigated for use in optoelectronic devices including photovoltaic cells due to their increased stability as compared to their 3D counterparts. However, quantum and dielectric confinement effects increase the exciton binding energies in these materials to as much as 100s of meV.[1] These increased binding energies correspond to an increase in exciton population at ambient temperatures, and the presence of a large population of excitons can greatly alter the optoelectronic properties. Optical Pump/THz-probe (OPTP) spectroscopy measurements have revealed decreased effective charge-carrier mobilities and significantly shortened charge-carrier lifetimes for 2D perovskites.[2] We further investigate 2D perovskites by analyzing the fundamental properties of $PEAPbI_4$ (PEA = phenylethylammonium) and evaluating a mixed phase Pb-Sn and FA-PEA perovskite using both OPTP and visible transient absorption spectroscopy. Through these investigations, we see similar fast charge-carrier cooling and exciton formation in timescales of about 300 fs in all compositions, which result in decreased effective charge carrier mobilities at later times. However, mixed-phase materials exhibit increased charge-carrier, but these lifetimes are sensitive to morphology and preparation method.

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10:30 AM EL02.11.02
Understanding Factors that Induce Static and Dynamic Stress in Metal Halide Perovskites Gabriel McAndrews[1,2], Boyu Guo[3], Benjamin Lefler[3], Aram Amassian[3] and Michael D. McGehee[1,1]; [1]University of Colorado Boulder, United States; [2]National Renewable Energy Laboratory, United States; [3]North Carolina State University, United States

The operational stability of metal halide perovskite devices hinders their commercial viability despite promising, competitive initial efficiencies. Mechanical stress in perovskites is often overlooked but significantly influences degradation as the presence of tensile stress has been shown to accelerate undesirable PbI_2 formation.[1,2] In addition, the brittle nature of polycrystalline metal halide perovskite films leaves them susceptible to fracture and delamination.[3] Therefore, it is crucial to identify and reduce sources of residual tension that arise from film formation processes. For one, several studies have highlighted the coefficient of thermal expansion (CTE) mismatch between the perovskite and rigid substrates, such as glass, which can induce tension.[2,4] Thermal annealing is essential to promote crystallization for solution processed perovskites, but during the cooldown the crystallites are confined to the substrate and unable to contract with their intrinsic CTE.

Strain engineering approaches to reduce tension or induce compression in perovskites have been primarily focused on molecular precursor or antisolvent additives. However, many strategies lack explanations grounded in thin-film mechanics.[5] Here, we demonstrate perovskite residual stress dependent on composition that cannot be explained solely by variations in CTEs. For example, with standard processing conditions a tin-containing narrow bandgap perovskite ($Cs_{0.25}FA_{0.75}Sn_{0.5}Pb_{0.5}I_3$) exhibits a residual stress of ≈100 MPa whereas the heavily studied “Triple Cation” perovskite ($Cs_{0.05}MA_{0.16}FA_{0.79}Pb(I_{0.83}Br_{0.17})_3$) has near zero stress. Additional sources of stress beyond the CTE mismatch are identified in connection with film formation kinetics to explain the varied stresses in perovskites. Specifically, grain coalescence, adatom/impurity insertion into grain boundaries, phase transitions, and partial attachment of crystallites to the substrate are likely contributors to stress.

We present a broadened perspective on stress engineering and propose new connections between stability and stress. For example, moisture and oxygen uptake can induce compression in perovskites that could be explain the accelerated PbI_2 formation with tension. Finally, the impact of temperature cycling on stress and mechanical stability for perovskite photovoltaics in both terrestrial and space applications are discussed. Due to the CTE mismatch, biaxial tensile stress can be substantial at subzero. Using strategies to have the stress be near zero or compressive at room temperature will be essential to avoid cracking at low temperature extremes.

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10:45 AM EL02.11.03
Effective Surface Passivation by *In Situ* Thermal Phase Transition for Highly Efficient Perovskite Solar Cells Dohyun Kim, Seung Un Ryu and Taiho Park; Pohang university of science and technology (POSTECH), Korea (the Republic of)

In this work, we investigated an effective interfacial engineering of perovskite solar cells (PSCs) by adopting in Situ thermal phase transition of alkylammonium formates (AAFos). AAFo, which consists of large organic cation with pseudo-halide anion, can participate in passivation proced as liquid phase at relative low temperature due to the weak coordination between the cations and anions. Thanks to this property, AAFo can give several advantages for the interfacial engineering: (1) Increase of liquid-like behavior of AAFo can effectively passivates into the grain boundaries to reduce trap densities of perovskites. (2) formate anion has relatively higher affinity with iodide vacancies than other halides, leading effective passivating at iodide vacancies for improved thermal stability. (3) Long alkyl chain of decylammonium cations improve moisture stability by preventing the moisture permeation into the perovskite layer. As a result, we achieved 25.0% of power conversion efficiency (PCE) with dodecylammonium formate and superior thermal stability maintaining over 92% of initial effieciency under 85°C N_2 condition. Finally, we achieved a high efficiency of 20.82% will superior fill factor (80.77%) in module PSC with an active area of 23.75 cm^2, proving the suitability of the strategy for manufacturing large-area devices.

11:00 AM DISCUSSION TIME

11:15 AM EL02.11.06
Visualizing Voltage Losses in Highly Efficient and Stable Perovskite-based Tandem Solar Cells Esma Ugur[1], Jiang Liu[1], Erkan Aydin[1], Michele De Bastiani[1], Mingcong Wang[1], Sam Teale[2], Bin Chen[2], Randi Azmi[1], Hao Chen[2], Aidan Maxwell[2], Edward H. Sargent[2], Frédéric Laquai[1] and Stefaan Dewolf[1]; [1]King Abdullah University of Science and Technology, Saudi Arabia; [2]University of Toronto, Canada

To achieve higher electricity generation at low cost, the most substantial impact on the energy generation from solar cells is to make existing technologies more efficient per area. This forms the focus of tandem solar cells, which utilize different photoactive materials with different bandgaps, allowing to benefit from a broader range of the solar spectrum. To make efficient and stable perovskite-based multi-junction (e.g. perovskite/silicon and perovskite/perovskite tandem) solar cells – also single-junction ones –, it is important to understand the losses under device operational conditions.[1] To do so, we used absolute (photo- and electro-) luminescence imaging techniques with high spatial resolution.
On the device level, recombination losses could occur either in the bulk of the perovskite or at the adjacent transport layer interfaces. Here, we visualized the interfacial recombination losses using hyperspectral imaging system by analyzing the data with home-built MatLab code. We investigated how the different passivation routes affect the quasi Fermi level splitting (QFLS) of the samples together with device performance, also the stability under different external stressors. In the case of single junction perovskite devices, the focus was on 2D perovskite layers at the electron-selective interface that passivate the trap states and suppress the ion migration. Also, the alternative passivation routes for wide bandgap perovskites such as ammonium-based passivation molecules were studied. These molecules regulate this interface that results in absolute 90 meV enhancement in QFLS. Finally, we further investigated the p-i-n perovskite/silicon monolithic tandem solar cells. Reducing the trap states at perovskite/C_{60} interface both for single-junction and tandem solar cells not only enhances the device performance but also the stability of the devices after damp-heat testing (85°C at 85% relative humidity).[2, 3] Further, origin of the perovskite top cell degradation in perovskite/silicon tandem devices after field test experiments was demonstrated via PL imaging.[4]

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SESSION EL02.12: Perovskite Solar Cell
Session Chairs: Xuedan Ma and Yuanyuan Zhou
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3002

1:30 PM *EL02.12.01
The Origin of Moisture Instability in Perovskite Solar Cells Chunqing Ma[1], Felix T. Eickemeyer[2], Sun-Ho Lee[1], Dong-Ho Kang[1], Seok Joon Kwon[1,1], Michael Grätzel[2,1] and Nam-Gyu Park[1,1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]École Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Since the seminal work on 9.7% efficient solid-state perovskite solar cell in 2012, its power conversion efficiency reached over 25% within a decade. Organic lead halide perovskite as a light absorber for PSCs, however, is unstable under moisture, where the moisture instability was assumed to be due to its ionic nature without in-depth understanding. Although a preponderance of methodologies have been proposed to improve the moisture stability of perovskite films, the origin of moisture instability is still unveiled. We found for the first time that a specific facet in perovskite film was responsible for the moisture instability. Among three facets of (100), (110) and (111) in a cubic structured film, a certain facet was unstable but a certain facet was quite stable under moisture. Experimental combined with theoretical studies revealed that a crystal facet with moisture instability provided a strong water adhesion via the hydroxylation of Pb atoms, leading to phase transformation. Perovskite film where moisture-tolerant crystal facet is abundant was designed and successfully prepared, which showed exceptional stability against moisture without additional surface passivation.

2:00 PM EL02.12.02
Encapsulation of Perovskite Solar Cells Robert Witteck[1], Tobias Abzieher[1], Xiaopeng Zheng[1], Ashley Gaulding[1], Min Chen[1], Brian Habersberger[2], Joseph Luther[1] and Lance M. Wheeler[1]; [1]National Renewable Energy Laboratory, United States; [2]Dow, United States

We study the effect of varying encapsulation polymers and vacuum lamination processes on the electrical properties of perovskite (PSK) solar cells with varying hole transport layer (HTL). In order improve the performance and long-term stability of perovskite solar cells (PSC) it requires a suitable encapsulation material. Yet there is very little work done for understanding what appropriate materials and processing conditions for PSC are.
In this work we investigate PSC with pin architecture, which consists of a glass/ITO/HTL/PSK/LiF/C60/BCP/Ag structure. We employ four different HTL

materials to investigate the effect of the high temperature lamination process on the PSC performance. The PSC are encapsulated at varying lamination conditions with a peak lamination temperature of 125 or 150°C and a total process duration of 12 or 20 min. We employ different polymers for the encapsulation using a conventional peroxide-cured ethylene-vinyl acetate (EVA) and polyolefin elastomers (POE) as well as a low and high crystalline silane and anhydride grafted POE. Subsequent to the lamination we test the long-term stability of the encapsulated PSC in thermal cycling (TC) tests in N_2 atmosphere, where the environmental temperature is varied between -40°C and 85°C holding each temperature for 25 min. Besides *IV* characteristics we perform time resolved electroluminescence (EL) and photoluminescence (PL) imaging measurements.
Our results show that samples with 2PACz HTL yield the highest cell efficiency of 20.0% on average for all samples. Further these cells show the best process stability when comparing the pre and post lamination *IV* parameters. The lamination of the PSC with varying process durations and temperatures reveal that all PSC show a loss in power conversion efficiency, when measured immediately after the lamination. The efficiency loss correlates with the thermal budget of the lamination process, i.e., the hotter and longer the lamination process the higher the efficiency loss. All samples show a recovery in efficiency when stored in N_2 atmosphere after the lamination. However, only samples laminated with a cool and short process show a full recovery back to the initial efficiency. EL and PL images show the formation of dead areas after the lamination, where the size of the dead area grows with increasing thermal budget. We hypothesize that a dead area of a certain size may be able to recover when stored at RT in N_2 atmosphere, while for a dead area above a certain size the recovery is irreversible. A comparison of the various encapsulation materials shows no significant differences when comparing the *IV* parameters before and after lamination. However, we observe slight advantages in stability for the silane grafted POE after 40 TC. At the conference we will present further details on our lamination experiments and the various TC tested encapsulation polymers with up to 200 TC.

2:15 PM EL02.12.03
2D Pb-Halide Perovskites Can Self-Heal Photodamage Better Than 3D Ones Sigalit Aharon[1], Davide R. Ceratti[2], Naga P. Jasti[3], Llorenç Cremonesi[4], Yishay Feldman[1], Marco A. Potenza[4] and David Cahen[1]; [1]Weizmann Institute of Science, Israel; [2]Institut Photovoltaïque d'Ile-de-France, France; [3]Bar-Ilan University, Israel; [4]University of Milan, Italy

Adding a 2D character to halide perovskite (HaP) active layers in ambient-protected cells can improve their stability drastically, which is not obvious from the hydrophobic large cations that force the HaP into a 2D structure. We report now, using two-photon confocal microscopy to study the interior of single crystal, inherent photo-stability of pure 2D Pb iodide HaPs. Compared to 3D HaP crystals, the 2D ones have higher photo-stability and, under conditions equivalent to a few suns, they self-heal efficiently after photo-damage. Using both photoluminescence (PL) intensities (as function of time after photo-damage), and spectra, we compare the self-healing dynamics of 2D HaPs with n=1 or 3 ($(C_4H_9NH_3)_2PbI_4$, $(C_4H_9NH_3)_2(CH_3NH_3)_2Pb_3I_{10}$) and 3D $MAPbI_3$. We find differences between the 2D HaPs in their response to photo-damage and ability to self-heal from different degrees of photo-damage. Based on our findings we suggest a possible chemical mechanism for photo-damage and self-healing of these 2D HaPs: the layered lattice arrangement limits out-diffusion of degradation products, facilitating damage reversal, leading to increased 2D HaP photo-stability, also improving self-healing uniformity. One of the implications of the layered structures' resilience is transfer of their increased stability to devices, based on them, such as photovoltaic solar cells and light-emitting diodes.

2:30 PM BREAK

SESSION EL02.13: Mechanism and Characterization II
Session Chairs: Laura Schelhas and Yuanyuan Zhou
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3002

3:30 PM *EL02.13.01
***In Situ* and *Operando* Scattering Studies on Perovskite Solar Cells** Peter Muller-Buschbaum; Technical University of Munich, Germany

The first application of hybrid organo-metal halide perovskites as sensitizer in hybrid solar cells marked the cornerstone for what has now become a broad field of extensive research. After overcoming initial challenges, power conversion efficiencies (PCE) of hybrid perovskite photovoltaics strongly increased to above the 25 % mark and now outperform many conventional inorganic thin film technologies for solar cell fabrication. The easy and versatile processing towards an improved stability and reproducibility further increases the massive interest in this type of material. The abundance of precursor materials in combination with the wet chemical processing are rendering hybrid organo-metal halide perovskites as candidates for a low-cost, mass-production photovoltaic technology. However, still the limited reproducibility of the device fabrication and the limited device stability impose challenges to bringing perovskite solar cells to real world applications.
With advanced in-situ x-ray and neutron scattering methods, the perovskite film formation is followed with a very high temporal and spatial resolution. In particular, with multi-modal grazing incidence small- and wide-angle X-ray scattering (GISAXS and GIWAXS) studies, we gain information on the kinetics of inner structures forming during processing. From these data, models about the morphology evolution are extracted and these models guide the fundamental understanding to increase reproducibility in the solar cell fabrication. [1]
Extensive studies have focused on improving the operational stability of perovskite solar cells, but few have surveyed the fundamental degradation mechanisms. One aspect overlooked in earlier works is the effect of the atmosphere on device performance during operation. Here, we investigate the degradation mechanisms of perovskite solar cells operated under vacuum and under a nitrogen atmosphere using synchrotron radiation-based operando GISAXS and GIWAXS. [2]

[1] Nat. Commun. **12**, 5624 (2021)
[2] Nature Energy **6**, 977-986 (2021)

4:00 PM *EL02.13.02
Light-Induced Structural Dynamics in the Hybrid Perovskites—From Femtoseconds to Seconds Aaron Lindenberg; Stanford University, United States

I will describe recent results focused on elucidating the atomistic response of the hybrid perovskites to light, probing both the ultrafast dynamics that potentially underlies their unique optoelectronic functionalities and the dynamical processes that underlie how these materials degrade. In the first part of the talk I will focus on time-resolved x-ray and electron scattering approaches as applied to a range of material systems including single crystals, thin films, and nanocrystals and describe how these efforts enable new understanding of electron-phonon coupling processes. In the second part I will describe new efforts using cryo-electron microscopy coupled to light to capture structural intermediates during the phase segregation process in mixed-halide perovskite films.

4:30 PM EL02.13.03

Using Multimodal *In Situ* Spectroscopy to Understand the Influence of the Ionic Liquid BMIMBF$_4$ on the Film Formation and Optoelectronic Properties of MAPbI$_3$ Thin Films Simon Biberger, Konstantin Schötz, Nico Leupold, Philipp Ramming, Maximilian Spies, Ralf Moos, Anna Kohler, Helen Grueninger and Fabian Panzer; University of Bayreuth, Germany

Today, metal halide perovskite solar cells are one of the most promising emerging photovoltaic technologies. A key to such highly efficient devices is to realize high-quality perovskite layers, which requires a deep understanding about the perovskite formation and good process control. In-situ experiments have been proven to give important insights into the formation process of the perovskite absorber layer. We use multimodal optical in-situ spectroscopy to further develop an understanding of the thin film formation of the model halide perovskite methylammonium lead iodide MAPbI$_3$ during the one-step processing and the solvent engineering approach. Further, we investigate how the identified formation processes change when we mix a passivating additive, the ionic liquid (IL) BMIMBF$_4$ into the perovskite precursor solution.

One-step processing experiments reveal that IL in the precursor solutions does not affect the formation of perovskite–solvent complexes, but higher IL contents delay the perovskite transformation and decrease growth rates. For solvent engineering, the perovskite growth rate decreases with later anti-solvent (AS) dripping as the properties of PbI$_4^{2-}$ species in the precursor solutions change during drying. Here, the IL also affects the evolution of the PbI$_4^{2-}$ properties, as the IL cation interacts with the PbI$_4^{2-}$. This interaction appears to reduce the perovskite crystallite growth rates after initiating perovskite formation by AS dripping.[1]

Thus, this work shows the sensitive interconnection between precursor properties, film formation process, and final optoelectronic properties of perovskite thin films and how small amounts of additive can impact this relationship. Further, this work highlights the potential of optical in-situ spectroscopy to facilitate more tailored solution processing strategies in the future.

[1] Biberger et al., J. Mater. Chem. A, 2022, 10, 18038

4:45 PM EL02.13.04

Backscattered Electron Imaging for the Instability Analysis of the Structure and Composition of Perovskite Device Cross Sections Abigail Carbone, Mathilde Fievez, Austin Flick, Omar Elsafty, Robert Sinclair and Reinhold H. Dauskardt; Stanford University, United States

The primary obstacle to commercialization of organic-inorganic lead halide perovskites is instability of device performance under operational conditions. Ongoing research efforts are focused on understanding degradation mechanisms of the perovskite absorber, where the structure and chemistry of charge transport interfaces and diffusion of metal species are of particular interest. What has been lacking in these efforts is the application of electron microscopy to directly image and quantify compositional variations and microstructural changes. These would greatly enhance our understanding of phenomena like iodine ion migration, undesirable PbI$_2$ formation, and diffusion of species from adjacent charge transport and electrode layers, all of which lead to diminishing power conversion efficiency.

The goal of this research is to use high-resolution electron imaging techniques to address the fundamental mechanisms that underpin perovskite instability. Scanning electron microscopy (SEM) is a powerful tool for making direct connections between microstructure, composition, and overall device properties. However, using SEM to its full potential is particularly difficult for perovskites because they readily degrade upon incident electron irradiation; they are susceptible to cracking along grain boundaries caused by inelastic-scattering radiolysis of the electron beam[1,2] as well as phase transformations due to localized heating effects[2]. Acquiring compositional information in the SEM using energy dispersive X-ray spectroscopy (EDXS) is not ideal because of diminished elemental sensitivity at the low accelerating voltages and currents required to prevent beam-induced perovskite damage. Additionally, the interaction volume of EDXS is larger than the length scales of our device cross sections.

We circumvent these limitations by employing backscattered electron (BSE) imaging with meticulously optimized beam conditions (e.g., accelerating voltage and beam current), a rigorous set of controls, and delicate sample preparation. We use a low-energy argon mill to create a flat cross-sectional face of photovoltaic cells deposited via a Rapid Spray Plasma Process[3] with the following architecture: ITO/NiO/CsFAPbI$_3$/C$_{60}$/BCP/Ag. We acquire BSE images of as-fabricated devices and devices subjected to accelerated aging conditions to probe the effect of aging on perovskite layer composition. Monte Carlo simulations are implemented to understand the interaction volume of the backscattered electrons generated at our specified beam conditions, and therefore informs the intensity of our subsequent BSE images. We generate intensity profiles along the device cross section using ImageJ. These intensity profiles are compared to a set of controls, which are analyzed in tandem with nano-SIMS depth profiling data to correlate change in BSE image intensity with chemical profiles obtained by SIMS. We studied the correlation of lighter intensity regions on the BSE images to the formation of PbI$_2$ on accelerated thermal aging. These results elucidate the limiting degradation mechanisms of perovskites by leveraging the full potential of SEM imaging in a unique way, and therefore inform direct process engineering solutions for bulk manufacturing of perovskite modules. Additionally, developments in sample preparation of device cross-sections contribute to the ongoing effort to image perovskites using transmission electron microscopy and related analytical techniques.

SESSION EL02.14: Poster Session II

Session Chairs: Robert Hoye, Maria Antonietta Loi, Xuedan Ma, Wanyi Nie and Sergei Tretiak
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL02.14.04

Sub-Diffraction Limited Measurement of Carrier Recombination Dynamics on Lead Halide Perovskite Semiconductors Madeleine Breshears, Rajiv Giridharagopal and David S. Ginger; University of Washington, United States

Traditional optical methods of measuring the spatial heterogeneity of carrier lifetimes—such as fluorescence lifetime imaging (FLIM)—are diffraction-limited, whereas perovskite materials of interest exhibit grain structure at lengthscales far below the diffraction limit. Here, we use time-resolved electrostatic force microscopy (trEFM) to achieve nanoscale spatial resolution of carrier dynamics. trEFM captures the response of the scanning probe cantilever to a perturbation of the electrostatic force gradient between the tip and sample; by monitoring the cantilever oscillation during photoexcitation as a function of wavelength and intensity, we can measure carrier recombination with sub-microsecond temporal resolution. Using this method, we observe slower recombination dynamics in $FA_{0.83}Cs_{0.17}Pb(Br_{0.15}I_{0.85})_3$ on a phosphonic acid-based hole transport layer (HTL) as compared to indium tin oxide substrates, which we correlate these findings with bulk lifetime measurements and FLIM. Finally, we apply trEFM to investigate the spatial heterogeneity in carrier dynamics of a $FA_{0.83}Cs_{0.17}Pb(Br_{0.15}I_{0.85})_3$ when passivated with (3-aminopropyl)trimethoxysilane (APTMS), demonstrating that APTMS-passivation extends carrier recombination lifetimes in perovskite.

5:00 PM EL02.14.05
Additive-Enhanced Aerosol Treatment for Improved Nanoscale Homogeneity, Efficiency and Stability of Perovskite Solar Cells and Photodetectors Joe Briscoe[1], Tian Du[1], Sinclair R. Ratnasingham[1], Thomas J. Macdonald[1], Felix Kasasih[2], Ruoxi Yang[3], Meng Li[4], Zhongyao Jiang[5], Lokeshwari Mohan[1], Adriana Augurio[1], Huda Ahli[5], Shengda Xu[5], Weidong Xu[5], Zhenhuang Su[6], Xingyu Gao[6], Richard Whiteley[1], Chieh-Ting Lin[5], Ganghong Min[5], Saif Haque[5], Kristin Persson[3], Caterina Ducati[2], James Durrant[5] and Martyn A. McLachlan[5]; [1]Queen Mary University of London, United Kingdom; [2]University of Cambridge, United Kingdom; [3]Lawrence Berkeley National Laboratory, United States; [4]Henan University, China; [5]Imperial College London, United Kingdom; [6]Shanghai Institute of Applied Sciences, China

We have previously demonstrated a new approach to solvent-based post-treatment of perovskite films that achieves excellent reproducibility and uniformity by exposing a perovskite film to vapourised solvents delivered via an aerosol-assisted chemical vapour deposition system [1]. Using this process we achieved enhancement of both photovoltaic power conversion efficiency (PCE) and stability in a range of perovskite compositions and device architectures, which we have linked to improvements in both the nanoscale and macroscale uniformity of the material, including a reduction of defects and associated trap states.
Here I will discuss our more recent developments of this process to include organo-halide salts in the solvent aerosol, such as MACl, leading to substantial enhancement of the post-crystallisation grain growth and recrystallisation process [2]. This leads to films that are comprised of ultra-large grains (~1-5 µm) where local traps are almost completely eliminated, as confirmed at the nanoscale via photoconductive atomic force microscopy. The large grains have also allowed us to visualise local variations in photoluminescence (PL) emission at the grain boundaries using hyperspectral PL mapping. Finally, the substantial reduction in trap states and increase of film homogeneity leads to photodetectors that can operate at ~1.5 orders of magnitude lower light levels than those made with conventional spin-coated films.
Expanding beyond solvent post-treatment, we have also applied this technique to pure formamidinium lead iodide ($FAPbI_3$) [3]. Using aerosol-assisted crystallization (AAC) of the $FAPbI_3$ films enhanced by Lewis base additives in the solvent aerosol we are able to crystallise pure black-phase α-$FAPbI_3$ in only 2.5 minutes at 100°C, compared to 20 minutes at 150°C for conventional thermal annealing. Not only does this open up wider processing options for the material, but we demonstrate improvement in PCE and, importantly, phase stability of pure α-$FAPbI_3$ compared to thermally annealed control samples. Using X-ray diffraction, X-ray scattering and density functional theory simulation, we identify that relaxation of residual tensile strains due to the lower annealing temperature and post-crystallization crystal growth during AAC are key factors that facilitate the formation of phase-stable α-$FAPbI_3$.
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5:00 PM EL02.14.07
Highly Stable Inorganic 0D and Quasi-2D Perovskite/Cellulose Nanocrystal Luminescent Films Chih Hao Chiang and Meng Lin Tsai; National Taiwan University of Science and Technology, Taiwan

In the past two decades, 0D perovskite quantum dots (PQDs) attract a lot of attentions in optoelectronic industry and academia due to the narrow emission full width at half maximum (FWHM), tunable bandgap, and high photoluminescence quantum yield (PLQY). Owing to these advantages, PQDs are regarded as the new blue ocean for developing next-generation displays. However, the poor stability of PQDs is the most serious drawback for the further application and commercialize. In order to overcome the stability issue, we developed a strategy to stabilize PQDs by applying surface functionalized cellulose nanocrystals (CNCs) to replace traditional ligands and successfully synthesized the highly stable and color-tunable PQDs/CNCs luminescent films. Nevertheless, the PLQY of the PQDs/CNCs luminescent films is limited due to large crystals formed during the synthesis process. After investigation, we incorporate phenethylammonium halide (PEAX, X = Cl, Br, and I) during the synthesis process to format quasi-2D perovskite structures instead of the PQDs and the PLQY of $CsPbBr_{1.5}Cl_{1.5}$, $CsPbBr_3$, and $CsPbBr_{0.5}I_{2.5}$ films with PEAX passivation can be enhanced more than 10 (from 1.2% to 10%), 3 (from 22% to 69%), and 18 (from 3% to 55%) times, respectively. Moreover, the stability of PEAX passivated inorganic perovskite/ CNCs luminescent films also slightly increase. By combining the advantages of CNC and PEAX, this study demonstrates highly stable light emission/conversion films with largely enhanced PLQY, and it holds the potential for developing full-color, stable, and high PLQY displays in the future.

5:00 PM EL02.14.08
Thermally Stable and Efficient Perovskite Solar Cells employing an IDTT-Based Organic Semiconductor Additive Hyuntae Choi, Dohyun Kim and Taiho Park; Pohang University of Science and Technology, Korea (the Republic of)

Perovskite solar cells (PSCs) have received a lot of attention because of their fascinating optoelectronic features and solution processability, but they still have shortcomings that limit their efficiency and stability. Here, a new small molecule additive (IDTT-ThCz) based on indacenodithieno[3,2-b]thiophene that can interact with perovskite layers is designed. In particular, IDTT-ThCz is introduced into the perovskite layer to significantly suppress the perovskite defects through anti-solvent treatment. In addition, this facile surface passivation greatly improves the charge extraction ability, preventing perovskite degradation. As a result, IDTT-ThCz-treated PSCs showed enhanced power conversion efficiency (PCE) of 22.5% and superior thermal stability by maintaining 95% of the initial PCE after storage for 500 hours under thermal conditions (85°C).

5:00 PM EL02.14.09
Minimizing Energy Loss via Perovskite Heterostructure Fabricated by Transfer Printing Technique for Efficient Perovskite Solar Cells Chih Wei C. Chu, Anisha Mohapatra and Anjali thakran; Academia Sinica, Taiwan

Despite the efficiency of perovskite solar cells (PSCs) has been increased rapidly from 3.9% in 2009 to 25.7% in 2022, the conversion of solar energy into electricity is still not efficient enough due to the energy loss originates from the non-absorption of low-energy photons and thermalization losses of high-energy photons ascribed to the Shockley-Queisser limit. As a result, stacked perovskite architectures including tandem, heterostructure, and prismatic configurations have been proposed to minimize non-absorption and thermalization losses. However, fabricated multi-layer heterostructure through solution process suffers from the dissolution problem in which bottom layer will be destroyed by subsequently deposited perovskite layers. In this work, a grafting-assisted PDMS transfer process was demonstrated for constructing heterostructure perovskite layers for solar cell devices. As a proof of concept, an layer $MAPbSnI_3$ was stacked on top of an $MAPbBrI_2$ layer to fabricate a cascaded heterostructure-based cell. The $MAPbBrI_2/MAPbSnI_3$ heterostructure showed power enhancement of ∼15% as compared to single-layer films MAPbBrI2 (∼13%) and $MAPbSnI_3$ (∼10%), presumably because of minimized thermodynamic and non-absorption losses. Such printed heterostructures suggest a new pathway for minimizing thermalization and non-absorption losses in PSCs and resolving the bottleneck of solution-processable perovskite heterostructures for the realization of efficient perovskite optoelectronics.

5:00 PM EL02.14.10
Hidden Structural Characteristics of Metal Halide Perovskites Monty R. Cosby[1], Nutifafa Y. Doumon[2], Amy E. Louks[2,3], Minh T. Nguyen[4], Michael D. Irwin[4], Joseph J. Berry[2], Laura T. Schelhas[2] and Kevin Stone[1]; [1]Stanford Synchrotron Radiation Lightsource, United States; [2]National Renewable Energy Laboratory, United States; [3]Colorado School of Mines, United States; [4]CubicPV, United States

Formamadinium lead idodide, $FAPbI_3$, is at the forefront of metal halide perovskite (ABX_3) research boasting an impressive 25% efficiency (as of this writing). The structural makeup of an $FAPbI_3$ thin film has been presumed to be primarily the $FAPbI_3$ cubic structure with potentially a low percentage of PbI_2. Using comprehensive powder and grazing incidence diffraction methods, we have characterized these perovskite thin films in great detail to determine the subtle structural parameters which play a role in the material performance. Performance differences in the literature are typically ascribed to changes in processing conditions while the level of characterization is insufficient to determine if there are accompanying structural changes. Our work seeks to address this open question as to whether there are structural differences which correlate to the observed differences in material performance.

5:00 PM EL02.14.12
Monolithic All-Perovskite Tandem Solar Cells with Minimized Optical and Energetic Losses Kunal Datta[1], Junke Wang[1], Dong Zhang[1], Valerio Zardetto[2], Bruno Branco[1], Willemijn H. Remmerswaal[1], Christ H. Weijtens[1], Martijn M. Wienk[1] and Rene A. Janssen[1]; [1]EIndhoven University of Technology, Netherlands; [2]TNO-Solliance, Netherlands

Solution-processed all-perovskite tandem solar cells present an effective device platform to maximize power-conversion efficiencies by combining complementary wide-bandgap mixed-halide perovskites and narrow-bandgap lead-tin perovskites in monolithic architectures to minimize the loss in chemical potential observed in single-junction solar cells due to thermalization and transmission losses.[1] Currently, the open-circuit voltage of such devices is limited by the low radiative yield in the wide- and narrow-bandgap sub-cells. Furthermore, optical losses reduce short-circuit current density contribution of the narrow-bandgap sub-cell, which increases the current-mismatch between sub-cells, thereby decreasing the effective short-circuit current-density of the tandem device.

This work, firstly, identifies sites of non-radiative recombination in the wide-bandgap ($E_g \sim 1.77$ eV) top-cell using absolute photoluminescence spectroscopy and pinpoints the interface between the perovskite and the electron transport layer (C_{60}) as a dominant surface for energetic losses.[2] Using surface treatment strategies based on the use of quaternary ammonium salts, the non-radiative loss is recovered, leading to high open-circuit voltages in single-junction, wide-bandgap solar cells. Compositional engineering, such as potassium substitution, is further used to improve the photostability of devices against light-induced halide segregation. Similarly, in narrow-bandgap ($E_g \sim 1.23$ eV) single-junction solar cells, the interface with the C_{60} layer is improved, as confirmed by electroluminescence spectroscopy, by compensating for sublimed halide ions at the surface, leading to an improvement in the open-circuit voltage. At the same time, high short-circuit current density is ensured by using thin, optically benign, hole-transport layers, such as self-assembled monolayers,[3] that minimize parasitic absorption, and by reducing external quantum efficiency losses due to optical interference by optimizing the perovskite layer thickness.

The monolithic tandem combining the wide-bandgap and narrow-bandgap sub-cells is integrated using a dense, atomic layer deposition-based SnO_x recombination junction that improves stability against solvent ingress during processing. A thin gold monolayer is used to maintain high conductivity across this interface.[4]

Free-carrier absorption in the front electrode of the tandem device is reduced by opting for hydrogenated indium oxide (IOH) instead of commonly used indium tin oxide (ITO),[5] which increases the near infrared response of the narrow-bandgap sub-cell, reducing the current-mismatch between sub-cells. Further decreases in parasitic absorption by using thin hole-transport layers and highly transparent interfacial layers additionally ensures improved light absorption in the narrow-bandgap sub-cell, which leads to current-matched tandem devices. A key highlight of this work is the effective light management strategy that ensures a high NIR response of the narrow-bandgap cell, despite using a low active layer thickness (600 nm). Collectively, these pathways to limit non-radiative recombination and reduce optical losses ensure 23% – 24% efficient tandem solar cells in small (0.09 cm^2) and large (1 cm^2) device areas which mark a > 7% (abs.) and > 6% (abs.) gain in the power conversion efficiency compared to the performance of single-junction wide- and narrow-bandgap solar cells.

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5:00 PM EL02.14.14
***In Situ*, High-Throughput Optical Monitoring of Spray-Coated Perovskite Photovoltaics Under Thermal Stress** Mathilde Fievez, Jessica Huxel, Alan Liu, Thomas W. Colburn, Austin Flick and Reinhold Dauskardt; Stanford University, United States

Hybrid organic-inorganic perovskite thin-film solar cells are of great interest as the light-absorbing perovskite layer can be easily deposited via simple solution processing, allowing for low-cost photovoltaic manufacturing. Under operation, prolonged exposure to UV light and elevated temperatures are known to cause premature device failure. Failure mechanisms include the degradation of the perovskite absorber itself and chemical reactions between device layers. Current research focuses on tracking device performance over time which provides an estimate of the degradation timescale. This approach is slow and requires numerous tedious measurements. Therefore, a high throughput characterization method is needed to quantify rapidly the thermal stability of perovskite devices. Optical imaging is an efficient method to screen for stable perovskite absorber compositions but has not yet been applied at a device or module scale.

In this work, we developed an optical imaging platform inspired by previous work [1] to monitor the thermal aging (85°C) of unencapsulated spray-coated perovskite solar cells ($glass/ITO/NiO/CsFAPbI_3/C_{60}/BCP/Ag$) in an inert atmosphere. The importance of studying full cell structures that include all charge transport and electrode layers, together with the constraint on both sides of the cell are included. Our primary goal is to identify the device structures and processing parameters of scalable deposition methods such as spray-coating that minimize photovoltaic devices degradation under thermal stress. This work includes the design of the system and the development of an automated Python image processing algorithm. During aging of devices at 85°C, the RGB and LAB (lightness, red-green and yellow-blue scales respectively) color space values were extracted and averaged over the device active area. This analysis was applied to time series of images acquired during thermal aging to determine the evolution of RGB and LAB values over time.

Upon aging, we observed an overall device lightening and yellowing in certain areas with rates quantified by the respective increase of the L and B mean values. X-Ray diffraction (XRD) confirmed that the yellowing was linked to an increased quantity of lead iodide (PbI_2) or of the non-photoactive $FAPbI_3$ tetragonal (yellow) phase. The monitoring of the L and B distributions over each active area also informed us of the spatial homogeneity of the degradation process. We distinguished homogeneous degradation and defect-induced degradation using the distribution skewness values. We compared the color evolution of devices fabricated using different plasma curing parameters (height, duty cycle), as well as the effect of including additional barrier layers (e.g. phenylammonium iodide) in the device structure. Finally, we demonstrated the scalability of our imaging method through the thermal aging of perovskite mini-modules. This work provides a high throughput optical imaging platform to quantify the effect of thermal stress on perovskite photovoltaics. The resulting high-fidelity visual data set provides insights on perovskite degradation mechanisms with high temporal and spatial resolutions.

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5:00 PM EL02.14.15
Multi-Objective Optimization of Open-Air Spray-Plasma Processed Perovskite Solar Cells Austin Flick[1], Mathilde Fievez[1], Thomas W. Colburn[1], Qiaohao Liang[2], Alexander E. Siemenn[2], Tonio Buonassisi[2] and Reinhold H. Dauskardt[1]; [1]Stanford University, United States; [2]Massachusetts Institute of Technology, Afghanistan

Rapid spray plasma processing (RSPP) has been demonstrated as a successful method to deposit and rapidly cure homogeneous metal halide perovskite thin films over large areas in open-air conditions.[1] An ultrasonic spray coater accompanied by an atmospheric pressure nitrogen blown-arc discharge plasma dynamically moves over the substrate to rapidly form a compact perovskite film in under a second. One of the key challenges towards optimizing the processing space of the RSPP system is the high-dimensional processing space and the complex relationships between input variables (coating and curing distances, speed, etc.) and output film morphology and optoelectronic properties. Furthermore, developing a pathway for commercialization of perovskite technologies using the RSPP system requires a multi-objective approach to achieve both high power conversion efficiency and long-term stability.

In previous work, a sequential learning framework using Bayesian optimization was adopted to evaluate the initial performance of RSPP perovskite films in a p-i-n photovoltaic device architecture (glass/ITO/NiO/$CsFAPbI_3$/C_{60}/BCP/Ag). This optimization study focused on six individual processing parameters: substrate temperature, linear process speed, spray flow rate, plasma gas flow rate, plasma height, and plasma duty cycle.[2] Probabilistic knowledge constraints built from prior knowledge with the RSPP system informed a regression-based model to refine the high-dimensional processing space towards an optimal regime; however, this initial optimization lacked the complementary stability characterization for a multi-objective approach.

In this work, we advanced the multi-objective optimization through a complementary evaluation of the long-term stability of the previously explored six-dimensional processing space. Over 400 unencapsulated RSPP perovskite devices spanning a broad range of initial power conversion efficiencies were aged for over 400 days in inert atmospheric conditions and evaluated for their performance retention. Within the previously refined processing space, optimal device stabilities were found to retain >90% initial power conversion efficiency, up to 100% performance retention in devices with initial efficiencies of >15%. Furthermore, continued exploration within the refined processing space, incorporating optimization studies of previously fixed processing parameters, enabled further increases in device efficiency >19%. The long-term stability and elevated performances of the RSPP perovskite devices demonstrate a strong foundation towards developing a pathway for commercialization of RSPP perovskite technologies.

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5:00 PM EL02.14.16
Structural and Size Effects on $CsPbI_3$ Nanocrystals Luminescence—A Temperature and Pressure Dependent Study Giulia Folpini[1], Olivera Vukovic[1,2,3], E Laine Wong[1], Luca Leoncino[4], Giancarlo Terraneo[5], Annamaria Petrozza[1,6] and Daniele Cortecchia[1,7]; [1]CNST@IIT, Italy; [2]Eindhoven University of Technology, Netherlands; [3]Université de Pau et Pays Adour, France; [4]Istituto Italiano di Tecnologia, Italy; [5]Politecnico di Milano, Italy; [6]King Saud University, Saudi Arabia; [7]Università di Bologna, Italy

Metal halide perovskite nanocrystals (NCs) are promising for photovoltaic and light emitting applications thanks to the tunability of their optoelectronic properties and high photoluminescence quantum yield [1,2]. NCs’ size plays a critical role not only by affecting the optical and electronic characteristics through quantum confinement, but also by changing the surface-to-volume ratio and consequently the structural properties[3]. The soft nature of the metal halide lattice can result in a wide range of structural distortions and defects that also impact the material optoelectronic properties [4], [5], particularly for $CsPbI_3$ where the perovskite g-phase is only stable at room temperature due to the strain induced by the small NC size. Therefore, accurate size-dependent study of perovskite NCs is required to single-out the complex contribution of particle size, quantum confinement, structural distortions, defect losses and phonon scattering, retrieving fundamental structure-property relationships that allow a more precise material’s design.
The size-dependent investigation of perovskite NCs optical and structural properties are limited by the poor size selectivity of the standard hot injection synthesis [3]. We employ the hot injection synthetic method and adapt a size-selective precipitation strategy [6] to controllably isolate $CsPbI_3$ NCs with sizes ranging between the strong and weak quantum confinement regime (7-17 nm), and combine photoluminescence (PL) spectroscopy and X-Ray diffraction (XRD) characterization to elucidate their size-dependent structural and photophysical properties under different thermodynamic conditions controlled by temperature and pressure.
Using temperature dependent PL measurements, we identify the role of exciton-phonon coupling and surface defect passivation by the organic ligands: we find that the level of surface coverage not only directly affects the availability of nonradiative loss channels but also the NPs luminescence through more subtle phonon coupling effects, stressing the need for the careful consideration of the chosen ligands. Pressure on the other hand is an ideal post-synthesis method to investigate the structure-properties relationship by adjusting interatomic distances, lattice deformation and band to band electronic overlap, controlling these parameters independently from NC size [7]. We perform pressure dependent PL and XRD measurements up to 2.5 GPa, observing changes in recombination dynamics and PL quenching at high pressures, as well as a size dependent solid-solid phase transition from the γ-phase to the non-perovskite δ-phase. The relationship between size dependent pressure effect and PL quenching further demonstrate that the lattice deformation

mechanism strongly affects the material's bandgap and recombination dynamics, stressing the importance of the structural engineering of these class of soft semiconductors. By highlighting the key role of particles' size, our findings shine light on a fundamental relationship between structural and optoelectronic properties of CsPbI$_3$ NCs that can likely be applicable to a wide range of perovskite systems.

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5:00 PM EL02.14.17
Investigating the Formation Dynamics of Mixed 2D/3D Perovskite Films via Multimodal *In Situ* Analysis Meredith Goudreau[1], Mahdi Malekshahi Byranvand[2], Tim Kodalle[1], Michael Saliba[2] and Carolin M. Sutter-Fella[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of Stuttgart, Germany

Within the current landscape of solar energy materials, hybrid metal halide perovskite thin films have rapidly emerged as an extremely interesting photovoltaic technology due to their continually improving power conversion efficiencies and ease of fabrication [1]. However, instability under conditions of thermal stress or high humidity still remains a significant obstacle to the production of optimized, high-quality hybrid perovskite solar cell devices [2]. The deposition of bulky, organic cations onto the 3D perovskite layer during or after thin film synthesis generating 2D perovskites has recently emerged as a potential solution for this lack of stability [3]. As the method of incorporating these bulky molecules into the 3D hybrid perovskite film has yet to be optimized [4], and considering the known impact that varying properties of these bulky cations and their counterions have on the formation of the 2D layer [3], it is thus of significant interest to gain mechanistic insights into the formation dynamics and the influence of the concentration of the bulky molecules used on these mixed 2D/3D perovskite thin films.
In this study, in-situ transmission, photoluminescence (PL), and grazing incidence wide angle X-ray scattering (GIWAXS) measurements were employed during spin-coating and annealing of the perovskite films to investigate the evolution of the optical and structural properties.The deposition of the 2D material was combined with the antisolvent (AS) drop in lieu of the typical two-step process in which the 3D perovskite layer is completed prior to deposition of the 2D material to reduce both the processing time and the complexity of the deposition process. By varying the concentration of phenethylammonium chloride (PEACl) being deposited during the AS-step we find that the 2D-treated samples exhibit slower and smoother formation dynamics across all growth stages with nucleation and growth rates inversely proportional to the PEACl concentration. For concentrations higher than 1.5 mg/ml, we see a slight shift in the diffraction peaks of the precursor-solvent phase towards larger q-values, indicating that the intermediate solvate-phase has smaller lattice parameters than in the reference case. In the PEACl-treated samples, the PbI2-related diffraction peak temporarily disappears upon attainment of the maximum annealing temperature, and diffraction peaks corresponding to the n=1 and n=2 phases of the layered 2D-structures emerge. The duration of interruption of the PbI$_2$ signal is longer with increasing PEACl concentration, which we propose derives from consumption of excess PbI2 via reaction with PEACl during formation of the n=1 2D-layer. In addition, the GIWAXS images acquired for the 2D-treated samples indicate strongly pronounced crystal orientation, demonstrating that the simplified combined antisolvent and PEACl drop promotes the formation of 2D-structures. Our results demonstrate the utility of in-situ techniques for obtaining a detailed mechanistic understanding of the 2D layer formation and its subsequent interaction with the 3D triple cation perovskite.
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5:00 PM EL02.14.20
Chloride Gradient Renders Carrier Extraction of Hole Transport Layer for High *Voc* and Efficient Inverted Organometal Halide Perovskite Solar Cell Kai-Chi Hsiao[1], Ting-Han Lin[1], Wei-Fang Su[2,3] and Ming-Chung Wu[1]; [1]Chang Gung University, Taiwan; [2]Ming Chi University of Technology, Taiwan; [3]National Taiwan University, Taiwan

A carrier transport layer and its interfacial effects on an organometal halide perovskite light harvesting layer play an influential factor in either photovoltaic performance or long-term stability of a perovskite solar cell (OHPSC). Although the understandings of the carrier transport layers and interfacial effects on regular structured OHPSCs have been explored, knowledge of an interface between hole transport layer of NiO$_x$ and perovskite in an inverted OHPSC is still necessary to be developed. Here, we performed a universal NiO$_x$ film with the sequential passivation strategy of NiCl$_2$ (SPS-NiCl$_2$ treatment) for either wide bandgap or narrow bandgap of OHPSCs. The SPS-NiCl$_2$ treated NiO$_x$ film not only implements the passivation at the perovskite layer/NiO$_x$ film interface but also confers itself a gradient energy level of valance band inducing by chloride. Comprehensive characterizations reveal that the SPS-NiCl$_2$ treated NiO$_x$ film suppresses non-radiative recombination at the interface and enlarges the splitting of the quasi-Fermi level at the interfaces. The photoconversion efficiency (PCE) of the champion device comprised of the SPS-NiCl$_2$ treated NiO$_x$ film can achieve 19.53% with a record *Voc* of 1.16 V, the lowest *Voc* deficit of 390 mV in NiO$_x$ based inverted OHPSCs. The corresponding devices with encapsulation also exhibit superior long-term stability, and over 80% of initial PCE can be maintained after 1500 h damp-heat test. This study sheds the light on managing the interfacial issues of an inverted OHPSC and offers a feasible path to develop a universal hole transport layer for perovskite layers with different energy bandgap.

5:00 PM EL02.14.21
Realize the Counterbalance between Sustainability and Photovoltaic Performance of Organometal Halide Perovskite Solar Cell Jia-Mao Chang, Kai-Chi Hsiao, Shun-Hsiang Chan, Kun-Mu Lee and Ming-Chung Wu; Chang Gung University, Taiwan

The containing toxic Pb in perovskite solar cells may obstacle the pace of its further progress. Based on appropriated ionic radius and stable valence electron, barium is the most suitable alkaline earth element for lead substitution in perovskite material. To enhance the tolerance of lead substitution in perovskite material, a bulky cation of phenylethylammonium (PEA$^+$) was induced into the perovskite to serve as A-site cation. The bulky size and dipolar intrinsic properties render it to simultaneously induce a quasi 2D/3D structure ($n>40$) and to passivated the ionic defects in such perovskite material. Herein, we induced PEA$^+$ into perovskite to enlarge the limitation of barium substituted ratio. In addition, the optoelectronic properties and morphology were also improved as 1 mol.% of PEA adopted into the lead reduced perovskite. Taking these advantage, the ratio of barium substitution in dual cation perovskite system can reach to 10 at.% and the corresponding photovoltaic performance can attain 19.1% in a n-i-p configuration. These results shed the light on how to delineate a framework for lead reduction in organometal halide perovskite solar cell and guide a direction for counterbalancing sustainability and photovoltaic performance of perovskite solar cells.

5:00 PM EL02.14.22

Isoelectronic Cations: A Toolset to Study Hydrogen-Halide Interactions in Lead Halide Perovskite Excluding Other Variables Yunping Huang[1,2] and Christine Luscombe[3,2]; [1]University of Colorado Boulder, United States; [2]University of Washington, United States; [3]Okinawa Institute of Science and Technology, Japan

Cations in lead halide perovskite (LHP), though at first considered to merely charge balance the PbX_6 octahedra, have been revealed to have significant impacts on device efficiency and stability. Cs ion, methylammonium, and formamidinium are the common cations in LHP materials. These cations have different sizes and varied numbers of hydrogen atoms interacting with the surrounding PbX_6 octahedra, and so far there are no experimental studies that investigate how LHP properties in correlate with hydrogen-halide interaction independently. To bridge this knowledge gap and provide more fundamental understanding of LHP materials, we designed two ligands based on guanidinium ($C(NH_2)_3^+$) and uronium ($C(NH_2)(OH)^+$), and studied their differences in efficacy and mechanism in LHP thin-film passivation. Guanidinium and uronium are a pair of isoelectronic cations and therefore of nearly identical sizes, while guanidinium has one more hydrogen atom interacting with the PbX_6 octahedra. In addition, these two ligands share the same counter ion (methanesulfonic group) and the same alkyl chain attached to cations ($-C_{12}H_{25}$). These deliberate designs allowed us to exclusively investigate the effects of hydrogen-halide interaction in LHP without other inferences.

After passivating wide-bandgap LHP films ($(Cs_{0.17},FA_{0.83})Pb(I_{0.75}Br_{0.25})_3$) with the alkylated guanidinium ligand (GA), we observed a 12-time increase in photoluminescence (PL) intensity along with the PL lifetime improved from 134 ns to 337 ns compared to the untreated film. On the other hand, the passivation efficacy of the alkylated uronium ligand (UA) is less pronounced, with a 5-time enhancement in the PL intensity and a slight improvement of the PL lifetime (134 ns to 176 ns). In solar cell devices, the GA increased fill factors of the solar cells from 72.37 % to ~80 % and power conversion efficiency from 15.48 % to 17.71% compared to the untreated devices, while the UA passivated devices showed little improvement. These drastically different results indicate that guanidinium and uronium adopt different mechanisms in LHP thin-film passivation despite their nearly identical sizes.

X-ray diffraction and atomic force microscopy suggested a formation of a crystalline guanidinium-rich 3D perovskite phase at the original grain boundary after GA treatment, supported by the (110) diffraction peak shifting to lower angles and an increase in Young's modulus in the GA-treated film. Compared to the original amorphous phase at the grain boundary, the newly formed crystalline phase significantly reduces surface trap density and facilitates charge extraction, leading to a boost in fill factors. On the other hand, the lower passivation efficacy of the UA suggested UA passivates LHP thin films via filling cation vacancies at the amorphous grain boundary. In addition, we observed a slightly reduced open circuit voltage in the GA-treated device, indicating a reduced bandgap of the guanidinium-rich phase, which is consistent with previous theoretical simulations that show hydrogen-halide interactions reduce LHP bandgaps through enhancing spin-orbit interaction and modulating octahedral tilting. The interaction between hydrogen and the PbX_6 octahedral was further confirmed by nuclear magnetic resonance, as we observed all hydrogen signals from guanidinium broaden after filling in the cation sites in the LHP lattice.

In conclusion, by using a pair of isoelectronic organic cations, we excluded other variables to exclusively study how the hydrogen-halide interactions between cations and PbX_6 octahedra affect the surface passivation and the optoelectronic properties of LHP materials, meanwhile providing a novel approach for LHP passivation via surface recrystallization. This project also underlines the value of in-depth interdisciplinary collaborations between the organic and inorganic communities in unfolding the fundamental aspects of LHP materials.

5:00 PM EL02.14.23

Deposition of Conformal Perovskite Films on 100cm^2 Textured Silicon Surface Using Sequential Dry Process Jae-Keun Hwang[1], Sang-Won Lee[2,1], Wonkyu Lee[1], Solhee Lee[1], Seok-Hyun Jeong[1], Sujin Cho[1], Donghwan Kim[1], Yoonmook Kang[1] and Hae-Seok Lee[1]; [1]Korea University, Korea (the Republic of); [2]Stanford University, United States

Perovskite solar cells are currently recording an efficiency of 25.7%, achieving an efficiency close to that of silicon solar cells. Recently, in order to overcome the theoretical limit efficiency of single-junction solar cells, research on tandem solar cells has attracted great interest, especially silicon/perovskite tandem solar cells have reported an efficiency of over 30%. In order to fabricate high-PCE silicon/perovskite tandem solar cells, it is important to maintain the pyramid shape of the textured silicon surface for maximizing the current density. However, it is difficult to deposit conformal perovskite film along a pyramid shape of ~μm on a textured silicon surface through a conventional solution process. Therefore, the dry process is necessary for the fabrication of high-efficiency silicon/perovskite tandem solar cells.
In this study, a uniform perovskite film was conformally deposited on a 100 cm^2 textured silicon surface using two-step sequential sputtering and chemical vapor deposition processes. In addition, a perovskite solar cell with a glass/FTO/TiO_2/$MAPbI_3$/spiro-MeOTAD/Au structure was fabricated to analyze the device characteristics.

5:00 PM EL02.14.24

Sputtered Nickel Nitride on p-NiO_x Stabilizes Halide Perovskite, p-i-n Solar Cells Anat Itzhak[1], Xu He[2], Adi Kama[1], Sujit Kumar[1,3], Michal Ejgenberg[1], Antoine Kahn[2] and David Cahen[1,3]; [1]Bar Ilan University, Israel; [2]Princeton University, United States; [3]Weizmann Institute of Science, Israel

Stability is one of the significant barriers to commercialize halide perovskite, HaP, devices. Interfaces between inorganic selective contacts, preferred in terms of stability, and HaPs are one of the greatest challenges for making stable and reproducible devices. Nickel oxide (NiO_x) is an attractive hole-transport layer as it fits the electronic structure of HaPs, is highly durable, and can be produced at low cost. We demonstrate RF sputtering of NiO_x as a hole transport layer, followed by *in situ* deposition of an ultra-thin nickel nitride (Ni_yN) passivation layer. The Ni_yN coating protects Ni^{3+} (in the oxide) from being reduced to Ni^{2+} during Ar plasma cleaning, thus maintaining NiO_x conductivity.
Additionally, the Ni_yN forms a buffer layer that passivates the interface between NiO_x and the HaPs, protecting the HaP from the reactive Ni^{+3} species. This double effect improves the perovskite solar cell efficiency from an average of 16.5% (with 17.4% record) to 19% average (with 19.8% record) and increases the device stability, as shown by measurements over several days. We conclude that RF sputtering to deposit inorganic passivation layers is an innovative and viable step towards a scalable process of stable HaP-based solar cells.

5:00 PM EL02.14.25

Insights From the Perovskite Database Project. What we Can Learn From Data Collected From 45000 Perovskite Solar Cells Reported in the Literature T. Jesper Jacobsson; Nankai University, China

The recent development of halide perovskite solar cells has been impressive, both in terms of increased performance and in the number of published papers. The sheer number of papers does, however, make it increasingly difficult to get a good overview of the field. It is also difficult to truly take advantage of all device data generated when it is inconsistently formatted and scattered over thousands of papers. We therefore initiated the Perovskite

Database Project, which is an open-source communal bottom-up effort to gather all generated perovskite device data in one place, provide consistent formatting, and make it adhere to the FAIR data principles. So far, we have collected device data for around 45000 photovoltaic devices with up to 100 parameters per device. In this talk I will introduce the Perovskite Database Project and give examples of insights gained from analyzing the present dataset. Specific examples will include a quantitative discussion about a discrepancy between short circuit currents extracted from JV and EQE measurements, and a reflection about herd behavior in experimental design. I will also discuss what we can expect from the future in terms of follow up studies, challenges, opportunities, and how we can continue to make as good use as possible of our collective research efforts.

5:00 PM EL02.14.26
Exploring the Origin of Degradation at the NiO-Perovskite Interface and its Impact on Perovskite Solar Cells Hye Ri Jung, Hanseul Lee, Namhee Kwon, Soohyung Park and Gee Yeong Kim; Korea Institute of Science and Technology, Korea (the Republic of)

Nickel oxide (NiO_x) has been widely used as a hole transport layer in inverted perovskites solar cells owing to its high-mobility, low cost, and superior stability. Unfortunately, NiO_x tends to form unpleasant reactants in contact with perovskite depending on the valency of nickel ion. Reactants formed by de-protonizing with cationic ammonium and oxidizing iodide species act as hole extraction barriers in the NiO_x-perovskite interface [1]. These reactants lower the V_{OC} and promote device degradation, especially when operating the device. In previous studies, various insertion layers have been proposed to alleviate the interfacial reaction at the NiOx-perovskite. However, the origin of the reaction process depending on the surface state of NiO_x and its effect on perovskite solar cell's stability has not been fully understood. Therefore, in this study, we fabricated perovskite solar cells and investigated the reaction process and decomposition mechanism with different surface states of NiO_x (one is for nanoparticle NiO layer the other one is for sputtered NiO_x thin-film). The origin of this reactant is identified through *in-operando* XPS, TEM and electrical measurements. From *in-operando* XPS, we observed compositional changes and carrier transport in NiO_x-perovskite by applying an external voltage to elucidate charge transfer and decomposition mechanisms in real-time device operation. The result shows that two different types of NiO_x displayed a significant difference in the Ni^{3+}/Ni^{2+} ratio, which in turn affects the stability of the device. The decomposition is induced by the reactants in NiO_x-perovskite and the insertion layer retards the decomposition of perovskite solar cell. We also measured the formation of reactants and the morphology variation of the NiO_x-perovskite interface through TEM over time. As a result, our experiment suggests that the proper insertion layer can control interface degradation and improve hole extraction, thereby efficiently promoting charge separation and suppressing recombination. These results provide insight into the origin of degradation at the NiO_x-Perovskite interface.

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5:00 PM EL02.14.27
Ionic Effects on Space Charge Formation at Halide Perovskite Interfaces with Contact Materials Mina Jung, Davide Moia and Joachim Maier; Max-Planck-Institute, Germany

Understanding interfacial effects, such as charge recombination and injection, is a crucial issue to improve the photo conversion efficiency of hybrid perovskite solar cells (PSC) [1,2]. The space charge equilibrium at the interface between hybrid perovskites and contact layers is commonly interpreted according to electronic equilibration only. However, it has been shown that halide perovskites are mixed ionic-electronic conductors and that ionic adsorption at their interface with oxides can have a critical role in the determination of the space charge situation[3]. The resulting ionically-induced charge carrier redistribution may have significant repercussions on device behavior. Therefore, it is important to understand whether such ionic effects are relevant to interfaces involving other materials that are commonly used in high-performance solar cell applications, and how they can be controlled.
In this study, we discuss experimental investigation of ionic effects at the interface between $CH_3NH_3PbI_3$ (MAPI) and a number of insulating, electron or hole transporting oxide materials. We use zeta potential measurements to establish the expected ionic interaction on the surface of oxide particles. We then perform electrical measurements to quantify the ionic and electronic conductivities of composite films, where nanoparticles of the oxide material are embedded in MAPI, as well as of structures where a mesoporous oxide film is infiltrated with MAPI. We study the iodine partial pressure dependence of ionic and electronic conductivities in these films, allowing us to extract the sign of the space charge potential in MAPI when in contact with the oxide phase. Secondly, we demonstrate that molecular functionalization can successfully modify the space charge behavior at the oxide-MAPI interface in both composite and mesoporous films.
With this study, we aim to provide a complete model including both ionic and electronic effects to describe the equilibrium space charge situation at the interface between halide perovskites and contact materials. Our results will help the design of photovoltaic architectures and the interpretation of experimental data accounting for the mixed conducting properties of halide perovskites.

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5:00 PM EL02.14.28
Regulated Lattice Structure of Quasi-2D/3D Tin-Perovskite Absorbers by Fluorinated Phenethylammonium Cation for Stabilized Lead-Free Perovskite Solar Cells Donghan Kim and Jae Woong Jung; Kyung Hee University, Korea (the Republic of)

Lead-free perovskite solar cell is a promising next-generation eco-friendly photovoltaic technology. Particularly, much effort has been devoted in tin-based perovskite solar cells due to idealtical outer electric and ionic radius configuration of Sn^{2+} to Pb^{2+} cation. However, there remains a detrimental oxidation issue of Sn^{2+} to Sn^{4+} causing accelerated self-doping within the interface or grain boundaries of the perovskite absorber layer in ambient conditions. In this work, a fluorinated phenethylammonium iodide (4FPEA) was introduced in a typical quasi-2D/3D tin-perovskite absorber layer to enforce strong hydrogen bonding in the octahedral lattice, which can effectively passivate the defective antisites and retain enhanced oxidation resistance of the perovskite absorber layer. As a result, 4FPEA could contribute to enhancing the oxidation stability of tin-perovskite absorbers and resulting perovskite solar cells. The optimized 4FPEA-based tin-perovskite solar cells achieve promising photovoltaic performance of >4% PCE as the trap state density within defective grain boundaries were successfully passivated. Moreover, the optimized concentration of 4FPEA demonstrated antioxidation properties that were being worked over 1,000 hours under the atmospheric condition of 25 °C and RH 17%.

5:00 PM EL02.14.31
Tailoring the Grain Boundaries Grooves for High-Performance Perovskite Solar Cells Mingwei Hao and Yuanyuan Zhou; Hong Kong Baptist University, Hong Kong

Grain-boundary groove (GBG) is an inherent microstructural feature of grain boundaries in metal halide perovskites, which has not been quantitatively studied. In this work, we leveraged high-resolution characterization methods to qualify the characteristic GBG angles and revealed their impact on properties of perovskite heterointerface and performance of PSC devices. We showed that flattening GBGs can lead to significantly enhanced optoelectronic properties, chemical stability, and most importantly opto-mechanical reliability of perovskite heterointerfaces. Highly efficient and stable perovskite solar cells are thus fabricated via the GBG optimization.

5:00 PM EL02.14.33
Deuteration Improved Stable and Efficient Perovskite Solar Cells Yu Gao[1], Xin Hong[2], Man-Chung Tang[2] and Guodan Wei[1]; [1]Tsinghua-Berkeley Shenzhen Institute, China; [2]Tsinghua University, China

Traditional solution-processed perovskites often suffer from defects-induced nonradiative recombination, which has severely hindered the improvement of device performance, especially the fill factor (*FF*). Herein, we have successfully applied a deuterated precursor as a facile additive not only to improve the perovskite multigrain size with high crystalline order, but also passivate the surface defects. Time of Flight Secondary Ion Mass Spectrometry shows that this deuteration has successfully induced an intermediate to the $CsFAPbI_3$ crystal and exhibiting an increase in grain size and in phase crystallinity. Suppressed iodide ion migration was observed in the deuterium additive-treated devices after aging tests, indicating improved structural stability of perovskite crystals. As a result, these translation into a high fill factor of 83.85% and a power conversion efficiency of 23.45% based on an inverted planar heterojunction device. Also, the devices operate for over 1,000 h at the maximum power point under simulated AM 1.5 illumination, possess a better light soaking stability.

5:00 PM EL02.14.34
Effect of Electrical Bias in the Dark on the Flexible Perovskite Modules Jiyeon Nam, Wonkyu Lee, Hae-Seok Lee, Donghwan Kim and Yoonmook Kang; Korea University, Korea (the Republic of)

In this study, the electrical bias stability of the perovskite flexible module was conducted in the dark state. In general, the solar cell is maintained in the MPP state, but when the module is disconnected during illumination, a voltage close to Voc is applied. Electrical bias causes module degradation by ion migration, charge carrier accumulation, and trap generation, so it is necessary to study the electrical bias stability when the perovskite module is operating and disconnected. The perovskite module was fabricated on a PEN/ITO flexible substrate. The structure of this module is a standard n-i-p structure and uses SnO2 as the ETL material and Spiro-OMeTAD as the HTL material. Au was deposited as the top electrode and all patterns were scribed using a laser and connected monolithically. The cell width is about 0.5cm wide with 5*5cm2. Module A was biased with voltage at the maximum power point(MPP) under 1sun and Vmpp was applied to module B in the dark.
The initial efficiency of module A was 12.82% (Voc: 9.89V, Jsc 2.04mA/cm2, FF: 63.58%) Maximum Power Point (MPP) is tracked in ambient air. The temperature was maintained at approximately 33°C and the humidity was kept below 40%. Modules encapsulated with a diffusion barrier were placed under 1 sun. After 3h MPPT, the efficiency decreased to about 75% of the initial efficiency. The biggest cause of the decrease in efficiency is the decrease in Jsc, which is most likely caused by the decomposition of the perovskite layer, which is a light absorption layer, at a specific location. When the perovskite layer decomposes, Jsc appears to decrease because light absorption and carrier generation decrease. The distribution of elements in the module along the depth direction was measured through SIMS analysis. Measurements were performed on fresh, 25-hour working modules. The intensity of Au near the pattern was higher than that of the neat area. This shows that Au diffused from P2 and the top electrode. In addition, the I2 peak broadened as a result of perovskite decomposition. We obtained electro-luminescence (EL) images before and after MPPT and the intensity of EL decreased around the P2 pattern. Non-radiative recombination sites can be distinguished from EL images in which the perovskite layer disintegrates after ion migration has occurred. Series resistance increased significantly due to the increase of non-conductive materials such as PbI2, which is a by-product of perovskite layer decomposition. Also, the shunt resistance decreased slightly, showing a similar trend to LIT (Lock-in Thermography) results. A thermal imaging camera attached to the LIT system detects Joule heating in the shunt. The number and temperature of hot spots increased.
In the case of module B, the initial efficiency was 14.11% (Voc: 10.43V, Jsc: 2.24mA/cm2, FF: 60.44%). Vmp was applied in the dark state. The temperature was maintained at 24.9°C and the humidity was kept below 50%. Modules are encapsulated in the same way as module A. After 16 hours of application, the efficiency decreased to 11.73(Voc: 9.97V, Jsc 2.17mA/cm2, FF: 54.11%). The biggest change is the reduction of Voc and FF. When a voltage is applied in the absence of light, ions are expected to move along the direction of the electric field, creating non-radiative recombination centers. The result is a decrease in Voc due to recombination. However, ions migrate in the opposite direction when the electric field disappears. When the recovery characteristics were measured again 3 days after the end of the voltage application of the module, the efficiency was 15.23% (Voc: 10.72V, Jsc: 2.23mA/cm2, FF: 63.84%), similar to before voltage application. In the perovskite module, electric bias causes ion migration, creating non-radiative recombination centers, resulting in Voc losses, and light causes decomposition, resulting in Jsc losses.

5:00 PM EL02.14.35
Fully Dry-Processed and Powder-Based Halide Perovskite Solar Cells by Powder-Aerosol-Deposition and Hot-Pressing Christina Witt, Konstantin Schötz, Simon Biberger, Nico Leupold, Meike Kuhn, Philipp Ramming, Eva M Herzig, Ralf Moos, Anna Kohler and Fabian Panzer; University of Bayreuth, Germany

The lifetime and stability of halide perovskite solar cells is well known to be reduced by high internal strain, which correlates with a high degree of energetic disorder. Here, we present a novel method to prepare perovskite solar cells with a low level of internal strain and disorder using a fully dry processing approach suitable for upscaling.
For this, we first prepared perovskite powder with remarkable stability by dry mechanochemical synthesis. Subsequently, this powder is deposited by a dry powder-aerosol-deposition method and pressed at elevated temperatures. This hot-pressing approach increases the grain size and reduces the disorder and strain in the films. Strain and disorder are analyzed using XRD as well as detailed Urbach analyses of temperature dependent photoluminescence and absorption spectra. These detailed Urbach analyses enable us to accurately determine even low static disorder values. We find values as low as 3.7 meV for the dry-processed, pressed films. Moreover, hot-pressing improves the surface roughness and compactness of the films to such an extent that their integration into a solar cell configuration becomes feasible. We demonstrate fully working dry-processed powder-based perovskite solar cells - the first of their kind.
The solvent-free approach allows to separately optimize the synthesis of the material, and the processing of the film. This contrasts with the currently used approaches where the perovskite forms only as the film is formed. Our results thus pave the way for a novel fabrication method of thin-film perovskite solar cells that is suitable for upscaling and that has strong potential to advance the stability of perovskite-based devices.

5:00 PM EL02.14.36
Bulk and Micro-Photoluminescence Studies of Perovskites Stuart Thomson and Matthew Berry; Edinburgh Instruments Ltd., United Kingdom

Perovskite based solar cells are the subject of intense research interest due to the attractive properties of perovskite; high carrier mobilities, large absorption coefficients, tuneable bandgaps, and long carrier diffusion lengths. One of the challenges in any solar cell design is how to get the charge carriers efficiently out of the device. To aid charge extraction, electron and hole extraction layers are routinely incorporated into the device stack.

One promising material being investigated as a hole extraction layer are vertically aligned carbon nanotubes (VACNTs). The VACNTs can be grown in a grid pattern of 'towers' atop the ITO electrode in order to achieve improved charge extraction while maintaining high optical transmission through the ITO/VACNTs. Photoluminescence response from perovskite materials is proportional to the number of charge carriers in the layer and therefore sensitive to charge extraction into adjacent layers. This makes photoluminescence based techniques invaluable for investigating the performance of new extraction layers. In this work steady-state and time-resolved confocal photoluminescence microscopy and photoluminescence quantum yield studies were used to quantify hole transfer efficiency into the VACNT towers.

5:00 PM EL02.14.37
Additives Engineering for High-Performance All-Inorganic Cs Based Perovskite Solar Cells Gulzhan Bizhanova, Vladimir Pavlenko, Zhuldyz Yelzhanova, Gaukhar Nigmetova, Damir Aidarkhanov, Hryhorii Parkhomenko, Askhat Jumabekov, Mannix Balanay and Annie Ng; Nazarbayev University, Kazakhstan

The emerging perovskite solar cells (PSCs) have made a breakthrough in the photovoltaic community. To date, the power conversion efficiencies (PCEs) of the single junction PSCs have been increasing from 3.8% in 2009 to the latest record of 25.7%. Despite the impressive PCEs of PSCs, the material instability and short device lifetime are the major obstacles of future commercialization. For conventional organic-inorganic hybrid PSCs, the presence of methylamine ions (MA^+), formamidine ions (FA^+) and other organic components causes poor thermal stability of the perovskite thin films due to the volatile nature of the organic components at 80 – 100 °C. The preparation of all-inorganic perovskites such as $CsPbX_3$ (X = I, Br) can prevent the use of the volatile organic components, which is believed to be the potential solution for enhancing the thermal stability of perovskite thin films. However, the photovoltaic performance of all-inorganic Cs based PSCs is still below the conventional type of organic-inorganic hybrid PSCs. The quality of the all-inorganic perovskite film is one of the important factors in determining the device efficiency and stability. In this work, the ionic liquids (ILs) are used as the additives during the preparation of $CsPbI_2Br$. It is found that the crystallization of $CsPbI_2Br$ and its surface morphology are significantly enhanced by using the controlled amount of ILs. A systematical investigation has been performed on the materials and devices. The experimental results show that incorporation of ILs is an effective method to fabricate high-performance $CsPbI_2Br$ based solar cells.

SESSION EL02.15: Solar Cell
Session Chairs: Maria Antonietta Loi and Nakita Noel
Friday Morning, April 14, 2023
Moscone West, Level 3, Room 3002

8:00 AM *EL02.15.01
Towards Standardization of Accelerated Stress Testing Protocols for Metal-Halide Perovskite Photovoltaic Modules Laura T. Schelhas; National Renewable Energy Laboratory, United States

Metal-Halide Perovskite (MHP) photovoltaic (PV) modules are at the cusp of commercialization. One major hurdle that remains is establishing confidence in long-term field performance and durability of MHP modules. A lot of progress has been made in addressing many performance stability issues in MHP cells and modules; however, in the absence of established protocols for MHPs, many of the studies have been conducted using the International Electrotechnical Commissions 61215-series (IEC61215) of standardized tests. IEC61215 lays down requirements for the design qualification of terrestrial photovoltaic modules suitable for long-term operation in open- air climates and test results are not construed as a quantitative prediction of module lifetime. While some of the testing protocols outlined by IEC61215 are likely to be relevant to MHPs and do provide some insight to potential degradation mechanisms, they should not be used to infer any estimation of durability or field performance without a more rigorous understanding of how those test conditions affect the MHP and whether those conditions are even relevant. In addition, counterpart field-exposure and a thorough analysis of the degradation pathways introduced by external stressors will be needed to validate any accelerated stress testing conditions. Here I will discuss an initial accelerated stress testing protocol that can be used as the foundation for the development of a standardized test procedure for qualification of commercial MHP modules. We apply the protocol to different MHP module architectures to identify the critical degradation pathways that will inform future testing development. In addition, the modules are exposed to outdoor environments such that a cross- examination with indoor results can be used to verify the relevance of the indoor stress conditions. This work is part of the recently established Perovskite PV Accelerator for Commercializing Technologies, PACT, program.

8:30 AM EL02.15.02
Blade Coated Inverted Perovskite Solar Cells and Minimodules with Vacuum Assisted Nucleation Approach He Wang and Xinwen Zhang; University of Miami, United States

Solar cells using metal halide perovskite as the absorber are attracting significant attention due to their high power conversion efficiency, and potential low fabrication cost. A key obstacle to commercialization is represented by the difficulty in fabricating highly efficient and stable large area solar cells. As such, to bridge the gap between laboratories and industry for perovskite solar cells, it is crucial to develop devices in an ambient environment using materials and methods that can be scalable. One of the key steps is to control the nucleation and crystallization of perovskite on a large area. Antisolvent can be used to quickly extract the solvent during the spin coating process for nucleation and crystallization, but it is inherently limited to small areas, making it a poor candidate for large area. In addition, the fast and crucial nucleation process is very sensitive to the time when the antisolvent is added, greatly hampering its reproducibility.

We utilize a vacuum assisted approach to obtain mirror-like, pinhole-free, crystalline and uniform blade-coated perovskite films.[1] The vacuum replaces the antisolvent to quickly remove the solvent to initiate the nucleation process and produce the intermediate phase. We have conclusively proven that this method can be applied to many perovskite compositions. In order to improve thermal stability, MA^+ (methylammonium) is substituted by FA^+ (formamidinium) or a mixture of cations. One difficulty is that FA ink is not straightforward to develop, since $FAPbI_3$ favors the yellow phase at room temperature in air. Our solution involved using solvent N-methyl-2-pyrrolidone (NMP) to replace the conventional co-solvent dimethyl sulfoxide to fabricate perovskite film under ambient environment, since NMP exhibits a stronger interaction with PbI_2 and FAI.

Besides the perovskites layer, hole transport material (HTL) is also of importance for efficient and stable device. Organic HTL poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA) has been the premier choice for the p-i-n device architecture. One drawback is that PTAA is hydrophobic, limiting the choice of solvents for perovskite precursors. Therefore, we choose an inorganic semiconductor NiOx as the HTL in our work. It exhibits high photostability with a hydrophilic surface, and can be easily scalable. On the other hand, NiOx has relatively low open-circuit voltage caused by the surface traps. Based on the physical properties of NiOx, we optimize it by tuning the composition in perovskite precursors to improve the device efficiency. In addition, the passivation effect with phenethylammonium iodide at the top and bottom interfaces of perovskite layer based on p-i-n structure has been studied. The optimized device blade coated under an ambient environment exhibits an efficiency of 20.7%. The encapsulated solar cells exhibit long-term photostability, keeping 96% of the original efficiency after 648 hours under one sun, 45°C, 50%-60% RH.[1] Our work demonstrates a highly scalable process, promising for manufacturing, and we have also applied the blade coating followed by vacuum quenching approach to minimodules.

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8:45 AM EL02.15.04
Stabilization of Formamidinium Rich Halide Perovskites for Highly Efficient and Stable Perovskite Photovoltaics Satyawan D. Nagane; University of Cambridge, United Kingdom

Halide perovskite-based solar cells have achieved record-breaking efficiencies of 25.7% in single junction and 32.5% in tandem configurations [1]. Formamidinium (FA) lead triiodide ($FAPbI_3$)-based single junction solar cells are the most efficient single junction devices to date. However, the conversion of the black-phase $FAPbI_3$ perovskite phase to unwanted non-perovskite phase of $FAPbI_3$ has hindered its widespread acceptance as an absorber for photovoltaic applications. Cation alloying is one of the most efficient routes to stabilize the FA-rich halide perovskite phase. The outstanding example of this is the triple cation, $Cs_{0.05}FA_{0.78}MA_{0.17}Pb(I_{0.83}Br_{0.17})_3$, composition which has delivered highly reproducible photovoltaic devices with improved ambient stability [2]. Even though this composition delivers highly reproducible devices, this approach is non-ideal as it compromises the bandgap and the mixed-cation and mixed-halide nature can lead to spatial compositional heterogeneities [3]. Here I will reveal the role of functional organic molecule in stabilization of corner-sharing photoactive black phase of pure $FAPbI_3$. A functional organic molecule-based approach allows us to stabilize $FAPbI_3$ perovskite phase without the issues associated with cation alloying. By introducing functional organic molecules into the perovskite precursors, we can template black-phase perovskites that are highly stable in a variety of operational conditions even without any other cation alloying [4]. I'll step through the mechanism of this additive-assisted stabilization approach and outline the road map from here on to go towards highly efficient, highly stable $FAPbI_3$ based PV devices.

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3. Lu, H. et al. Vapor-assisted deposition of highly efficient, stable black-phase $FAPbI_3$ perovskite solar cells. Science 370, (2020).
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9:00 AM *EL02.15.03
A Look into a Sustainable Future by Understanding Perovskites Stability Laura Miranda Perez and Severin Habisreutinger; Oxford PV, United Kingdom

Perovskite PV has been at the center of photovoltaic discussions during the last ten years for a variety of reasons. In one hand, it is the major breakthrough on PV in the last decades, it has achieved efficiencies unseen before, without having reached its full potential yet. On the other hand, the technology is questioned based on the intrinsic stability of the material and sustainability factors, as the presence of hazardous elements. Oxford PV has been focused on the integration of perovskite PV in tandem configurations with silicon since 2014, holding the world record in large area at 26.8%. Our results show that it is possible to have a reliable product meeting the industry standards, as well as proving it to be the most sustainable option at hand. The perovskite-on-silicon technology is a technological disruption without a business disruption. In this presentation, I will show the Oxford PV advances on materials, device integration, and product designs that had led to the success of a sustainable and reliable new technology, ready for its market entry.

9:30 AM BREAK

SESSION EL02.16: Device Fabrication III
Session Chairs: Robert Hoye and Wanyi Nie
Friday Morning, April 14, 2023
Moscone West, Level 3, Room 3002

10:00 AM *EL02.16.01
Bi-Functional Inorganic Interlayers via Low-Temperature Atomic Layer Deposition Toward Highly Stable and Efficient Perovskite Solar Cells (>23%) Hyoungmin Park[1], Sooeun Shin[1], Pronoy Nandi[1], Dipayan Pal[1] and Hyunjung Shin[1,2]; [1]Sungkyunkwan University, Korea (the Republic of); [2]SKKU Institute of Energy Science & Technology, Korea (the Republic of)

Power conversion efficiency (PCE) of Perovskite solar cells (PSCs) is over 25.7%. Despite PSCs' high PCEs, their operational as well as environmental instability remains to be solved and restrict PSCs' commercialization. Currently, the state-of-the-art PSC is used almost pure α-$FAPbI_3$ (Formamidinium lead tri-iodide) as an absorber and 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) as hole transporting layer (HTL) in the *n-i-p* normal structure of PSCs. A chemical-deriven phase transition from photoactive α-$FAPbI_3$ to non-photoactive δ-$FAPbI_3$ is pointed as a significant challenge. In addition to phase transition issue, much lower stability of Spiro-OMeTAD is critical for the device performance degradation. As an interlayer in between top metallic electrodes (i.e., Au and/or Ag) and Spiro-OMeTAD/α-$FAPbI_3$, inorganic HTLs prepared by a low-temperature atomic layer deposition (ALD) technique provide bi-functionality to stabilize the PSCs during operation in ambient. Transition metal oxide (TMO) as an inorganic interlayer can be a strong candidate. Most of TMO layers generally require a high processing temperature and the lack of *p*-type characteristics inhibits application to PSCs as hole-transporting interlayers. In this study, we adopt ALD to fabricate TMO layers at low temperatures (~ 50 °C) and intentionally induce oxygen deficient traps to form empty *d*-bands to induce and further enhance hole transporting properties. With their oxygen deficient trap assisted hole transporting properties, we fabricated n-i-p normal structure PSCs of α-$FAPbI_3$ and Spiro-OMeTAD with ALD grown TMOs (amorphous-TiO_2, MoO_x and V_2O_{5-X}) on top of Spiro-OMeTAD to enhance device stability. During fabrication, we adopt funnel like 2D perovskite passivation layers for defect passivation and enhance perovskite's stability coming from hydrophobic characteristics. [1] As a result, highly efficient PSCs of PCE of over 23%

with TMOs are fabricated with pin-hole free hole transporting and protection bi-functional ALD layers. [2,3] The environmental stability of PSCs with ALD-V_2O_{5-x} interlayers is over 90% initial PCE after ~ 600 hrs, while without the interlayer started to be degraded under 80% of initial PCE just after around 200 hrs without any special encapsulation. In conclusion, this study demonstrates the application of TMOs as hole transport/protective bi-functional interlayers and ALD as an optimal deposition method without damaging the underlying perovskite absorber. Furthermore, this study shows the possibility that ALD TMOs can be also applicable to tandem device fabrication with p-i-n type PSCs and stable PSCs' commercialization.

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10:30 AM *EL02.16.02
Refining Perovskite Solution Chemistry—Repurposing Degradation Products for Improved Efficiency and Stability Nakita K. Noel; University of Oxford, United Kingdom

Since the first demonstration of efficient halide perovskite solar cells, there has been sustained and growing research interest in this class of materials. With facile deposition processes and excellent optoelectronic properties, these materials have found applications not only in photovoltaics, but in a myriad of optoelectronic devices. While research into halide perovskites for light emission and X-ray detection is just beginning to surge, perovskites are most well known for their remarkable PV performance, achieving certified power conversion efficiencies approaching 26%. Despite their truly impressive device performance, these materials have not yet reached their true potential. The major obstacle to this is an incomplete understanding of crystallisation processes, as well as defects which exists on surfaces and at interfaces in perovskite thin-films. For solution-processing, arguably the most researched deposition modality, defect control may start with the ability to control precursor ink chemistry. In this talk, I will illustrate how understanding ink chemistry and degradation processes can yield the ability to precisely control crystallisation kinetics and phase transformations; and in particular, how we can use this approach to fabricate halide perovskite films with improved optoelectronic quality, yielding devices with not only enhanced performance, but notable improvements in operational stability.

11:00 AM EL02.16.03
Scalable, One-Step Manufacturing of Robust Perovskite Thin Films in Open-Air with Rheological Modification Nicholas Rolston[1], Carsen Cartledge[1], Muneeza Ahmad[1], Saivineeth Penukula[1], Antonella Giuri[2] and Aurora Rizzo[2]; [1]Arizona State University, United States; [2]CNR Nanotec - Institute of Nanotechnology, Italy

Metal halide perovskites hold the potential for making the next generation of high-efficiency, low-cost solar cells through solution processing of Earth abundant materials. The U.S Department of Energy has identified four major challenges facing PVSKs: stability, scalability, manufacturability, and accelerated test protocols for reliability validation. Typical processing utilizes an antisolvent or gas quenching step.

Unmodified perovskite inks designed for spin coating produce pinholed, uneven, and shunted films when processed in air or with scalable processing methods. Novel polymeric modifiers have recently been used to improve film uniformity and density. These additives not only act as rheological modifiers by increasing ink viscosity, thus allowing longer periods for crystallization and smooth films, but the long chains of the polymer create an organizational scaffold that increases resistance to humidity. Furthermore, additives from the food industry, such as cornstarch, have been found to enhance mechanical integrity and the operational lifetime of devices in addition to inducing spherulitic domains that can be tuned in size by temperature and precursor concentration to increase performance.

In this work, the effects of gellan gum, a nontoxic polymeric modifier from the food industry, are studied on improving PVSK stability using scalable, one-step processing in open air. The use of a nontoxic solvent system further extends the wetting period, thus improving crystallization control. We measure the film stress to be tunable and compressive based on the additive concentration. We find that the additive enables reproducible and scalable perovskite devices to be produced in ambient conditions that match state-of-the-art performance on areas >25 cm^2 with efficiencies exceeding 15%. The devices are stable under both thermal cycling and continuous operation (1000 hours). We attribute the compressive stress in the films along with significantly reduced ion migration based on impedance spectroscopy and transient photocurrent measurements as key reasons for the improved device stability. We validate the effect through aging perovskites with different film stresses and additive concentrations for mechanistic understanding of how film stress influences ion migration and device stability.

11:15 AM EL02.16.04
Iodine Exchange and Spontaneous Self-Doping in Iodide Perovskite Semiconductors Julian A. Vigil[1], Nathan Wolf[1], Adam Slavney[1], Nicholas J. Weadock[2], Michael Toney[2] and Hemamala Karunadasa[1]; [1]Stanford University, United States; [2]University of Colorado Boulder, United States

The successful incorporation of lead-halide perovskites and lead-free halide double perovskites in various optoelectronic devices has spurred remarkable discoveries and innovation in recent years. Research-scale perovskite-based devices boast efficiencies competitive with more established technologies, including as thin-film solar absorbers and light-emitting diodes. However, despite these impressive efficiencies, areal scale-up and long-term stability continue to lag and present outstanding questions. Indeed, many of the recognized limitations are intrinsic to the perovskite crystal, including thermodynamic phase instability, mobile ions, and an abundance of point defects. These characteristics manifest in many ways in devices, including moisture and temperature sensitivity and current-voltage hysteresis, underscoring the necessity for investigations of the perovskite structure and defect chemistry.

Here, we highlight the predominant role of halogen vacancies and present our characterization of spontaneous iodine exchange in iodide double perovskites. This unique type of external defect reaction is mostly appreciated for its role in oxide crystals at high temperature; we show that the analagous exchange between iodine vacancies and gaseous iodine is spontaneous at room temperature and directly influences the electronic charge carrier concentration. We provide evidence that the iodine vacancy is a shallow electron donor, leading to striking *n*-type self-doping effects by manipulating the external pressure of iodine. Furthermore, single-crystal measurements allow for analysis of the thermodynamics of the exchange equilibrium and modeling of the diffusion-limited kinetics associated with transport of vacancies and iodide anions in the bulk crystal. Finally, we introduce complementary *in situ* X-ray diffraction and single-crystal diffuse X-ray scattering studies to correlate defect chemistry with the structural response at various length scales. A broad and critical evaluation of the mixed ionic-electronic conductivity and defect chemistry of the halide perovskites is discussed in the context of this underappreciated external defect equilibrium.

11:30 AM EL02.16.05
Highly Efficient and Stable Perovskite Solar Cells with Exceptional Thermal Cycling Performance Min Chen and Joseph Luther; National

Renewable Energy Laboratory, United States

We have witnessed the rapid development of perovskite solar cells from initially reported 3.8% to the 25.7%. However, the current perovskite solar cells still suffered from the low stability especially in the thermal cycling test. The layered structure of perovskite solar cells will experience continuous mechanical stress/strain during the thermal cycling, resulting in the failure of the photovoltaic performance. Herein, we reported an improved thermal cycling performance by adding the large organic cations molecules during the deposition of perovskite layers. As a result, the stress state of the perovskite thin films could be relieved, and the modified perovskite solar cells dropped to 85% of initial efficiency of 23.5% after 500 cycles. This approach will lead to an new avenue in improving the thermal cycling performance and have great potential in space engineering.

11:45 AM EL02.16.06
Vapor Deposited Wide Bandgap Metal Halide Perovskite Semiconductors for Multijunction Photovoltaics Jay Patel, Siyu Yan, Laura Herz, Nakita K. Noel and Michael Johnston; University of Oxford, United Kingdom

Hybrid perovskites semiconductors provide an opportunity to create highly efficient low-cost, lightweight, photovoltaics that have a high power-to-weight ratio. Physical vapor deposition is the technique that enables the creation of a multilayer heterostructure that contains hybrid perovskites semiconductors, small-molecule organic and metal oxide semiconductors. However, to develop such an intricate architecture that can reach close to the theoretical limit, the metal-halide perovskite semiconductors need to have minimal defects and phase stability. We have shown that by manipulating, the substrate material [1] the temperature [2] and the addition of additives [3] can aid in growing highly crystalline, low defect density perovskite thin films.
In this study, using physical vapor deposition, we develop an all-inorganic 2eV perovskite semiconductor which is phase stable and has minimal voltage losses. We then use X-ray diffraction analysis to show how and why the material is phase stable. We then use this technique to create the phase stable perovskite composition and integrate it into a solar cell.

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SESSION EL02.17: Interface III
Session Chairs: Xuedan Ma and Hsinhan Tsai
Friday Afternoon, April 14, 2023
Moscone West, Level 3, Room 3002

1:30 PM DISCUSSION TIME

1:45 PM EL02.17.03
Monolithic Perovskite-Silicon Tandem Solar Cells for Continuous Solar-Assisted Water Splitting Kunal Datta[1], Bruno Branco[1], Yifeng Zhao[2], Valerio Zardetto[3], Nga Phung[1], Andrea Bracesco[1], Luana Mazzarella[2], Martijn M. Wienk[1], Mariadriana Creatore[1], Olindo Isabella[2] and Rene A. Janssen[1]; [1]Technische Universiteit Eindhoven, Netherlands; [2]Delft University of Technology, Netherlands; [3]TNO-Solliance, Netherlands

Photovoltaic (PV)-driven hydrogen (H_2) evolution through electrochemical (EC) water splitting is an effective method to store energy and compensate for the intermittency of solar irradiation.[1] However, the high cost of present-day concentrated inorganic multijunctions used in such systems undermines their future commercial competitiveness. Solution-processed perovskite-based multijunctions, on the other hand, present cheap, easy-to-process alternatives that can deliver high current without light concentration and, when coupled to a flow EC system, can provide an efficient method for H_2 generation.[2]

This work describes the design and development of 1 cm^2 monolithic perovskite-silicon tandem solar cells that are well-suited for this application. First, compositional engineering strategies (cationic and anionic substitution) are used to tune the optical bandgap of the perovskite layer and to stabilize it against light-induced halide segregation. By introducing bromide to replace iodide in the perovskite lattice, the optical bandgap (E_g) is widened to ~ 1.7 eV, ideal for multijunction applications. Potassium substitution is then used to stabilize the crystal against photo-instability, that can decrease the long-term performance of devices.[3] Thereafter, the polymeric hole transport layer (PTAA) is substituted for a self-assembled monolayer (2PACz), whose favorable energetic alignment with the valence band of the perovskite minimizes energetic losses and increases the open-circuit voltage of devices.[4] Using absolute photoluminescence spectroscopy, the perovskite/C_{60} interface is further found to dominate non-radiative recombination; choline chloride or LiF interfacial layers are used to improve radiative yield and open-circuit voltage.

The perovskite top-cell is then integrated with a silicon heterojunction (SHJ) bottom-cell to build the monolithic tandem device. Here, an interfacial atomic layer deposition-based NiO layer is used to increase the surface hydroxyl content, characterized by X-ray photoelectron spectroscopy, which benefits the binding of the self-assembled hole transport monolayer.[5] As a result, tandem devices with low voltage losses are developed using a perovskite top- and a SHJ bottom-cell.

Optical simulations are then used to optimize the light incoupling and the current-mismatch between subcells. Specifically, the role of anti-reflective coatings (MgF_2) in minimizing reflection losses, and parasitic absorption in interfacial layers (ITO, C_{60}), is explored in order to identify materials and layer thicknesses that maximize absorption in the active layers of the device. Subsequent experimental development based on the optical simulations yield current-matched tandem solar cells with a power conversion efficiency of over 25%; a voltage loss of < 70 mV compared to the sum of the open-circuit voltages of single-junction perovskite and SHJ solar cells emphasizes the lossless recombination junction based on NiO. The efficiency represents > 6% (abs.) gains compared to the efficiencies of both perovskite and SHJ single-junction solar cells.

Lastly, the fabricated tandem solar cell is coupled to a flow EC cell using RuO_2 and Pt for O_2 and H_2 evolution respectively. The polarization curve of the EC cell overlaps with the current density-voltage curve of the PV cell close to the maximum power point indicating minimal additional losses in the coupled PV-EC system during operation. As a result, a stable solar-to-hydrogen (STH) conversion efficiency of > 21% is recorded both in continuous (18 h) and day-night cycling (72 h) operation.

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5. *ACS Appl. Mater. Interfaces* **2022**, *14* (1), 2166–2176.

2:00 PM EL02.17.04

Transparent Conductive Composites—A New Class of Encapsulants for Durable Perovskite Photovoltaics Kai C. Outlaw-Spruell[1], Jackson Xu[1], Qi Jiang[2], Kai Zhu[2] and Nicolas Gaillard[1]; [1]University of Hawaii, United States; [2]National Renewable Energy Laboratory, United States

Since the first report of perovskite solar cells (PSCs) in 2009, tremendous research efforts on absorber chemistry have boosted the power conversion efficiency of this material class from 3.9% to 25.7%. Although impressive, this attribute alone cannot guarantee the commercial success of PSCs, as any emerging technology must also meet the 20-25 yrs. stability already achieved by other mature photovoltaic (PV) classes. To date, the durability of best performing PSCs is limited to few months at best, constituting an important roadblock in their deployment.

In this communication, we report on our efforts with using transparent conductive composites (TCCs) as gas-barrier to repell moisture and oxygen while preventing out-diffusion of volatile species in PSCs. Unlike most conductive flexible polymers, where media are coated on top providing only *in-plane* conductivity, TCCs innovate by allowing simultaneous high optical transparency (%T>90% in the 370nm-2000nm region) and high *out-of-plane* electrical conductivity (R<0.2 W.cm^2). This unique characteristic is permitted by highly conductive 50-micron Ag-coated PMMA spheres protruding out of a transparent non-conductive polymer host.

To demonstrate that TCCs can effectively isolate PSCs from the outside environment while permitting electrical current to pass through, we will first report on an experiment in which PSCs were immersed in a 0.5M sulfuric acid electrolyte solution (pH0.3) and used as photocathodes to drive photoelectrochemical water splitting. Under such harsh conditions, unprotected PSCs discolored within seconds upon immersion and were unable to produce any appreciable photocurrent. In contrast, PSCs coated with TCCs were able to sustain continuous water splitting for over 5 hours at a steady photocurrent density of 20 mA/cm^2. The fact that PSCs protected by TCCs were able to drive an electrochemical reaction for such extended period in highly corrosive aqueous solution is a testament of TCCs' potential to protect PSCs when operating under less strenuous ambient conditions.

To further validate this novel protection concept, we will report on the effect of weathering on TCCs made of various polymer hosts, including polyepoxy, EVA, and polyolyflin. We will present optical transparency and electrical conductivity data measured periodically on TCCs during 1,000+ hrs. exposure to outdoor Hawaii climate (tropical semi-arid climate with average annual temperature, insolation, and relative humidity of 23.5^{o}C, 5.4 kWh/m^2 and 68%, respectively). Finally, we will discuss durability data of high-efficiency PSCs coated with TCCs and measured under accelerated testing conditions (50^{o}C, ambient air with 40-60% RH, 1-sun illumination).

SESSION EL02.18: Virtual Session
Session Chairs: Robert Hoye and Xuedan Ma
Tuesday Morning, April 25, 2023
EL02-virtual

8:00 AM *EL02.18.01

Intrinsically Stable and Versatile Co-Evaporated Halide Perovskites Solar Cells Annalisa Bruno; Energy Research Institute @ Nanyang Technological University (ERI@N),, Singapore

Metal-halide perovskites (MHP) are one of the most promising low-cost optoelectronic materials, due to their excellent optoelectronic properties and fabrication versatility. Since the advent of the first perovskite solar cells (PSCs) in 2009, their power conversion efficiency (PCE) has now reached 25.6% [1], for active areas smaller than 1 cm^2 and their operational stability is constantly improving [2-4]. The interest in transferring the existing technology into large-area perovskite modules using industrial-compatible techniques is exploding.

In this talk, I will show why thermal evaporation is a promising MHP fabrication technique to bring this technology closer to reliable and extended production, relying on excellent size scalability, promising stability, fine composition control, and surface adaptability [5]. The co-evaporated perovskite thin films are uniform over large areas with low surface roughness and a long carrier lifetime. I will present our highly efficient, large-area, PSCs where the $MAPbI_3$ perovskite is deposited by thermal co-evaporation. Developing optimization strategies customized for n.i.p [6-8] and p.i.n [9] architectures the PSCs achieved PCEs above 20% in both configurations and with different perovskites compositions. Moreover, the co-evaporated $MAPbI_3$ is formed intrinsically strain-free, and the PSCs showed remarkable structural robustness and impressive thermal maintaining over ≈80% of their initial PCE after 3600 under continuous thermal aging at 85 °C without encapsulation [8].

Extrapolating the optimization strategies over large areas, the co-evaporated mini-modules achieved record PCEs of up to 18.7% for active areas larger than 10 cm^2. Looking toward building-integrated photovoltaics we have also developed colored semi-transparent PSCs and mini-modules with a wide range of colors.

I will further discuss how these results represent a significant step toward the commercialization of the perovskite technology in comparison with other vacuum-based and hybrid technologies.

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8:30 AM EL02.18.02
Bias-Free Solar to Chemical Conversion using Perovskite Photocathodes Rashmi Mehrotra, Dongrak Oh, Yuri Choi, Sang-Hak Lee, Sung-Yeon Jang, Jungki Ryu and Ji-Wook Jang; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Considering the increasing consequences of climate change, utilizing fuels synthesized by mere use of solar flux, water, and ambient air seems to be advanced option for the simultaneous capture and storage of vast amounts of solar energy at ambient temperature and pressure. Solar hydrogen production is one of ultimate technologies needed to realize a carbon-neutral, sustainable society [1]. However, an energy-intensive water oxidation half-reaction together with the poor performance of conventional inorganic photocatalysts have been big hurdles for practical solar hydrogen production [2]. In first part of work, we present a photoelectrochemical cell with a record high photocurrent density of 19.8 mA cm^{-2} for hydrogen production by utilizing a high-performance organic-inorganic halide perovskite as a panchromatic absorber and lignocellulosic biomass as an alternative source of electrons working at lower potentials. Additionally, the system was able to generate H_2 without applying any additional bias while utilising raw waste itself [3].

To further draw the application of perovskite photoelectrodes, we applied the photocathode to generate bias-free hydrogen peroxide (H_2O_2). It is an eco-friendly oxidant and a promising energy source comparable to H_2. It stands an irrefutable chance due to its wide application for wastewater treatment, the paper industry, and pulp bleaching with numerous in-situ production of other chemicals including propylene. However, currently, more than 95 % of H_2O_2 production relies on the anthraquinone oxidation process [4], which requires a significant energy supply at several steps and numerous organic chemicals. In addition, precious Pd-based catalysts and high-pressure H_2 used during the hydrogenation reaction increase the cost of the process and introduce many safety issues. Therefore, developing single-step oxygen reduction to H_2O_2, with a simple and eco-friendly method can pave a promising route [5]. However, utilising inorganic semiconductors impedes solar-to-chemical conversion efficiency (SCC) lower than 1 % due to several factors including their low absorption coefficient, sluggish kinetics owing to the charge diffusion length, and low stability and selectivity of the H_2O_2 production's electrocatalyst. In second part of work, we utilized an inorganic-organic-based lead halide perovskite photocathode for demonstrating bias-free solar H_2O_2 production without the need for additional bias or sacrificial agents. To further improve the stability and selectivity of this photocathode, we passivated the photocathode with oxidised buckypaper as the H_2O_2 electrocatalyst and the field's metal as an intimate junction for the subsequent transfer of photogenerated electrons towards oxygen reduction reaction. With such an efficient strategy, an SCC of ~1.463 % is attained in such a system, attaining 100 % selectivity toward H_2O_2 for 12 h. Moreover, the integrated photocathode was able to produce a stable photocurrent for 45 h continuously under one-sun simulated conditions [6].

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8:35 AM EL02.18.03
ACI 2D Perovskite Enabled Dual Passivation for Efficient and Stable Perovskite Solar Cells—From Interface to Bulk Pengfei Wu[1,2], Shirong Wang[1,2], Xianggao Li[1,2] and Fei Zhang[1,2]; [1]Tianjin University, China; [2]Collaborative Innovation Center of Chemical Science and Engineering(Tianjin), China

Here, we report an alternating-cation-interlayer (ACI)-phase 2D (n=2) passivation layer modulating the bulk and interfacial defects in the perovskite films simultaneously by the mixed GAI and MAI (MGM) treatment, leading to the suppressed nonradiative recombination, longer lifetime, higher mobility, and reduced trap density. Consequently, the devices' performance is enhanced for both p-i-n and n-i-p structures, with the highest reaching ~24.0%. In addition, the MGM treatment can be applied to a wide range of perovskite compositions, including MA-, FA-, MAFA-, and CsFAMA- based lead halide perovskites, making it a general method for preparing efficient perovskite solar cells. Without encapsulation, the treated devices show improved shelf life (ISOS-D-1 stability) and real-life stability.

8:40 AM EL02.18.05
Interface Engineering with Polymer Hole Transport Layer for 3D Perovskite Solar Cells Thomas Mather, Ehsan Ghavaminia and Anupama B. Kaul; University of North Texas, United States

Perovskite solar cells have demonstrated impressive efficiency, but their susceptibility to moisture ingress and ion-transport must be reduced in order to attain a lifetime sufficient for a commercially viable photovoltaic technology. New approaches have been used to create PSCs, including with triple cation absorbers, lowering the dimensionality of the absorber or alternate electrode layers, in order to address the stability issue. Another way in which stability is enhanced is via interface engineering to block moisture access to the hygroscopic photoabsorbers used in PSCs. In this work, we explored the use of polymer interface layers between the 3D perovskite absorber and the conventional hole transport layer, Spiro-OMeTAD. Specifically, poly-[bis-(4-phenyl)-(2,4,6-trimethylphenyl)-amin] (PTAA) and Poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PTB7) were examined in the regular structure, but these are mostly utilized as hole transporting layers in an inverted structure. Specifically, the effect of inserting PTAA and PTB7 layers, as buffer layers at the interface between the absorber layer and hole transporting layer in perovskite solar cells is investigated. The power conversion efficiency of perovskite solar cells decreased from 16.49% in case of using PTAA to 12.73% by using PTB7.

8:45 AM EL02.18.06
Lattice Distortion Suppresses Phase Segregation in Triple-Junction Perovskite Photovoltaics Zaiwei Wang, Lewei Zeng and Edward H. Sargent; University of Toronto, Canada

The tunable band gaps and facile fabrication of perovskites make them attractive for multi-junction photovoltaics. However, light-induced phase segregation limits their efficiency and stability: this occurs in wide bandgap (> 1.65 eV) I/Br mixed perovskite absorbers, and becomes even more acute in the top cells of triple-junction solar photovoltaics that requires a fully 2.0 eV bandgap absorber. We report herein that lattice distortion in I/Br mixed perovskites suppresses phase segregation, generating an increased ion migration energy barrier arising from the decreased average interatomic distance between A-site cation and iodide. Using a ~2.0 eV Rb/Cs mixed-cation inorganic perovskite with large lattice distortion in the top subcell, we fabricated all-perovskite triple-junction solar cells and achieved an efficiency of 24.3% (23.3% certified quasi-steady-state efficiency) with an open-circuit voltage of 3.21 V. The triple-junction devices retain 80% of their initial efficiency following 420 hours of operation at the maximum power point.

9:00 AM EL02.18.07
Unraveling Electron Dynamics in Perovskite Nanocrystals from Milli-to Femtoseconds Fredrik Johansson[1,2], Azmat Ali[2], Birgit Kammlander[1], Alberto García Fernández[1], Mariam Ahmad[3], Elin Berggren[4], Hervé Cruguel[2], Morten Madsen[3], Emmanuel L'Huillier[2], Ute Cappel[1] and Nadine Witkowski[2]; [1]KTH Royal Institute of Technology, Sweden; [2]Sorbonne Université, CNRS, Institut des NanoSciences de Paris, INSP, France; [3]University of Southern Denmark, Denmark; [4]Uppsala University, Sweden

The fundamental understanding of carrier dynamics in- and between photovoltaic materials is of utmost importance for the advancement of material and device engineering. These dynamics includes both transfer of electron and holes through the material and between layers of different materials. The focus herein will be on charge transfer and relaxation of excited electrons in nanocrystals of the lead halide perovskite $CsPbBr_3$. $CsPbBr_3$ is material that has shown promise as absorber layer in devices and it is also relatively stable under x-ray illumination compared to its hybrid cousins. This allows for long measurements that often is a requirement for studies of electron dynamics. Furthermore, nanocrystals allows for efficient tuning of its electronic properties by changing their size and shape [1,2].

Reviewing the timescales in which charge transfer occurs in lead halide perovskites that are similar to our system, it is shown that it varies through several orders of magnitude. For an interface between methylammonium lead iodide and the 2D material WS_2, pump-probe measurements with 45 femtoseconds time resolution did not capture the charge transfer process, indicative that it occurred on a shorter timescale. However, a small fraction of the electrons remained in the perovskite layer for up to 2 ns [3] showing that multiple processes are competing and for nanowires of $CsPbBr_3$ it has been reported that the exciton radiative recombination is in the few nanosecond regime [4]**.**

We have used time resolved x-ray photoelectron spectroscopy on $CsPbBr_3$ nanocrystals to study the longer time scale and specifically recombination processes and have measured a decay constant in the range of 0.5 millisecond for the $CsPbBr_3$ nanocrystals on a gold substrate which can be compared with 20 microseconds that we recorded for a spin-coated $CsPbBr_3$ thin film on TiO_2.

To study the other faster end of the timescale we used two photon photoemission, were the decay of the valence excited state of $CsPbBr_3$ nanocrystals with two different ligands was followed. The technique allows for studies of hot electron cooling and polaron formation, processes that occur in the picosecond range [5]. Our measurement revealed several time dependencies, showing hot electron cooling in the 0.5 picosecond range independent of which ligand was attached to the nanocrystal and a slower component, that could describe trap states, with decay constants in the several picosecond range. However, this slow component is dependent on which ligand is attached to the nanocrystals.

For the truly ultrafast timescale inside the nanocrystals, on the few femtosecond and even attosecond scale, core-hole clock spectroscopy was used [6,7]. This chemically specific, resonant x-ray spectroscopy uses the core-hole lifetime as an internal clock and allows for studies of pure electronic charge transfer *i.e.* tunneling. Our results indicate that charge transfer occurs on the few femtosecond timescale when resonantly exciting both the cesium L_3-edge and the lead M_5-edge.

To summarize, we have measured charge transfer and electron dynamics in $CsPbBr_3$ on timescales spanning twelve orders of magnitude, from femtoseconds to milliseconds using different spectroscopic techniques. Providing a comprehensive review of the electron dynamics in this promising material system.

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9:15 AM *EL02.18.08
Emerging Metal-Halides for Energy-Resolving X-Ray Detection and Imaging Yang Yang; Zhejiang University, China

In this talk, I will first briefly introduce the backgrounds of X-ray detection and metal-halide materials, then give a few examples of why metal-halide-based scintillators and semiconductors are very promising candidates for indirect and direct X-ray imagers. Those examples cover several lead-free metal halides scintillators materials, featuring with negligible self-absorption loss and high X-ray light yield. One the basis of those emerging materials, energy-resolving large pannel X-ray imaging are demonstrated in our group.

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SESSION EL03.01: Electrochromics—Plasmonics, Nanostructures, Structural Colors

Session Chairs: Jianguo Mei and Anna Österholm
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3012

10:30 AM *EL03.01.01
Electrochromic Transition Metal Oxide Nanocrystals Delia Milliron; The University of Texas at Austin, United States

Transition metal oxide thin films are the active elements of electrochromic smart glass used in commercial building applications and more. Colloidal nanocrystal synthesis can produce and tune structures at both the atomic and nanoscale that are not readily accessible by conventional physical vapor deposition, providing new opportunities to develop structure-property relationships for electrochromic materials. Nanocrystal inks are readily coated to make optical quality films, facilitating spectroelectrochemical analysis and potentially providing a pathway for low-cost manufacturing compatible with flexible form factors. We discovered that the crystal structure and morphology of niobium oxide nanocrystals play a dominant role in controlling their spectral response upon electrochemical reduction. Depending on the atomic scale structure, niobium oxide can darken selectively in the range of visible wavelengths or near infrared wavelengths or both, selectively as a function of the applied bias. The coloration efficiency can also vary by about 5 fold. Combining experimental and computational analysis, we relate these dramatic differences in electrochromic response to the nature of the electronic states populated when ions are electrochemically inserted. The most promising niobium oxide nanocrystals have been incorporated in prototype electrochromic devices.

Transition metal oxide thin films are the active elements of electrochromic smart glass used in commercial building applications and more. Colloidal nanocrystal synthesis can produce and tune structures at both the atomic and nanoscale that are not readily accessible by conventional physical vapor deposition, providing new opportunities to develop structure-property relationships for electrochromic materials. Nanocrystal inks are readily coated to make optical quality films, facilitating spectroelectrochemical analysis and potentially providing a pathway for low-cost manufacturing compatible with flexible form factors. We discovered that the crystal structure and morphology of niobium oxide nanocrystals play a dominant role in controlling their spectral response upon electrochemical reduction. Depending on the atomic scale structure, niobium oxide can darken selectively in the range of visible wavelengths or near-infrared wavelengths, or both, selectively as a function of the applied bias. The coloration efficiency can also vary by about 5-fold. Combining experimental and computational analysis, we relate these dramatic differences in electrochromic response to the nature of the electronic states populated when ions are electrochemically inserted. The most promising niobium oxide nanocrystals have been incorporated into prototype electrochromic devices.

11:00 AM *EL03.01.02
Plasmonic Electronic Paper Oliver Olsson, Marika Gugole and Andreas Dahlin; Chalmers University of Technology, Sweden

Micro- and nanostructures are widely used by nature to create vivid colors. An example of this is the morpho butterfly with its blue wings created not by a pigment, but by a nano-structure. Adjacent to this, humans have generated colors by plasmonics for thousands of years. An example of this is the metal nanoparticles in old church windows whose resonances create the colorful glasses which still can be seen today.

In our group, we use plasmonic structural colors to create highly reflective pixels in red, green, and blue. We later modulate the reflection with an electrochromic material incorporated inside or on top of the structures.

The plasmonic metasurfaces are made by an evaporated back reflector made of silver or aluminum (~100 nm) and a spacer layer of aluminum oxide (60-110 nm). A thin film (20 nm) of semi-transparent gold is evaporated on top to create a Fabry-Pérot cavity resonator that extinguishes one part of the visible spectra. Patterns such as a nanohole array can be introduced in the gold film by colloidal lithography. This generates a plasmonic effect that scatters red light to further enhance the coloration.
Both tungsten oxide and conjugated polymers are used to modulate the reflection and shut the pixel ON and OFF. The inorganic tungsten oxide gives the best contrast for all three colors[1]. However, the switching speed was faster for the conjugated polymers, under some conditions reaching video speed[2].

By substituting the aluminum oxide spacer layer with an electrochromic material, the metasurface can be dynamically tuned. Tungsten oxide's electrochromism is accompanied by a change in the real part of the refractive index which alters the resonant frequency of the cavity[3]. A similar effect is achieved by the thickness change of conjugated polymers upon doping[4]. Tungsten oxide can alter the colors by shifting the peak reflection wavelength around 100 nm while the polymer alternative (PT34bT) can span the whole visible spectra [3, 4].

To further show how metasurfaces could be incorporated into a reflective display the colored structures were prepared on a commercial flexible TFT backplane. Conjugated polymers can then be selectively polymerized on individual pixels and can be controlled individually without cross-talk.

As an alternative to active matrix addressing, we are also working on a passive matrix that has the potential to greatly simplify the fabrication of pixelated devices. The configuration utilizes an electrochemical reaction on a counter electrode based solely on ITO. The reaction on ITO introduces hysteresis into the electrochromic device which makes it possible to use in a passive matrix configuration. The reaction which occurs is likely associated with trace amounts of water.

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2. Xiong, K.; Olsson, O.; Svirelis, J.; Palasingh, C.; Baumberg, J.; Dahlin, A., Video Speed Switching of Plasmonic Structural Colors with High Contrast and Superior Lifetime. *Advanced Materials* **2021**, 2103217.
3. Gugole, M.; Olsson, O.; Rossi, S.; Jonsson, M. P.; Dahlin, A., Electrochromic Inorganic Nanostructures with High Chromaticity and Superior Brightness. *Nano Letters* **2021,** *21* (10), 4343–4350.
4. Rossi, S.; Olsson, O.; Chen, S.; Shanker, R.; Banerjee, D.; Dahlin, A.; Jonsson, M. P., Dynamically Tuneable Reflective Structural Coloration with Electroactive Conducting Polymer Nanocavities. *Advanced Materials* **2021**, 2105004.

11:30 AM EL03.01.03
Silver Electrodeposition Based Multicolor Electrochromic Device toward Plasmonic Nanophotoelectronics Norihisa Kobayashi, Shun Uji and Kazuki Nakamura; Chiba University, Japan

We reported silver electrodeposition-based electrochromic device (ECD) which exhibited reversible color change from transparent to chromatic color, black and silver-mirror in a single device. This coloration is based on the absorption by localized surface plasmon resonance (LSPR) enhanced by the silver nano deposit. In this paper, we review a relationship between optical properties, deposition process and morphology of silver nanoparticles toward plasmonic nanophotoelectronics as well as color reflective display.

11:45 AM EL03.01.04
Low Power Structural Color Tuning in a-Si Dielectric Metasurface via Li Ion Insertion Elena Kovalik[1], Janna Eaves-Rathert[2], Cary L. Pint[3] and Jason G. Valentine[2]; [1]Vanderbilt University, United States; [2]Vanderbilt University, United States; [3]Iowa State University of Science and Technology, United States

Optical metamaterials allow for wavefront manipulation through the precise geometry of subwavelength scatterers. The incorporation of active materials into these structures enhances functionality by tuning wavefront response with an applied stimulus. However, next-generation device architectures require active elements that are readily available, can be applied at optical frequencies, and consume minimal power. Here, we employ Li-ion insertion into amorphous silicon Fabry-Perot films and metasurfaces, utilizing both change in refractive index and accompanying lattice expansion as tuning mechanisms. We show reversible color change with the application of -0.2 V vs. Li/Li+ for the thin film structure, much less than the 2V required for the previously established electrochromic oxide WO_3. We then pattern the thin film into a metasurface and demonstrate reversible color bleaching and restoration in individual structural-color pixels. These devices show dynamic coloration ability well-suited for novel low-power reflective displays.

SESSION EL03.02: Inorganic and Metal Oxide Devices
Session Chairs: Brandon Faceira and Aline Rougier
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3012

1:30 PM EL03.02.02
Novel Approaches of Doped Metal Oxides Nanostructuration and Surface Engineering Towards More Sustainable and Autonomous Plasmonic Electrochromic Systems Anthony Maho; ICMCB - University of Bordeaux, France

Plasmonic nanostructures of doped metal oxides such as indium-tin oxide ITO are well-known for their selective and controlled modulation ability of NIR radiations in advanced electrochromic systems, as a consequence of the capacitive tuning of their carrier concentration through external electrical bias. Such materials are integrable in dynamic heat-filtering smart windows devices, additionally showing extremely fast switching kinetics as well as high optical contrasts, coloration efficiency, and cycling durability.

The present contribution will highlight different colloidal synthesis methodologies of ITO nanocrystals based on Schlenk line thermal decomposition and on hydro/solvothermal protocols, leading to stable and easily-workable dispersions in highly polar and low-toxic media. Such dispersions can then be used as “precursor inks” in wet deposition processes, especially spray coating, leading to uniform and highly-covering electrochromic thin films onto glass substrates. Ultimately, optical and electrochemical properties of the generated NIR-modulating layers are shown to be strongly dependent on the synthetic and post-synthetic treatments and conditions.

The talk will also address the challenge of directly interfacing ITO nanostructured films with pentacene molecular layers, well known as light absorbing, electron donor materials in many optoelectronic and photovoltaic applications in view notably of their spin-allowed singlet fission properties. Practically, ITO and pentacene can be processed into bilayers from consecutive spin coating and organic molecular beam deposition, respectively, allowing for *in-situ* electron generation in pentacene as organic photodonor and transfer towards ITO as inorganic photoacceptor. Materials microstructural and optoelectronic properties are carefully assessed through SEM, AFM, XRD, Raman, VIS-NIR spectrometry and transient absorption spectroscopy TAS, with obtained results highlighting their high-impact potential as self-powered NIR electrochromic filters, all in all targeting more and more materials sustainability and device autonomy.

This work involves research contributions recently achieved and/or under progress by University of Liège – GREEnMat in Belgium (Prof. Rudi Cloots), University of Texas in Austin (Prof. Delia J. Milliron), Imperial College London (Prof. Sandrine Heutz) and University of Bordeaux / ICMCB-CNRS (Dr. Aline Rougier).

1:45 PM EL03.02.03
Hybrid Molybdenum-Tungsten Oxide as Novel Dual-Band, VIS-NIR Selective Electrochromic Material in Advanced Smart Windows Florian Gillissen[1], Jennifer Dewalque[1], Pierre Colson[1], Rudi Cloots[1] and Anthony Maho[2,1]; [1]GREEnMat - University of Liège, Belgium; [2]ICMCB - University of Bordeaux, France

The energy efficiency of smart fenestration devices used in modern buildings could be greatly improved by the integration of advanced electrochromic materials. In particular, the ability to selectively control the amount of visible and near infrared (NIR) radiations transmitted through the windows could allow for independent control of light and heat supplies, offering a better suitability to respond to different climates, seasons, and users comfort. Such advanced smart windows typically involve electrochromic layers made of nanostructured highly doped metal oxides (tin-doped indium oxide ITO, aluminum-doped zinc oxide AZO), in which the selective modulation of NIR independently from the VIS behavior can be supported through localized surface plasmon resonance (LSPR) effects. In that configuration, the electrochromic material is only capacitively charged and discharged through electrochemical bias, with no redox reactions and cation insertion / extraction occurring like in conventional electrochromic metal oxides.

Therefore, there is a strong need to develop novel formulations and/or structures of electrochromic materials coupling conventional and plasmonic behaviors, so to reach a selective, dual-band modulation ability of VIS and NIR. In this context, specific formulations of nanostructured tungsten oxide (Cs-doped WO_3, WO_{3-x}) have already been highlighted as promising. Moreover, the plasmonic optical features of hybrid molybdenum – tungsten oxide have been shown to be strongly enhanced in comparison to the parent oxides, displaying an intense absorption peak around 700 nm. This resonance frequency, coupled with the stronger intensity of the signal, makes this "MoWOx" hybrid oxide a very interesting candidate as dual-band VIS/NIR-selective electrochromic material.

In this work, hybrid Mo-W oxide is successfully synthesized through a one-step hydrothermal route, with the recovered powder being dispersed in low toxic solvent and coated onto glass substrates by spin or bar coating. The morphological, structural and optoelectronic properties of the powders and films are investigated through SEM, XRD, XPS, EPR, UV-VIS-NIR spectrophotometry and electrochemistry. Following the developed protocols, a "parent", non-hybridized WO_{3-x} formulation testifies for a "traditional" dual-band signature between "clear" (62% transmittance in VIS, 82% in NIR), "cool" (61% in VIS, 44% in NIR) and "dark" (42% in VIS, 18% in NIR) states. On the other hand, some of our selected "MoWOx" formulations - typically obtained with initial Mo/W atomic ratios of 2/1 - offers the possibility of a "warm" dual-band commutation mode that implies a darker state in VIS (modulable from 43 to 11% transmittance) and a fully-tunable NIR transmittance (from 76 to 8%). Such behavior can be directly corelated to the ratio of oxygen vacancies and the stoichiometry of metallic elements specifically observed in hybrid Mo-W formulations in comparison with the parent oxides. Preliminary cycling assessments also indicate an improved electrochemical reversibility and durability of the "MoWOx" compounds.

This research is funded by FRS – FNRS (Projet de Recherches PDR "PLASMON_EC" #T.0125.20) and involves collaborations with University of Namur (Prof. Luc Henrard & Dr. Michaël Lobet), ICMCB-CNRS (Dr. Aline Rougier & Dr. Mathieu Duttine) and Université Paris-Saclay (Dr. Mathieu Kociak).

2:00 PM EL03.02.04
Evaluation of All-Solid State Electrochromic-Supercapacitor with Varying Surface Roughness of WO_3 Film; Nanoparticle Deposition System(NPDS) vs Sputtering Jiseon Kim[1], Sungjun Choi[1], Dongwon Shin[1], Diao Xungang[2] and Caroline Sunyong Lee[1]; [1]Hanyang University, Korea (the Republic of); [2]Beihang University, China

Development of energy storage systems is essential since the need of renewable energy arises in order to reduce global carbon emissions. With the demand for lithium-ion batteries still overwhelming, safety of lithium-ion batteries is the issue since explosion of batteries often occur by overcharging or electrolyte leakage. Even though supercapacitors based on metal oxide are promising due to its higher stability compared to batteries, capacity loss of device under overcharging is inevitable. To overcome this problem, there are two-strategies; electrochromism and solid-state electrolyte. In this study, supercapacitor combined with electrochromic technology which can visually check the amount of charge/discharge are studied. From the point of energy storage perspective, WO_3 film is considered to be one of the electrochromic-capacitive bifuncitional material for a pseudo-capacitor. Moreover, solid-state electrolyte is an attractive alternative to prevent explosion. In addition, inorganic solid-state electrolyte has advantages for smaller volume, lighter weight and higher thermal stability compared to those for conventional liquid and gel electrolyte.
Herein, we have investigated the effect of WO_3 deposition methods on evaluating characteristics of electrochromic supercapacitor (ECS). We have used two dry deposition methods to fabricate WO_3 thin film to build ECS along with all-solid state electrolyte. Two types of full-cell ECS were produced by depositing inorganic electrolyte and positive layer such as $LiMn_2O_4$ in a series on WO_3 thin films which was fabricated by NPDS and sputtering method. Deposition methods change surface roughness greatly in WO_3 thin film owing to nanoparticle deposition system(NPDS) and sputtering method. NPDS is a novel dry deposition method which can produce films by accelerating powder to supersonic speed due to its pressure difference within the system. When powders were collided onto the electrode, powders broke and crushed while resulting highly rough surface. Since this method does not require any binder or solvent, it is an eco-friendly process. Moreover, low vacuum and low cost can make this system very attractive for the next generation deposition method. Second, sputtering method was used to deposit WO_3 thin film. Sputtering method is one of the commercialized thin film production method where It can fabricate various films under high vacuum with mass-production of thin films. Moreover, the advantage of high uniformity in film thickness, results in very low surface roughness.
Evaluation of WO_3 films deposited via NPDS vs. sputtering were compared with respect to optical, electrochemical and energy storage properties of full devices in comparison. It was found that the surface roughness of WO_3 thin film using NPDS is almost 10 times higher than that of WO_3 thin film using sputtering method. With high surface roughness of WO_3 film, WO_3 film using NPDS showed larger electrochemical reaction area. Finally, differences in surface roughness have affected device performances such as transmittance, charge capacity and areal capacitance. For instance, initial transmittance of the device with WO_3 film using NPDS was found to be lower than that of WO_3 film using sputtering due to increased light scattering caused by rough surface of WO_3 film using NPDS. However, charge capacity and areal capacitance were improved in the device due to high roughness film owing to its larger reaction area. Therefore, advantageous deposition of thin film for target performance of ECS devices can be selected with varying surface roughness of WO_3 thin film.

2:15 PM EL03.02.05
Investigation of the Memory Effect in Electrochromic Sputtered WO_3 Thin Films—A Combined Approach of Experiments and Machine Learning Brandon Faceira[1], Lionel Teulé-gay[1], Gian-Marco Rignanese[2] and Aline D. Rougier[1]; [1]Institut de Chimie de la Matière Condensée de Bordeaux, France; [2]Institute of Condensed Matter and Nanosciences, Belgium

Electrochromic materials and devices, able to modify reversibly their optical properties in response to an applied voltage are recognized as one of the key green technologies for sustainability and energy savings. The state of the art of electrochromic oxide is WO_3, which undergoes coloration upon reduction with insertion of small cations (H^+, Li^+ or Na^+) associated with a visual color change from colorless to dark blue. Aiming at low energy consumption applications, the unusual property of so-called the memory effect, known as the persistence of the colored state for electrochromic materials when the applied voltage is withdrawn, has recently received particular attention. This unusual property for electrochromic metal oxides allows to reduce power consumption of devices by avoiding to apply a permanent voltage in order to keep the desired color or optical state. Herein, amorphous WO_3 thin films were grown by Radio-Frequency Magnetron Sputtering (RFMS) using a WO_3 ceramic target. EC properties were estimated by cycling the films in lithium-based electrolyte while the memory effect was characterized by the evolution of the optical transmittance ΔT at 550 nm in 48h of Li_xWO_3 colored films in air-controlled environment (25°C and 50% R.H). By adjusting sputtering parameters such as power density, oxygen and total pressure films with a low

(ΔT_{550nm}~61%) or high color persistence (ΔT_{550nm}~16%) were obtained. Nevertheless, it was found that high color persistence WO_3 films could also present a low electrochemical reversibility (~23%) hence limiting practical applications. In order to optimize the compromise between these two properties, machine learning, ML, was used as a tool to design prediction maps depending on the sputtering conditions. By combining color persistence and reversibility in a single map, high performance WO_3 films with high color persistence and reversibility were targeted. From this ML mapping, WO_3 films with three different electrochromic properties were found : namely, films showing *(i)* an irreversible blue coloration and high color persistence, *(ii)* films with high reversibility but poor color persistence and *(iii)* films with a memory effect which present both high values [1]. As a result from the ML prediction maps, the total pressure during the deposition plays a key role on the memory effect since the three categories of WO_3 films were obtained by varying this parameter. In the meantime, by increasing the total pressure, films progressively go from a compact morphology to a porous one. As the morphology is more open, faster lithium diffusion and switching times are recorded. In return, the duration of the memory effect is shortened. Hence WO_3 films with a high memory effect with good EC properties requires a careful control of the morphology allowing to avoid irreversible coloration or poor color persistence. The relationship between the deposition conditions, morphology, stoichiometry and the memory effect property in WO_3 films will be discussed.

[1] B. Faceira, L. Teule-Gay, G.-M. Rignanese, A. Rougier, Toward the Prediction of Electrochromic Properties of WO_3 Films: Combination of Experimental and Machine Learning Approaches, J. Phys. Chem. Lett., (2022) 8111–8115.

2:30 PM EL03.02.06
Electro-Responsivity in Electrolyte-Free and Solution Processed Bragg Stacks Giuseppe M. Paternò[1,2], Liliana Moscardi[2] and Francesco Scotognella[1,2]; [1]Politecnico di Milano, Department of Physics, Italy; [2]Istituto Italiano di Tecnologia, Italy

Achieving an active manipulation of colours has huge implications in optoelectronics, as colour engineering can be exploited in a number of applications, ranging from display to lightning. In the last decade, the synergy of the highly pure colours of 1D photonic crystals, also known as Bragg stacks, with electro-tunable materials have been proposed as an interesting route to attain such a technologically relevant effect. However, recent works rely on the use of liquid electrolytes, which can pose issues in terms of chemical and environmental stability.
Here, we report on the proof-of-concept of an electrolyte free and solution-processed electro-responsive Bragg stack.[1] We integrate an electro-responsive plasmonic metal oxide, namely indium tin oxide, in a 1D photonic crystal structure made of alternating layers of ITO and TiO_2 nanoparticles. In such a device, we observed a maximum of 23 nm blue-shift upon the application of an external bias (10 V). Our data suggest that electrochromism can be attained in all-solid state systems by combining a judicious selection of the constituent materials with device architecture optimisation.

1. Moscardi et al., J. Mater. Chem. C, 2020,8, 13019-13024

2:45 PM BREAK

SESSION EL03.03: Electrochromic and Hybrid Devices
Session Chairs: Shangzhi Chen and Eric Shen
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3012

3:30 PM *EL03.03.01
Flexible Electrochromic Devices—Challenges and Progress Pooi See Lee; Nanyang Technological University, Singapore, Singapore

An electrochromic device (ECD) controls optical properties such as transmittance, reflectance, or emittance in a reversible manner upon electrical bias. This distinctive characteristic enables ECD to be utilized in a variety of applications, including green buildings and electrochromic displays. Flexible electrochromic devices encounter issues on electrolyte sealing, compatible transparent electrodes and cycling stability while subjected to mechanical strain. High performance electrochromic devices (ECD) have been assembled using tungsten oxides (WO_3) and iron-centered coordination polymer (FeCP) electrochromic materials, respectively. The electrolyte applied is based on an in-situ polymerization of poly(ionic liquid) (PIL) solid ionogel.[1] The resultant ECDs are of high color contrast, high thermal stability and cycling stability. Flexible form factor and deformability of the ECDs can be achieved. Meanwhile, we design and synthesis bimetallic oxides $Nb_{18}W_{16}O_{93}$ with tunable intracrystal cavity leading to superstructure motifs and uniform self supported electrochromic film.[2] On the other hand, developing a stable solid electrolyte with wide potential window and high ionic conductivity is desirable for solid-state reversible electrodeposition and dissolution of metal (REDM)-based ECDs. A heat-insulating black ECD based on reversible Ni–Cu electrodeposition and dissolution in a tailored organohydrogel has been achieved. The flexible black ECD fulfills a superior color neutrality and delivers an outstanding cycling stability and mechanical cyclic bendability.

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2. G. Cai, R. Zhu, S. Liu, J. Wang, C. Wei, K. J. Griffith, Y. Jia, P. S. Lee, Adv. Energy Mater 2022, 12(5), 2103106.

4:00 PM *EL03.03.03
Leveraging the Electrochromic Effect in Soft PhotoElectroChemical Systems (SPECS) Understanding Processes for Solar Fuels and Energy Storage Erin L. Ratcliff; University of Arizona, United States

Highly scalable, durable π-conjugated polymer materials provide control over local environments afforded through synthesis, long-lived charge carrier lifetimes, and flexible, low-cost, and scalable thin film formats which circumvent the shortcomings of inorganic materials (surface states, grain boundaries, challenges in processing, and mechanically unstable platforms). The Center for Soft PhotoElectroChemical Systems (SPECS) is a newly funded Energy Frontier Research Center that focuses on the basic science questions that underpin the development of low-cost, robust energy conversion and energy storage technologies based on new organic polymer (plastic) electronic materials. These materials are predicted to fill a critical position in the U.S. energy portfolio, providing for next-generation fuel-forming platforms (energy conversion) and batteries (energy storage) that cannot currently be achieved with conventional (hard) inorganic materials.

SPECS' mission is to understand the factors controlling charge and matter transport processes that underpin emerging energy conversion (i.e. catalysis) and energy storage technologies across spatiotemporal scales to guide durable soft material development and optimization. The realization of all-organic semiconductor systems that capture light energy and convert it into chemical energy requires a detailed understanding of structure-property relationships governing the interconnected dynamics of photo-generation, transport, and electron transfer across multiple interfaces. Dark electrochemical processes must be understood before increasing the complexity via light-matter interactions. This talk will focus on increasing complex, multiple interface platforms, towards the goal of photons-to-electrons-to-molecules energy conversion processes. A number of *in situ/operando* spectroelectrochemical and photoelectron spectroscopy capabilities will be discussed for this exciting new area of energy conversion.

4:30 PM EL03.03.04
Structure-Property Relationships in Organic Mixed Ion-Electron Transporting Materials Loren G. Kaake; Simon Fraser University, Canada

There are three major classes of models for ion transport in organic electrochromic materials. The first is based on equivalent circuits, the second uses the drift-diffusion equation, and the third emphasizes the morphological heterogeneity of organic electronic materials. Of these models, the drift-diffusion equation provides the appropriate balance of rigor and ease of understanding. A simple model for describing the dynamics of electrochromic devices that accounts for in-situ spectroscopic observations and frequency dependent cyclic voltammetry will be presented. The importance of ion drift versus ion diffusion remains a point of contention. Clearly, including drift is a more general perspective, but it will be shown that ion transport does not depend on the applied field, demonstrating that in at least one common conducting polymer, diffusion alone is the appropriate metric for quantifying the rate of ion movement. As is typical of diffusive processes in solids and liquids, the rate of ion diffusion in organic electrochromic materials depends on the solubility of the ion in the electrochromic material. When the charge density of the organic semiconductor is included in the expression for solubility, quantitative fits can be obtained that describe the voltage (not field) dependence of the rate of ion diffusion. We find that the fastest switching electrochromic materials can be obtained by increasing the solubility of the ion in the electrochromic material, which includes the use of hydrated ions for hydrophilic polymers.

SESSION EL03.04: Poster Session
Session Chairs: Sue Franz, Leroy Kloeppner, Jianguo Mei and Anna Österholm
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL03.04.01
Role of Solvent Composition During Processing of Stimuli-Responsive PNIPAM/Silyl Methacrlyate Copolymers Fabian Rodriguez[1], Jason Linn[2], Diana Zhang[2] and Michelle Calabrese[2]; [1]University of Texas Rio Grande Valley, United States; [2]University of Minnesota, United States

Electromagnetic radiation from the sun, can produce changes in the internal temperatures of infrastructures. Offsetting this increase in temperature requires greater energy consumption. Therefore, the use of smart glass windows has increased, as these windows restrict the passage of solar radiation that enters through exterior windows and thus providing greater energy efficiency. Despite these favorable qualities, implementation of smart windows is limited due to higher production and installation costs since traditional smart windows are pretreated and cannot be processed onto already existing windows. This means that standard windows would have to be removed and replaced with expensive smart windows. Therefore, cost becomes a barrier for businesses, schools, or individuals who are seeking green alternatives. To circumvent these costs while still meeting demands for greater energy efficiency, thermosensitive polymer coatings have been proposed as an alternative to traditional smart windows such as thermal glazes or hydrogel laminates.
In this study, poly(N-isopropylacrylamide-co-3(trimethoxysilyl)propyl methacrylate copolymer (PNIPAM -co-TMA) has been studied as thermal-responsive glass coatings due to optical properties stemming from thermally reversible phase changes. These phase changes result from the abrupt coil-to-globule transition where aqueous solutions shift from clear to opaque with increasing temperature. The thermoresponsive behavior of PNIPAM is favorable for sprayable smart window coatings for their ability to filter out light and heat from solar radiation. However, the presence of TMA, which allows PNIPAM coatings to bind to glass substrates, can lead to irrecoverable opacity due to crosslinking within the copolymer chain.
Cloud point testing was utilized to characterize the optical response of PNIPAM-co-TMA over several thermal cycles as irrecoverable transmittances can be observed when the TMA crosslinks within the copolymer chain. However, systems composed of 95% mol of water and 5% mol of DMSO were able to recover their original clarity across various concentrations of TMA. These results are significant because co-nonsolvency allowed access to the collapsed, opaque, state using solvent mixtures instead of temperature. This may be advantageous for coating processes. Various co-nonsolvent systems were processed into coatings through either spin or drop coating. When processing the co-nonsolvent systems into coatings, the solutions were kept at lower viscosities to better replicate a sprayable coating. This was a critical consideration when optimizing the spin coatings as the viscosity of the solution has a direct impact on the rpm required to spin. Finally, contact angles at 23°C and 60°C were collected for a coated slide. At room temperature, below the cloud point temperature, the coated slide had a contact angle of approximately 21°. When the coated slide was heated to 60°C a contact angle of 52° was measured. These results verify that the PNIPAM-co-TMA solution maintains the characteristic hydrophilic/hydrophobic phase change after the coating grafts onto the glass and subsequently permits this research to impact the use of polymer responsive coatings to improve energy efficiency.

5:00 PM EL03.04.02
Origin of Black Coloration in Reversible Metal Electrodeposition Dynamic Windows Cheon Woo Moon, Nikhil C. Bhoumik, Desmond Madu and Christopher Barile; University of Nevada; Reno, United States

Dynamic windows with electronically controlled transmission are a promising technology to increase the energy efficiency of buildings because they allow for the control of heat and light transmittance from the outside. Recently, our group has investigated dynamic windows based on reversible metal electrodeposition and designed devices that possess high contrast ratios and excellent cycleability. By modulating the structure and reactivity of the electrolyte and the electrode, uniform thin films of metals can be electrodeposited on transparent conducting oxides over a relatively large area, opening up the possibility of using reversible metal electrodeposition for practical smart window applications.[1]
To generate a black opaque state with privacy level transmission (< 0.1%), various metals have been investigated including Ag [2, 3], Cu-Bi [4], and Zn [5]. Reflection and transmission of the electrodeposits must be minimized to generate a dark black appearance. However, a deep understanding of the coloration principle in terms of the micro- and nanostructures of the electrodeposited metals has not been described. For example, Ag is a plasmonic material, and Zn is non-plasmonic material in the visible light region, but both metals can generate black colors. In this work, we explain the origin of black coloration in the reversible metal electrodeposition systems using electromagnetic simulation-based (finite-difference time-domain; FDTD) approaches.
As the size of the window increases, the coloration efficiency (CE) of device tinting is an important issue to consider. We therefore have designed nanostructures that maximize coloration efficiency. By considering the deposits as arrays of isolated nanoparticles, the nanoparticle size effect in terms of transmittance and reflectance is investigated after fixing the amount of metal in a unit cell. Next, optical characteristics are analyzed by modeling the experimentally-determined three-dimensional structure of the electrodeposits. Finally, the effects of metal oxides and other side products in the electrodeposits are carefully examined from the perspective of optical resonance modulation.

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5:00 PM EL03.04.03
Increased Cycleability for Reversible Zinc Electrodeposition for Dynamic Windows Nikhil C. Bhoumik[1,2], Desmond Madu[1], Profulla Mondol[1] and Christopher Barile[1]; [1]University of Nevada, Reno, United States; [2]Jahangirnagar University, Bangladesh

The energy crisis is a grand challenge facing our world. In the U.S., buildings are responsible for ~40% of total energy consumption. Dynamic windows, which switch between dark and clear states upon application of a voltage, can result in an average of 10% energy savings in buildings. In previous research, it has been demonstrated that Zn-containing aqueous electrolytes used on transparent conducting glass electrodes facilitate fast, reversible, and color-neutral Zn electrodeposition over thousands of cycles in dynamic windows.[1,2] However, for commercialization applications, some important challenges still need to be overcome. Common challenges for reversible Zn electrodeposition on dynamic windows are dendritic growth, parasitic H_2 evolution, irreversible Zn-ion loses, and low cyclability.
In this work, we improve the durability of 25 cm^2 Zn dynamic windows to 10,000 cycles and overcome all the above-mentioned challenges by using a unique electrolyte system. To achieve these results, we studied a series of electrolytes in different solvents and found relationships between the electrolyte and solvent compositions and the switching speed and cycleability of the devices. Proper control of the electrode-electrolyte interface results in the suppression of dendrite growth and enhances the reversibility of the Zn electrodeposition and stripping processes. The optimized electrolytes possess high Coulombic efficiency (> 99%) and promote the formation of smooth and compact electrodeposit morphologies that efficiently block light. This study also allows us to design prototype two-electrode 100 cm^2 Zn dynamic windows that switch uniformly to <2% within 30 s. Our results indicate that Zn is a promising metal for future practical dynamic windows based on reversible metal electrodeposition.

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5:00 PM EL03.04.04
Colorful E-Paper Based on Inorganic Nanostructures Marika Gugole; Chalmers University of Technology, Sweden

In recent years, reflective displays have gained a lot of attention due to their low power consumption and excellent visibility in sunlight. The market already offers viable options for reflective displays, mostly based on electrophoretic ink (E-ink). However, this technology has a number of limitations, including poor color quality. Therefore, black-and-white E-ink displays remain the most popular alternative [1].
We have investigated the integration of structural coloration and electrochromic materials for new types of reflective displays in color. We fabricated highly reflective red, green, and blue metasurfaces, based on Fabry-Perót cavities and plasmonics. In order to display dynamic images, we implemented electrochromic materials as on/off shutters [2].
To further improve the overall reflectivity, we aimed to reduce the number of subpixels needed to achieve a wide color gamut. Generally, this subdivision consists of three subpixels, normally red-green-blue. By fabricating a dynamic Fabry-Perót cavity, where one of the layers is made up of electrochromic WO3, we predicted to achieve full color with only two subpixels [3]. In this case, the electrochromic material tunes the resonance of the cavity, which in turn shows several colors depending on the degree of ion intercalation.
Furthermore, commercial alternatives have a slow refresh rate, which makes them unsuitable for displaying videos. To overcome this problem, we have incorporated electrochromic polymers into engineered nanostructures with positive curvature. By optimizing electrolyte and electrode configuration, the switching speed could be improved to the extent needed to enable video display [4].

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5:00 PM EL03.04.05
Oriented Surface-Anchored Metal-Organic Frameworks (SurMOFs) as Electrochromic Active Thin Films Antoine Mazel, Lucas Rocco, Nicolas Penin and Aline D. Rougier; CNRS ICMCB, France

Nowadays, electrochromic thin-films are mostly based on inorganic oxides (WO_3, V_2O_5…) or organic compounds (viologens, polymers…). Hybrid materials, combining inorganic and organic building blocks, are ideal candidates to expand the range of compounds for the development of original and performant EC thin films. Herein, we report the synthesis of novel hybrid EC thin films based upon highly oriented porous materials. The unusual property of the films lead to the design of an original electrochromic device.
Over the past two decades, porous coordination polymers and Metal-Organic Frameworks (MOFs) have emerged as an important family of crystalline materials with a broad range of applications[1]. These unique class of hybrid materials assembled from metal ions or clusters and organic ligands as building units allow the combination of functional ligands in a highly ordered three-dimensional fashion[2]. In these materials, the EC property can either originate

from the organic or inorganic component. Recently, a strategy based on the sequential and controlled immobilization of the key components of the MOFs led to the fabrication of highly homogenous materials where the ligands and the metals present a preferential orientation. These new MOF thin films are called Surface-Anchored Metal-Organic Frameworks (SurMOFs)[3]. Besides the generation of highly oriented and non-interpenetrated materials, this method is compatible with almost every substrates and uses a very small amount of precursors (few mg/cm*cm) making SurMOFs ideal candidates for the integration of highly sophisticated ligands into functional materials.

In this work, we developed novel electrochromic thin films based on oriented SurMOFs. Thin films were synthesized via spray-coating by using zinc acetate and a ligand from the perylene diimide (PDI) family. The electrochromic activity of the SurMOFs was recorded in imidazolium-based ionic liquids. Interestingly, two strikingly different behaviors were observed depending on the electrolyte composition. The as-deposited films switch reversibly from orange to dark blue in a lithium-based electrolyte while they adopt a cyan reduced state in salt free electrolytes. Taking advantages of this unusual property, a bi-color device with an original configuration was designed offering a uniform orange oxidized state and a bi-color cyan and dark blue reduced state. Clearly, two different mechanisms took place and the reduced species responsible of the color were identified. To our knowledge, this work represents the first one regarding the use of SurMOFs for electrochromic applications and opens the doors of a new category of EC materials as the combination between ligands and metals are infinite.

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5:00 PM EL03.04.06

Electrochromic Performance of Silver Nanowires Based Transparent Electrode Films: an Approach to ITO-Free Electrochromic Devices

Ambreen Ambreen[1,2], Brandon Faceira[1], Laetitia Bardet[2], Camilo Sanchez-Velasquez[2], Abderrahime Sekkat[2], David Munoz-Rojas[2], Daniel Bellet[2] and Aline D. Rougier[1]; [1]Institut de Chimie de la Matière Condensée de Bordeaux, France; [2]Laboratoire des Matériaux et du Génie Physique, France

Transparent electrodes (TE) have been widely studied as a key component of many optoelectronic devices such as solar cells, flexible light-emitting devices, transparent heaters and smart windows. Currently, indium tin oxide (ITO) is extensively used as transparent electrode for these devices owing to its high transparency, electrical conductivity and chemical stability. However, the scarcity of indium, the expensive deposition method and brittleness of ITO prompted the search for new flexible, stable and low-cost TEs. Silver nanowire (AgNW) networks appear as a promising alternative thanks to their high optical transparency, excellent electrical properties and mechanical flexibility [1], and are indeed gaining much attention in the last years. In order to improve the integration of AgNW networks into industrial devices, their stability against electrical and/or thermal stresses needs to be enhanced. One of the applications of TE is smart windows that have attracted great attention due to their potential applications in energy-efficient devices. Thanks to electrochromic materials that can alter their transparency as a response to an electrical input, [2] smart windows can decrease the need for energy-intensive heating or air conditioning in buildings. Strong direction of improvement in ECDs consists of replacing the commonly used ITO as transparent electrode with a flexible TE. In this context, AgNW networks are promising candidates however, their stability to oxidation and corrosion in electrolyte remains a key issue for the application. Moreover, the method and experimental conditions of electrochromic oxide deposition on AgNW networks also influence the stability of AgNW networks.

The aim of the present work is to prepare ITO-free electrochromic devices using stable AgNW networks as TE. The network is deposited through spray-coating on transparent glass substrates. To overcome the instability issues, AgNW networks are coated with a thin conformal protective oxide layer using atmospheric pressure spatial atomic layer deposition [3]. The influence of post deposition treatment on the properties and stability of AgNW networks are discussed. The electrochromic oxide is deposited through radio frequency magnetron sputtering (RFMS) technique and the electrochromic performance is determined through cyclic voltammetry and chronoamperometric characterizations. The performance of AgNW based electrochromic film is compared with the ITO based electrochromic film.

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5:00 PM EL03.04.07

Fabrication of Color Visualized Sensing System for NOx Gas Using Dry Deposition Method Sungjun Choi, Haritham Khan, Jiseon Kim, Jin-Goo Park and Caroline Sunyong Lee; Hanyang University, Korea (the Republic of)

As the emission of toxic gas continues to increase, the importance of monitoring the emission of toxic gas through a gas sensor is increasing continuously. Since most of these harmful gases are invisible, a system to give quick information about leakage is crucial. Conventionally, gas sensors should be heated to a high temperature to sense toxic gas by measuring its change in resistance. In this study, a gas sensor operable at low temperature with an electrochromic device that can display its presence of gas by changing its color at low voltage are implemented in one circuit to visualize sensing of toxic gas. When toxic gas is inserted, resistance of sensor is increasing, and the electrochromic device changes its color by changing its current. Therefore, the gas sensor to be used in this study should have high sensitivity at low temperature, while the electrochromic device operates at low voltage.

Ceramic oxides such as WO$_3$, ZnO, and TiO$_3$ are mainly used as active materials for gas sensors. In this study, a thin film was fabricated using a nanoparticle deposition system (NPDS) as a thin film deposition method to fabricate sensing films. NPDS is a method of dry deposition on a substrate by accelerating the powder in the nozzle to supersonic speed due to the pressure difference between the chamber and the nozzle in a low-vacuum atmosphere at room temperature. NPDS can control roughness of thin film to control reactive surface area. In addition, MoS$_2$ was coated on the surface of the thin film using a hydrothermal synthesis method after thin film production through NPDS. Through this, we tried to fabricate a gas sensor that has a highly reactive surface which can be operated even at low temperatures through MoS$_2$ coating.

In this study, three thin films of WO3, ZnO, and TiO3 were fabricated by NPDS method, followed by MoS$_2$ coating on each thin film through hydrothermal synthesis. We have used 200 ppm of NOx gas while we monitor the behavior of gas sensing while we vary temperature. The material with the best sensing sensitivity was selected. Finally, a sensor using the selected material with the highest sensitivity, and an electrochromic device were implemented in one circuit to build color visualized sensing system. We have used electrochromic gel (EC gel) based on mono-heptyl viologen (MHV, 1-heptyl-4-(4-pyridyl) pyridinium) which is capable of color-changing at low voltage for electrochromic device.

5:00 PM EL03.04.08

Modular Electrochromics – Designs for Facile Color-Mixing John M. Toribio, Omer Yassin and Gregory Sotzing; University of Connecticut, United States

Neutral states are quite lucrative in electrochromic design due to their versatile applications in different forms of shading and displays. Color neutrality is typically achieved as a result of subtractive color mixing, using a combination of chromophores having complementary absorption spectra to cover the entirety of the visible region. Several aspects of design should be considered when combining chromophores, including redox potentials, absorption spectra, migration effects during operation, and ease of synthesis or blending. Herein, we present a new system for achieving color neutrality in electrochromic devices by combining a set of complementary chromophores that can either be blended or co-reacted to form a new compound for polymerization that represents its component chromophores. As an example, we highlight a novel multichromophoric electrochromic polymer containing a conjugated 3,4-propylene dioxythiophene (ProDOT) backbone and a reversible redox active small molecule electrochrome tethered to the conjugated chain. The resulting electrochromic device exhibited a 55.7% photopic contrast with bleached and dark state transmittances of 70.4% and 14.7%, respectively. Furthermore, we briefly discuss approaches to develop melt-processable electrochromic polyesters as modular electrochromics.

5:00 PM EL03.04.09
Dynamic Switching of Optical Contrast in Structural Colors Based on Rayleigh Anomalies by Li-Ion Insertion Kyungnae Baek, Cheon Woo Moon and Jerome Hyun; Ewha Womans University, Korea (the Republic of)

To demonstrate dynamic on/off switching of structural colors, Li ion intercalation of WO_3 in Fabry-Perot cavities and gap plasmon resonators has been explored by many groups. Various structural colors can be prepared by controlling the arrangement or dimension of such resonators while the input and output of Li ions into the resonators can change the colors from dark to bright. One of the challenges has been achieving near 100% optical switching contrast, which can be achieved with a completely black off state. In this study, we prepare vibrant structural color pixels composed of WO_3 nano gratings and demonstrate various colors based on the Rayleigh anomaly (RA) under a cross-polarized excitation and detection configuration. From RCWA calculations, high switching contrast (>80%) between the intercalated and deintercalated states was confirmed at specific grating heights. To experimentally demonstrate these findings, we fabricated an electrochemical cell with a WO_3 grating on a metal working electrode and ITO counter electrode sandwiching an electrolyte including Li ions dissolved in propylene carbonate. The grating was oriented 45 degrees with respect to the input polarized and the refection was viewed with a separate orthogonal polarizer. With the appropriate grating parameters, this configuration enables one to view colors from the RA. With an applied cathodic bias, the Li_xWO_3 gratings appear black. The original colors from different gratings returned with an applied anodic bias. Based on these calculated and measured results, we suggest the use of this structural color pixel in high contrast dynamic reflective displays.

SESSION EL03.05: Organic Electrochromic Molecules and Polymers I
Session Chairs: Sue Franz and Leroy Kloeppner
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3012

8:30 AM *EL03.05.01
Flipping the Spectra—Optimizing Transmission, Contrast and Color in Anodically Coloring Electrochromes John R. Reynolds[1], Dylan Christiansen[2], Justine Wagner[1], Mason Butt[3], Abigail Dejneka[1], Simone Tennyson[1], Eric Shen[1], John Bacsa[4], Anna Österholm[1] and Aimee Tomlinson[3]; [1]Georgia Institute of Technology, United States; [2]Electrochromic Company, United States; [3]University of North Georgia, United States; [4]Emory University, United States

The ability to tune the electronic transitions of both molecular and polymeric electrochromes provides controlled absorption of ultra-violet, visible and near infrared light. Cathodically coloring conjugated polymers (CCPs) have been developed which exhibit a full palette of primary colors, and can also be mixed to form secondary colors and neutral (brown and black) states. Upon oxidation, light absorption for the these CCPs is moved into the near IR, with concurrent loss of the visible light absorption, yielding transmissive states. While high electrochromic contrasts are accessible with these polymers, a limit is reached as the near IR absorption bands tail in the visible providing some residual red-light absorption, causing the oxidized form to have a light blue or gray hue. Cathodically coloring molecular electrochromes, of which the viologen family is most prevalent, avoid this as the dication state absorbs in the UV, giving rise to a truly colorless state, and can be subsequently reduced to the visibly colored radical cation state with high optical density. Here, we report on our work in developing both unsymmetrically and symmetrically structured molecular Anodically Coloring Electrochromes (ACE). We start with unsymmetrically structured two-ring (EDOT-phenylene) molecules having neutral states that are UV absorbing and colorless with L*a*b* values of 100, 0, 0. The ACE molecules oxidize to vibrantly colored, cross-conjugated, radical cations with absorptions that span the visible spectrum creating green, yellow, and red chromophores. We subsequently extended the conjugation length of the ACE molecules to symmetric three-ring EDOT-Phenylene-EDOT structures, which exhibited varying degrees of hue and saturation within the blue color space in their oxidized form. By functionalizing the central 1,4-phenylene moiety with electron donating methoxy groups, we optimized the system to oxidize at a low potential, exhibit a single narrow radical cation absorbance in the visible region with a saturated blue color, and provide a high electrochromic contrast. As these ACE molecules are soluble, and have similar oxidation potentials, they could be mixed to create transmissive, colorless blends that switch to opaque black solutions. Finally, by functionalizing the ACE molecules with pendant phosphonic acid groups, they could be adsorbed onto nanoITO modified electrodes. Placing the chromophore in intimate contact with the electrode allows for rapid on-demand switching, with our first-generation ACE molecules reversibly switching from 98% transmittance to 30% transmittance within seconds over 100 cycles. These results establish the design strategies needed to further develop a complete palette of high contrast and user controlled molecular electrochromes with a truly colorless state.

9:00 AM EL03.05.02
Ultrahigh Optical Contrast Electrochromic Polymers Zhiyang Wang, Liyan You, Vaidehi Pandit, Jagrity Chaudhary and Jianguo Mei; Purdue University, United States

Electrochromic materials undergo reversible color changes upon application of an external potential bias. P-type cathodically coloring electrochromic materials absorb in the visible region in the neutral state, and the oxidized state absorbs in the NIR to IR region appearing transmissive by eye. However, the oxidized species exhibit an absorbance tailing into the visible region, thus never reaching a fully transparent state. In this work, we report a new concept for the design of p-type anodically coloring electrochromic polymers. The neutral states of these polymers are UV absorbing and completely transparent in the visible region. The color of the polymer in oxidized state is controlled by tuning the conjugation length. These polymers are mixed to create transparent-to-black electrochromic device. The device exhibits an ultrahigh optical contrast up to 95%, the highest value reported in literature.

9:15 AM EL03.05.03
Substituent Influence on Degradation of ProDOT Electrochromes Kuluni Perera, Wenting Wu, Atheena Jenkins, Michael Espenship, Matthias Zeller,

Liyan You and Jianguo Mei; Purdue University, United States

Molecular electrochromes are capable of switching between optically transparent and colored states through redox processes. Although the color of an electrochrome can be readily tuned using substituents, these alterations can also influence reactivity of the molecule, especially when in charged, open-shell forms. Increased susceptibility to undesired side reactions may affect reversibility of the color changes and diminish long-term cyclability of these electrochromic materials. This work focuses on a group of electrochromes designed based on the 3,4-propylenedioxythiophene-phenyl (ProDOT-Ph) π-conjugated core, whose stability in the oxidized, radical cation state is significantly influenced by the number and position of methoxy substituents placed on the phenyl ring. Radical cations were generated using both chemical and electrochemical doping and the subsequent degradation was tracked through a combination of UV-Vis-NIR spectroscopy, mass spectrometry and single crystal XRD analysis. Considerable deviations from expected radical cation characteristics were observed over time, depending on the substitution pattern. Two distinct irreversible degradation processes related to functional group loss and sigma dimerization were identified. Computational calculations reveal a trend in substituent-driven radical localization effects, which helps to explain the observed reactivity of the radical cations. While the judicious placement of substituents could successfully prevent rapid methoxy degradation, eventual radical dimerization could only be overcome by varying the end-capping group. These findings provide insights on the role of substituents in determining electrochrome stability and design considerations for durable redox-active molecular systems.

9:30 AM EL03.05.04
Probing Electron Density Modulation and Steric Interactions to Elucidate Color Control in Anodically Coloring Electrochromes Justine S. Wagner[1,1], Evan Smith[2], John Bacsa[3], Aimee Tomlinson[2] and John R. Reynolds[1,1,1]; [1]Georgia Institute of Technology, United States; [2]University of North Georgia, United States; [3]Emory University, United States

Recently, our group has made a significant contribution to the field of anodically coloring organic electrochromics (ACEs) through the autonomous manipulation of the band gaps of the neutral and radical cation forms. Here, we systematically evaluated the optoelectronic and structural effects of substituent alteration on a tunable centralized phenylene core on a symmetrical three ring conjugated thiomethyl-substituted bis(3,4-ethylenedioxythiphene)-1,4-phenylene molecule. In addition, we revisit the asymmetric EDOT-phenylene bi-aryl structural motif by accessing and modulating the lower energy (LE) radical cation peak position and oscillator strength through the incorporation of a sterically hindered electron rich moiety. We capitalize on the versatility of both constructs to demonstrate how steric interactions and electron density modulation impact the conjugation, torsional angles, and bond distances of both forms. As a consequence, there is an alteration in the optoelectronic properties and redox activity which controls color access and vibrancy of radical cation and dication states. These results, combined with our earlier work, increases our design rules thereby allowing for fine-tuning of the hue and saturation of molecular electrochromes. Ultimately, this work has allowed us to get closer to reaching our goal of developing a complete ACE color palette consisting of a fully transmissive colorless neutral state and a highly absorbing colored charged state.

9:45 AM EL03.05.05
Polyhedral Oligomeric Silsesquioxane Functionalized Viologen Hybrid Materials for Large-Area Flexible Electrochromic Devices Jong Seung Park[1], Fayong Sun[1], Joo Hee Eom[1], Do Yeon Kim[1], Gaurav K. Pande[1], Seung Geol Lee[1] and Sung Kyu Park[2]; [1]Pusan National University, Korea (the Republic of); [2]Chung-Ang University, Korea (the Republic of)

The electrochromic devices (ECDs) exhibit reversible color changes due to electron and ion transfers during the redox reactions. Viologen derivatives have been frequently employed in ECD fabrication due to their electron-accepting capability and facile synthetic routes. However, viologens have often disclosed slow switching speed, poor long stability, and mediocre coloration efficiency. Meanwhile, transparent conducting oxide (TCOs) electrodes are another vital component determining the visual contrast and switching behaviors of ECDs. Indium tin oxide (ITO) has been widely adopted as a TCO material. Still, the ECDs have often suffered from low conductivity and poor uniformity, especially in the case of ITO-PET films. Due to the inevitable voltage drop for large electrodes, the performance degradation has become even more severe.
Herein we present the polyhedral oligomeric silsesquioxane functionalized viologens (POSS-viologens) applicable for large-area flexible ECDs. The structural rigidity of POSS fillers and the synthetic versatility of viologen compounds are manipulated. The active layer formed using ion gel compositions by spray and bar coating methods displays good mechanical stability and high ionic mobility. Depending on the active device sizes, the electrochromic behaviors are investigated in-depth and compared with conventional viologens. Furthermore, the TCO electrodes are treated with semi-conducting nanoparticles to adjust and enhance the distribution in contact resistance. Different electrode patterns and power supply connections are applied for the device preparation. The current results may offer feasible approaches for mass production of large-area flexible ECDs at affordable costs by employing POSS-viologens and modified electrodes combined with the solution coating methods.

10:00 AM BREAK

SESSION EL03.06: Organic Electrochromic Molecules and Polymers II
Session Chairs: Jianguo Mei and Marco Schott
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3012

10:30 AM *EL03.06.01
Energy Saving Electrochromic Windows Based on Conjugated Polymers with Counter Electrode Modification Eunkyoung Kim; Yonsei University, Korea (the Republic of)

In the quest to reduce energy consumption, smart window devices present a core solution to reduce the massive energy loss through windows. Smart window devices can be designed on the basis of electrochromic (EC) principles, which offer simple integration mechanisms for color switching, optical sensing, and energy storage. An energy saving electrochromic window was explored based on charge-balancing concept and interfacial carrier transport control. A blue or black-to-transparent EC windows were achieved through the combination of EC polymers and a capacitive layer. A porous film was grown from aniline interfaced-graphene flakes, to provide a capacitive layer with a high surface area and electrical conductivity. As prepared EC windows afforded a highly transparent (>75%) and a large color-contrast EC window, which showed a high energy density enough to fuel an electronic clock and LED. A 10 × 10 cm2 size window was demonstrated, to feature the scalability of the electrochromic capacitive window. These electrochromic properties of CPs with counter electrode modification approaches make them very promising candidates for designing functional smart windows. Single cell type multi-functional windows have emerged based on CPs, to deliver electrochromic capacitive windows and photoelectrochromic windows. The progress of these efforts will be highlighted in this talk, along with guiding principles.

11:00 AM EL03.06.02
Optical Dispersion and Dynamic Thermoregulation Metasurface of IR-electrochromic Conductive Polymer Ting-Hsuan Chen[1] and Po-Chun Hsu[2]; [1]Duke University, United States; [2]The University of Chicago, United States

Personal thermoregulation is an energy-efficient innovation to address the need of human body temperature homeostasis. With its variable emissivity, mid-IR electrochromic conductive polymer can act as active material in a device to offer thermal comfort without energy input. Additionally, by incorporating the metal-insulator-metal (MIM) perfect absorber design, dynamic conductive polymer metasurface could provide larger emissivity contrast for personal thermoregulation. However, modelling the optoelectronic behavior of conductive polymer is challenging in the mid-IR due to the coupling of phonon and free carriers. Here, we present the spectroscopic ellipsometry and WAXS studies at various electrical potential and establish the correlation between charge transport properties, complex refractive index, and the morphology. The change in carrier concentration is successfully observed by fitting from various optical dispersion models. As a proof of concept, we also demonstrated the electrochemically dynamic metasurface for emissivity tuning by biasing and switching the structure between a high-emissivity perfect absorber and a metallic reflector.

11:15 AM EL03.06.03
Design Rules for High Contrast Mid-Infrared Electrochromism Eric Shen, Callie Goins, Austin L. Jones, Anna Österholm and John R. Reynolds; Georgia Tech, United States

The ability to modify a material's optical properties by varying the applied voltage is the foundation of the field of electrochromism. To date, most of the new material development is primarily focused on designing chromophores with strong and fast visible light modulation, where materials that can switch between a colored and colorless state, as well as those that switch between multiple colors, have generated opportunities in areas ranging from tinted windows, to color indicators paired with sensors, to user-controlled eyewear. However, the ability to modulate transmission in the mid-infrared (mid-IR) has been far less explored even though it has the potential of making a substantial impact in a range of applications including thermal camouflage and motion sensing. While several material classes can exhibit IR electrochromism, conjugated polymers can be synthetically tuned to readily investigate structure property relationships. This property has been utilized to develop a strong understanding of how their neutral state spectra can be predictably controlled. Their oxidized spectra however are far less well understood.
In this presentation we extend this understanding by evaluating several families of conjugated polymers. Thin films are spray-coated onto IR-transparent substrates and chemically treated to either neutralize the film through exposure to hydrazine or oxidized by exposure to a chemical dopant. In conjugated materials, oxidation gives rise to a rearrangement of bonds to accommodate the charge, accompanied by a shift in absorbance to longer wavelengths starting from the near-IR and continuing well into the mid-IR, arising from the optical signature of radical cations and dications. The intensity and width of the IR absorption is determined not only by the type and number of charge carriers, but also by how effectively they can delocalize along the chain. Theory suggests that the better stabilized the charged state of a conjugated material is, the greater the absorbance in the mid-IR. Here, we will summarize how we have been able to optimize IR switching in solution-processable EC polymers using some simple structural modifications resulting in champion systems exceeding 85% thin film contrast from 3-12 µm, areas where IR sensors commonly operate. This was achieved using a combination of an electron-rich backbone that has the ability to readily planarize and the incorporation of polar functionalities that we hypothesize are able to enhance polymer-electrolyte interactions and stabilize the charged state. The addition of electron-accepting repeat units is a common strategy for red-shifting the neutral state absorption for visible range electrochromism. Here, we find that these electron-deficient acceptor units compromise charge carrier delocalization and the stability of the oxidized state resulting in the mid-IR absorption rapidly tailing off above 3 µm. Replacing the polar functionalities with apolar analogs also does not have a significant impact on the visible electrochromism but, for the systems studied here, the intensity of the mid-IR modulation is noticeably compromised. Finally, we will show examples of IR-reflecting device prototypes and discuss some of the challenges that go beyond the active material, in particular how different device layers must be carefully considered based on their contribution to the mid-IR response.

11:30 AM EL03.06.04
In-situ Measurement of the Swelling, Mechanical Property, Damage, and Doping Kinetics of Poly(3,4-propylenedioxythiophene) Electrochromic Polymers Xiaokang Wang, Jianguo Mei and Kejie Zhao; Purdue University, United States

The doping of electrochromic polymers involves rich coupling between mechanics and electrochemistry. The drastic changes in the microstructure and properties originate from the electron transport and ion intercalation in the polymers. In our recent work, we quantify the breathing strain, the evolution of the mechanical properties, materials degradation and damage, and the doping kinetics of poly(3,4-propylenedioxythiophene) (PProDOT) thin films in-situ using customized environmental nanoindentation and optical microscopy. Upon oxidation, a breathing volumetric strain of 12–33% is persistent in different sets of electrolytes of various solvents, salts, and salt molarities. Also, the elastic modulus, hardness, and yield strength decrease by a factor of two. Heavily cycled PProDOT films show reduced volumetric strain and accumulated mechanical damage of channel cracks and dysfunctional regions of slow and inhomogeneous electrochromic switching. Interfacial engineering techniques are demonstrated to increase the lifetime of thin film electrochromic electrodes by two orders of magnitude. As the swelling-induced stress may bias the doping kinetics, we observe that an applied pressure as low as 2.8 MPa significantly retards the electrochromic switching in a designed moving front setup. Our work presents a systematic characterization of mechanical behavior and doping kinetics in a model electrochromic polymer and informs the mechanical and electrochemical reliability of organic electrochromic devices.

11:45 AM EL03.06.05
Synthesis and Conductivity Optimization of Ladder Polyaniline Featuring Extraordinary Stability, States-Delocalization Mingwan Leng and Lei Fang; Texas A&M University, United States

A highly stable, conductive ladder pernigraniline salts was synthesized. EPR and SQUID test were performed to prove that its conductivity comes from polaron delocalization. By comparing side chains with different electron donating/withdrawing group, parameter basicity is turn into a key design parameter for acid doped quinoidal structures. Meanwhile, the ladder structure enabled it good reversibility in Lithium salt and acid electrolyte, and extraordinary stable performance on electrochromic device. At the end, with assistant of robot and AI, the experiment of exploring acid additive to the polymer proved that liquid acids additive enabled it morphologies fitted for conductivity test.

SESSION EL03.07: Reversible Metal Deposition and Inorganic Electrochromic Devices
Session Chairs: Norihisa Kobayashi and Anna Österholm
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3012

1:30 PM *EL03.07.01
Design Factors that Enable High Performance Dynamic Windows Based on Reversible Metal Electrodeposition Michael D. McGehee[1], Andrew Yeang[1], Yuchun Cai[1], Gabriel McAndrews[1] and Christopher Barile[2]; [1]University of Colorado, United States; [2]University of Nevada, Reno, United States

Dynamic windows with adjustable tint give users control over the flow of light and heat to decrease the carbon footprint of buildings and improve the well-being of the people inside them. In this talk we will discuss the design of windows based on reversible metal electrodeposition. Topics will include the choice of metal (Cu, Bi, Ag or Zn), counterion (halides, nitrates, perchlorate), and solvent (water vs DMSO). We will also discuss how intercalation of lithium into nickel oxide or a metal mesh electrode can be used as the counter electrode. We will show how proper design can avoid irising, enable excellent resting stability, provide color neutrality, achieve light transmission below 0.1 % for privacy and result in good cycle life.

2:00 PM EL03.07.02
Investigation and Manipulation of Zinc Electrodeposition Morphology for the Construction of Reversible Zinc Electrodeposition Dynamic Windows Desmond Madu[1], Andrew A. Thompson[1], Madeline J. Leahy[1], Micah V. Lilo[1], Michael D. McGehee[2] and Christopher Barile[1]; [1]University of Nevada, Reno, United States; [2]University of Colorado Boulder, United States

Reversible metal electrodeposition (RME) is an underexplored and promising method for the design of dynamic windows with electronically controllable transmission. RME enables the construction of dynamic windows with fast switching and color-neutral tinting. A variety of metals have been explored, but each has thus far been associated with negative attributes. In this work, we investigate Zn RME due to its ability to produce viable windows despite the negative reduction potential of Zn. By systemically studying the chemical composition of aqueous Zn electrolytes and the structure of Zn electrodeposits on tin-doped indium oxide electrodes, we are able to create high contrast reversible 25 cm2 windows that possess >99% Coulombic efficiency. X-ray diffraction and scanning electron microscopy analyses allow us to link window optoelectronic performance to the electrolytes' composition and Zn electrodeposit morphology. Through the use of polymers such as polyethylene glycol , we are able to manipulate the deposited Zn morphology. This change in morphology allows for a large increase in cycle life from less than 100 cycles to more than 1,000 cycles with retention of other beneficial properties. With this increase in cycle life as well as a high contrast ratio, Zn RME is a viable option for further development of metal-based dynamic windows.

2:15 PM EL03.07.03
Understanding and Improving Mechanical Stability in Electrodeposited Cu and Bi for Dynamic Windows based on Reversible Metal Electrodeposition Gabriel McAndrews[1,2], Andrew Yeang[1], Yuchun Cai[1], Christopher Barile[3] and Michael D. McGehee[1,1]; [1]University of Colorado Boulder, United States; [2]National Renewable Energy Laboratory, United States; [3]University of Nevada, Reno, United States

Reversible metal electrodeposition (RME) is a growing field with applications ranging from batteries (e.g. Li, Zn) to dynamic glazings for thermal emissivity (e.g. Ag) or windows (e.g. Cu, Bi, Ag, Zn). Dynamic windows based on RME can enhance building efficiency up to 20% due to reduced lighting, heating, and cooling loads while reducing glare.[1] While a reductive potential is applied, RME windows based on Cu and Bi can adjust light transmission from ~ 70 % to < 0.1 % ("privacy state") when ~180 nm of metal is electrodeposited on the transparent conducting electrode.[2] Uniform, smooth, and compact films enable RME windows to reach low transmission states with color neutrality at large scale,[2] and the transparency of the window can be regained by switching the polarity of the potential.[3,4]

We find that films plated to privacy state transmission with a Cu-Bi ratio of ~2:1 fracture and delaminate within 24 hours resulting in a visually unattractive window with lost active metal and a reduced dynamic range. While the Cu-Bi film is stress free upon deposition, after 4 hours of resting 38 MPa of tensile stress develops. Likewise, pure Cu films exhibit 142 MPa of tension after deposition. The tension in Cu-Bi and Cu films combined with the $Cu(ClO_4)_2$ in the electrolyte results in severe, widespread sinusoidal cracks and delamination due to stress corrosion cracking (SCC). In contrast, electrodeposited Bi films have compressive stress, likely due to high self-diffusion and insertion of atoms into grain boundaries during plating. We emphasize the importance of stress characterization in electrodeposited films to identify susceptibility to mechanical failure driven by SCC. In turn, we demonstrate a Bi-based dynamic window with crack-free resting stability that exceeds 9 weeks.

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2:30 PM *EL03.07.04
Highly Opaque and Durable Dynamic Windows based on Reversible Zinc Electrodeposition Christopher Barile, Desmond Madu, Nikhil C. Bhoumik and Cheon Woo Moon; University of Nevada, Reno, United States

Dynamic windows harnessing reversible metal electrodeposition (RME) have emerged as a promising technology to enable energy-efficient windows with electronically tunable transmission. Metals are ideal materials for blocking light due to their high opacity and color neutrality. Most previous work on metal-based dynamic windows using aqueous electrolytes relies on the reversible electrodeposition of Ag, Cu, and Bi.[1-3] These metals are more noble than H_2, and thus H_2 evolution can be avoided during device switching.

Recently, we were inspired by work on secondary Zn batteries[4] to develop aqueous Zn electrolytes for reversible metal electrodeposition for dynamic windows. Despite being substantially less noble than H_2 with a standard reduction potential of -0.76 V vs. SHE, reversible Zn electrodeposition can be conducted with high Coulombic efficiency with properly designed electrolytes. We find that H_2 evolution can be kinetically passivated by Zn, ZnO, and $Zn(OH)_2$ electrodeposits. Moreover, because the solubility of common Zn salts in water is much higher than those of Ag, Cu, and Bi, high concentration electrolytes can be designed that results in rapid metal electrodeposition. Zn also can be electrodeposited with a much more compact morphology than other explored metals, which allows for Zn-based dynamic windows to reach privacy-level transmission in less than one minute. We also demonstrate that Zn-based dynamic windows can cycle 10,000 times without significant degradation, and they exhibit excellent bistability. Taken together, these results highlight that Zn is a promising candidate for practical metal-based dynamic windows.

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3:00 PM BREAK

SESSION EL03.08: Electrochromic and Hybrid Devices II
Session Chairs: Shangzhi Chen and Justine Wagner
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3012

3:30 PM EL03.08.01
Gel Polymer Electrolyte for Reversible Metal Electrodeposition Dynamic Windows Enables Dual-Working Electrodes for Faster Switching and Reflectivity Control Yuchun Cai[1], Tyler Hernandez[1,2], Andrew Yeang[1], Michael Strand[1,2], Francis M. Yavitt[1], Eldho Abraham[1] and Michael D. McGehee[1]; [1]University of Colorado Boulder, United States; [2]Stanford University, United States

Dynamic windows based on reversible metal electrodeposition (RME) represent an exciting, new class of electrochromic devices. These RME windows function by the electrochemical movement of metallic ions dissolved in a nearly colorless aqueous electrolyte between a transparent conducting working electrode and a metal mesh counter electrode. Metals are ideal light modulators for dynamic windows because they can be color neutral, inert, photostable, and opaque at 20-30 nanometer thicknesses. Our team has demonstrated metal-based dynamic windows that boast a dark state below 0.001% visible light transmittance in less than 10 minutes, an ultrawide range for optical and solar modulation (ΔT_{vis}=0.76 and ΔSHGC=0.56) with uniform and color neutral (C*<5) tinting in prototypes >900 cm^2 [1].

Though aqueous liquid electrolytes often have higher ionic conductivities than ones with high polymer content[2], dynamic windows with liquid electrolytes face problems of leakage and short-circuiting, especially for large-scale windows. Gel polymer electrolytes (GPEs) are attractive due to their ability to act as a physical separator between the two electrodes to help avoid short-circuiting[3,4]. For this study, a porous polyvinyl alcohol (PVA) GPE is synthesized as a physical separator where the polymer backbone provides the mechanical structure, and the pores are filled with BiCu ClO_4 liquid electrolyte. This highly transparent physically cross-linked PVA gel was implemented into RME dynamic windows, and the PVA GPE window can readily be tinted to below 0.1% visible light transmittance, exhibits color-neutral transmittance, and has similar coloration efficiency with liquid windows.

Importantly, the use of PVA GPE in windows provides opportunities for dual-working electrode (dual-WE) windows without short-circuiting. Dual-WE windows are made by incorporating a second piece of ITO-glass and integrating the Cu mesh counter electrode within the electrolytic matrix to the center layer of the window**.** Compared with single-WE windows, dual-WE windows are more susceptible to short circuits with a higher potential for the middle free-standing mesh to touch the WEs. Our dual-WE GPE windows switch about two times faster than single-WE liquid windows, i.e. the dual-WE window reaches the 0.1% transmittance state in 101 s while the single-WE liquid windows take 207 s. Additionally, each side of the dual-WE GPE window can be tinted individually to demonstrate varied optical effects (i.e., more reflective or more absorptive), providing users and intelligent building systems with greater control over the appearance and performance of the windows in single device architecture.

This work demonstrates the first application of GPE in the RME dynamic windows and strides toward commercialization by showing the dual-WE GPE architecture without short-circuiting concerns especially in large-scale windows, along with the benefits of twice the speed of switching and the controllable reflectivity states.

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3:45 PM EL03.08.02
Dual-Band Electrochromic Devices Utilizing Niobium Oxide Nanocrystal Benjamin Z. Zydlewski and Delia Milliron; The University of Texas at Austin, United States

Electrochromic window coatings that can modulate visible and near-infrared (NIR) light independently are important to the development of smart windows which can control solar heating and lighting to improve energy efficiency of buildings. Our work utilizes the electrochromism of monoclinic $Nb_{12}O_{29}$ nanocrystals to develop devices that can modulate the transmittance of NIR and visible light separately. The devices incorporate a secondary ion storage layer that allows for the charge and discharge of the electrochromic material, leading to reversible coloration. The configuration of the device consists of a working electrode composed the niobium oxide nanocrystals coated on a transparent conductive electrode, a non-aqueous gel electrolyte, and a counter electrode. The overall transmittance of the device can be modulated by applying different electrochemical potentials between the two electrodes. The dual-band electrochromic behavior of the niobium oxide nanocrystal allows for selective modulation of the NIR transmittance with low device potentials, along with significant visible modulation at higher potentials. In this work we study the performance trade-offs of varying film thicknesses, transparent conductive electrode materials, and ion storage layers. For optimum transmittance modulation, charge balance between the two electrodes is key. We compare the charge storage capacity and transmittance of NiO nanocrystals, CeO_2 nanocrystals, and amorphous VO_x thin films to determine optimum conditions for charge balance, allowing for full modulation of the electrochromic niobium oxide. We also show that these materials can be solution processed, without high temperature annealing steps, onto both rigid glass and flexible plastic substrates using blade coating. Optimal parameters for device assembly and overall performance will be discussed.

4:00 PM EL03.08.03
Back Injection Molding of Electrochromic Multilayer Films on Polycarbonate Substrates Christopher Johannes; University of Kassel, Germany

The integration/processing of flexible electrochromic multilayer films in common plastic injection molding processes could be advantageous with regard to the possible range of applications and mass production of electrochromic devices (ECDs). Especially light weight, slightly three dimensional formed and optically modulating windows are of interest in the transportation sector. Most optical applications based on amorph plastics, such as plastic windows or headlight coverings, are made of polycarbonate or polymethylmethacrylate (e.g. the well known brands Makrolon® and Plexiglas®). Especially polycarbonate as substrate material for ECDs could be advantageous regarding the optical properties compared to the often used PET substrate, particularly regarding the haze.
Therefore, a battery-type ECD multilayer structure based on polycarbonate substrate was developed aiming at good optical properties, especially a neutral colored and highly transmissive bleached state. For this reason, a neutral counter electrode of TiO2 and a highly transmissive polyurethane based gel electrolyte [1] was chosen. ITO was applied as current collector layer and PEDOT:PSS as working electrode.
Within a funded project an injection mold was developed and manufactured that allows to back mold the multilayer films (active area: 4 cm x 4 cm) and introduces a bending radius (200 mm). The integrated embossing unit leads to drastically lower injection pressure the cavity compared to standard processing. This results in lower shear and compressive stress on the multilayer film as well as reduced orientation and residual stresses in the injected component.
First back injection molding experiments with polycarbonate showed severel problems, especially considering the brittle metal oxide layers. After processing micro cracks all over the surface and macroscopic cracks at the kinks were detectable (beginning and end of radius). Due to different shrinkage of film and injected melt, the half cells partially detached from each other and deformed in most cases. In case of lamination defects at the multilayer films edges melt penetrated between the half cells. Most ECDs showed no function afterwards. Few surviving ECDs showed a non homogeneous coloring, defects, lower current responses and slower switching speed compared to the function before. Due to these findings the above described ECD configuration was adjusted and the brittle metal oxide layers were replaced. Instead of ITO a very conductive PDEOT:PSS formulation was used as current collector layer and TiO2 was replaced by Prussian Blue. The first ECD showed comparable transmittance changes, but considerable slower coloring/decoloring, probably due to lower conductivity of the current collector layer. The bright state was slightly blue colored and the total transmittance in the bright state was pretty low with 49 % compared to the original configuration with almost 70 %. Very promising on the other hand are the results with back injection molding since the major problems did not occur. Neither cracks were visible nor the cell detached. An accompanying peel study revealed that the new configuration had a 2.5 times better adhesion between the half cells (over the electrolyte). The total visible transmittance in the oxidized state at +1.5 V was 49 % before and 50 % after the process. The transmittance in the reduced state at -2.5 V after 60 s was 37 % before and 41 % after the process. So, the transmittance change was 12 % before and 9 % after back injection molding. Increasing the cycle time to 120 s led to a transmittance change of 14 % before and 13 % after the process. Accordingly, the switching speed decreased, but the total transmittance change only decreased little.

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4:15 PM *EL03.08.04
Fabric Electrochromics, Spandex and Nonwovens Gregory Sotzing; University of Connecticut, United States

Many advancements in electrochromics have been made over the decades, including adaptation of electrochromics to textiles. Many facotrs come into play when adapting electrochromics applied to rough, high surface area textiles that would bend and stretch. Further, the construction and implementation of such devices needs serious consideration for end use. Implementation of our very low sheet resistance polyethylenedioxythiophene-polystyrene sulfonate (PEDOT-PSS) prepared by our published screen printing and PEDOT/PSS phase segregation onto both spandex and unwoven synthetic leather, coupled with our conjugated polymer precursor technology, along with hole-through PEDOT-PSS connections, allowed for the construction of electrochromic displays on the front side of fabric while having electrical connections on the back. Here, we will discuss our open-air robust electrochromic fabric display technique, and the research necessary to adapt a technology from a relatively low surface area application using flat substrates to a very high surface textile having the ability to stretch and bend. The logic behind the choices made for electrical conductor, electrochromic material, electrolyte, and protective coating to seal the device, yet provide a fabric-feel, will be presented as well.

SESSION EL03.09: Electrochromic Polymers and Devices

Session Chairs: John Reynolds and Eric Shen
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3012

8:45 AM *EL03.09.01
Tunable Structural Colouration Based on Electrochromic Conducting Polymers Shangzhi Chen[1,2], Stefano Rossi[1] and Magnus P. Jonsson[1]; [1]Linkoping University, Sweden; [2]University of Cambridge, United Kingdom

Precise manipulation of light-matter interactions has enabled various strategies to produce vibrant and non-fading structural colours. However, dynamic tuning structural colours across the visible spectrum with high brightness has proven to be a great challenge. Here, we present a novel method based on electrochromic conducting polymers and Fabry-Perot cavity structures, to create reflective colours that can be tunable throughout the entire visible range and beyond[1,2]. The colour tuning mechanisms *via* electrochemistry can be attributed to the variation of the thin film thicknesses, the polymer's complex refractive index, or a combination of both. In addition, we will demonstrate a novel film patterning techniques based on vapour phase polymerization and ultraviolet (UV) exposure, which could modulate the conducting polymer thin film thickness and refractive index synergistically. Combing this method with a greyscale photomask enables facile fabrication of high-resolution and multi-colour structural color images within single steps. We believe our new proof-of-concept device structure and the UV-patterning method will be highly promising for the future electrochromic displays.

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9:15 AM EL03.09.02
Multicolored Display from Electrochromic PANI/PS-b-P2VP Thin Films Junxin Wang[1], Dashui Zhang[2] and Huiying Qu[2]; [1]University of Cambridge, United Kingdom; [2]Guangxi University, China

We fabricate an adaptive multicolored electrochromic display to tackle the limited color range in electrochromic materials. It is based on the synergetic effect of structural colors generated by polystyrene-block-poly (2-vinyl pyridine) (PS-b-P2VP) thin-film interferences and pigment colors arising from the electrochromic polyaniline (PANI) thin film. The pigment and structural colors are switchable by applying small external voltages ranging from -0.2 V to 1 V in the aqueous electrolyte. In contrast to the traditional coloration mechanism that mainly involves pigment color variations, our method uses pigment and structural color, achieving a wide range of color control and switchable vivid coloration. Evidence indicates that pronounced color changes of the PANI/PS-b-P2VP thin-film depend on the states of PANI, protonation/de-protonation of P2VP, and the thickness of each layer. The low energy consumed and excellent durability also satisfy the demand for applicable portable electronics. Our work provides new insights to design multiple-colored electronic devices with low energy consumption and high durability.

9:30 AM EL03.09.03
All Polymer Electrochromic Matrix Display Inho Song, Ke Chen, Liyan You, Won-June Lee and Jianguo Mei; Purdue University, United States

Emerging see-through display (i.e., transparent display) display is significant in future sophisticated displays such as wearable and portable electronics, augmented and virtual reality, electronic papers/billboards, digitized shopping displays, head-up display, and other new-generation displays. The non-emissive electrochromic (EC) materials and devices have received remarkable attention for use in the display electronics, due to the advantages such as their excellent outdoor readability, low power consumption, wide-viewing angle, and eye-saving features. However, optical signal crosstalk between multi-pixels in matrix display is serious problem, which originated from the unwanted charge transfer in EC components. In addition, the widely used inorganic-based transparent conducting electrodes (e.g., indium thin oxide and fluorine doped tin oxide) suffer from issues such as poor mechanical flexibility and an energetic mismatch between the organic-inorganic semiconductor interface. Thus, reduction of the signal crosstalk is a key factor related to the successful fabrication of matrix EC displays. In this research, we have successfully demonstrated a photolithographic patterning of all-polymeric EC components like matrix electrode, ion storage layer, solid-state electrolyte, and EC active materials. Highly capacitive and conductive conjugated polymers were used as matrix electrodes lines for passive matrix-based display operation. The transparent conductors exhibited low sheet resistance and high transmittance, which leads to fabrication of transmissive matrix displays. Great reduction of the crosstalk was shown by using the direct isolation of highly wettable and crosslinkable electrolyte thin film in high resolution *in-situ* photolithography. Ionic liquid based poly(ethylene glycol) diacrylate precursor solutions can be easily wettable on the ionic storage layers, plastic substrates, and EC polymers due to absence of polar solvent and addition of thiol based monomers. The whole polymer, patterned EC display pixels exhibited transparent/flexible display application with very low power consumption by an electrochemical behavior of the EC polymers in low voltage and their enlarged optical memory by robust electrical double layer in ionic liquid. A subtractive color can be actively tuned in matrix display, along with the laterally stacked subpixels based on micro-patterned EC polymers which have no interference with each other. These findings represent a novel strategy for fabricating flexible, dynamically color-tunable EC displays and are expected to advance the development of future see-through display applications.

9:45 AM EL03.09.04
Scalable Manufacture of Flexible Solid-State Electrochromic Devices by Physical Vapour Deposition Maimouna Diouf, Susan Impey and Adrianus Indrat Aria; Cranfield University, United Kingdom

The fight against climate emergency requires a solution to address the growing challenges of providing cost-efficient carbon emission reduction whilst improving the security of supply. Improving energy efficiency of residential and non-residential (schools, hospitals, shopping centres) buildings is at the heart of this fight due to the large carbon footprint of indoor lighting and thermal management including heating and air-conditioning. Electrochromic smart windows can be darkened or brightened as desired with a touch of a button to improve the energy efficiency of buildings. They allow a full control of visible light from outside, which reduces the dependency on indoor lighting systems, and simultaneously blocks infra-red energy from entering the room, which reduces the dependency on air-conditioning systems. Existing electrochromic smart windows, however, are rigid, bulky, and heavy, thus limiting their applications and consumer uptake. In addition, the commonly used liquid or gel electrolyte is susceptible to breakdown and leakage.

Here, we will present our recent work on the development and scalable manufacture of flexible solid-state electrochromic devices to enable light weight and economical smart windows. All device components, including transparent electrodes, electrochromic elements, and electrolyte, were made of submicron metal oxide thin films. These thin films were deposited on sub-mm flexible polymer substrates and stacked monolithically using physical vapour deposition technique. This allowed us to manufacture devices with active area of >255cm^2 and transmittance modulation of 37% in the visible range. Accelerated and field test were carried out to confirm the stability of the devices without any encapsulation. We will also present some challenges that occurred during device fabrication that resulted in device shorting and heterogeneous colouring.

10:00 AM BREAK

SESSION EL03.10: Metal Coordinated Electrochromic Polymers
Session Chairs: Eric Shen and Anna Österholm
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3012

10:30 AM *EL03.10.01
Metallo-Organic Thin Films Made in Israel Milko van der Boom; Weizmann Inst of Science, Israel

We demonstrate controlled charge trapping and release, accompanied by multiple color changes in metallo-organic coatings. The dual functionality of our metallo-organic materials provides fundamental insight into metal-mediated electron transport pathways. The electrochemical processes are accompanied by distinct, color-to-color transitions. Some of our coatings consist of two elements: 1) a nanoscale gate consisting of a layer of well-defined polypyridyl ruthenium complexes bound to a flexible transparent electrode, and 2) a charge storage layer consisting of isostructural iron complexes attached to the surface of the gate. This gate mediates or blocks electron transport in response to an applied voltage. Combining electrochemistry with optical data revealed mechanistic information: the coloration of the coatings directly relates to the formation of intermediate species, providing evidence for catalytic positive charge release mediated through the gate. These and other coatings can be functional elements in conventional electronic circuits.

11:00 AM *EL03.10.02
Recent Progress on Electrochromic Devices with Metallo-Supramolecular Polymers Masayoshi Higuchi; National Institute for Materials Science

(NIMS), Japan

Metallo-supramolecular polymers (MSPs) are coordination polymers in which metal ions and multitopic ligands are connected alternately with coordination bonds and was found to show reversible electrochromic (EC) properties (Chem. Rec., 7, 203-209 (2007)). The EC changes are triggered by electrochemical redox of the metal in MSPs. Since MSPs have specific colors caused by the metal-to-ligand charge transfer (MLCT) absorption, the color is tunable by changing the metal species and the ligands. Blue, purple, red, yellow, green and black colored MSPs were reported so far. In this presentation our recent research results on (1) design of MSPs and the EC properties, (2) design of EC decices (ECDs) with MSPs and their EC functions and (3) mass fabrication will be reported.

11:30 AM *EL03.10.03
Electrochromic Materials and Devices Based on Metal Coordination Polymers Marco Schott; Fraunhofer Institute for Silicate Research ISC, Germany

A new and exciting class of electrochromic (EC) materials are metal coordination polymers (MCPs) that can be synthesized via self-assembly of metal^{2+} ions (e.g. Fe^{2+}, Ru^{2+}) and bis(terpyridine) ligands resulting in linear polymer chains. By using different metal ions and/or ligands a broad color variation can be obtained. MCPs exhibit a strong absorption in the visible region attributed to a metal-to-ligand-charge transfer (MLCT) transition responsible for the intensive coloration. In particular, iron-based metal coordination polymers (Fe-MCPs) show excellent EC properties in terms of optical contrast, coloration efficiency, switching speed, low operating voltages and cycling stability as compared to inorganic state-of-the-art EC materials, such as tungsten or nickel oxides, used in most of the commercial smart window products. Fe-MCPs as cathodically coloring EC materials switch reversibly from a blue colored (reduced) state (Fe^{2+}) to a highly transmissive (oxidized) state (Fe^{3+}) over thousands of cycles.
MCPs can readily be deposited as thin films on transparent conducting glass or plastic substrates by means of wet-chemical processes, e.g. spin/dip coating, roll-to-roll slot-die coating or ink-jet printing. For Fe-MCPs, the fabrication of thin film electrodes was scaled-up from the laboratory to the pilot scale and their EC properties investigated in detail.
Novel EC device configurations based on Fe- and Ru-MCP thin film electrodes and different counter electrode materials, such as (mixed-) metal oxides or Prussian blue (PB), were realized with a focus on color variation (towards neutral tint), optical contrast, and cycling stability. Within the research project FLAIM, Fe-MCP inks are being investigated towards an automized and AI controlled production and optical characterization of EC thin film glass electrodes in a robotic platform.
Thus, MCPs are very promising materials for the use in future EC applications, such as architectural/automotive glazing, smart labels, sensors, displays, home appliances, and goggles/visors. However, they have to be further tested and validated, in particular under real use conditions, to prove their maturity and qualify them for a next generation EC technology.

SESSION EL03.11: Virtual Session

Session Chairs: Haizeng Li, Jianguo Mei, Fengling Zhang and Anna Österholm
Tuesday Afternoon, April 25, 2023
EL03-virtual

9:00 PM *EL03.11.01
Fabry-Perot-Type Multicolored Inorganic Electrochromic Materials and Devices Zhigang Zhao; Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, China

Tungsten oxide (WO_3) is the earliest discovered, and most widely used inorganic electrochromic material, which can change its optical properties (transmittance, reflectance, or absorption), or colors, induced by an electrical current or voltage. Owing to its high stability, strong weatherability, good adhesion to glass substrates, easy to large-scale production, and so on, the WO_3 material has a high commercial prospect. However, for a WO_3 material in its pure form, this compound only displays a onefold color modulation from transparent to blue, which is very difficult to achieve the utmost goal of full-color tunability for future electrochromic technology. Here, we introduced a Fabry-Perot cavity structure, changed the thickness, refractive index, and repetition period of the dielectric material in the cavities, and modulated the photonic bandgap, for realization of muti-color inorganic electrochromic devices. Such a simply structured device can significantly change to other more brilliant colours by changing the optical indices (n, k) of the tungsten oxide layer through ion insertion under applied potentials. Meanwhile, we emphasized the integration of multicolor electrochromic devices with other advanced energy, environment and electronic technologies to obtain new concept and multi-functional devices of new intelligent energy storage systems, high color purity devices and "Janus" devices.

9:30 PM EL03.11.02
Zinc Anode-Based Electrochromic Devices Haizeng Li[1], Wu Zhang[2] and Abdulhakem Y. Elezzabi[2]; [1]Shandong University, China; [2]University of Alberta, Canada

The development of electrochromic materials has opened the door to the development of numerous devices including smart windows, color displays, optical filters, wearable camouflages, among others. Although the current electrochromic devices do not consume energy while maintaining their colored or colorless states, their bistable operation requires external electrical energy to be consumed during switching. To reduce the energy consumption of an electrochromic device, an emerging Zn anode-based electrochromic device concept was recently introduced to partially retrieve the consumed electrical energy. In this talk, the speaker will introduce the mechanism of zinc anode-based electrochromic devices. The speaker will also introduce their group's research regarding zinc anode-based electrochromic devices.

9:45 PM *EL03.11.03
Bistable Electrochromic Materials and Devices Based on Proton-Coupled Electron Transfer Yumo Zhang; Jilin University, China

Bistable displays are considered a promising solution to reduce energy consumption in applications such as electronic shelf labels, electronic tags and smart windows because of their unique abilities to retain information (in particular images) without power input and their minimal power requirements for information change. Various strategies have been reported to implement bistable displays, including strategies based on cholesteric liquid crystals, e-inks and electrochromism. In particular, bistable electrochromic devices, in which colour change is controlled by redox reactions or the application of an electric field, are advantageous due to their simple structure and easy fabrication. However, unclear material design rules and several technical challenges intrinsic to the electrochromic switching mechanism, including undesirable drab colour, poor retention of bistability and low colour contrast, have hampered the development and widespread commercialization of bistable devices.

Recently, proton-coupled electron transfer (PCET) processes have been used to design ideal bistable electrochromic materials in our work. The PCET mechanism enhances the bistable properties of electrochromic materials by adjusting supramolecular interactions, broadening colour selection with available pH indicators and avoiding high-energy intermediates that may reduce the material's stability. The electrochromic devices show wide colour tunability and good bistable properties, and prototype devices of colourful bistable electrochromic electronic shelf labels, smart glasses, and rewritable e-paper with easy scaleup potential have also been developed.

10:15 PM *EL03.11.04
Investigation on Electrochromism of Transparent to Black Transition via Various Paths Chunye Xu; University of Science and Technology of China, China

Electrochromism is a phenomenon that optical properties of materials change stably and reversibly under an applied electric field. Electrochromic (EC) devices have attracted the attention of scholars because of their advantages of multiple colors, high energy efficiency, environmental friendliness and intelligent adjustment. Blackness of EC devices with high optical contrast is desired in automobiles, electronic displays, anti-glare mirrors, switchable window, etc. We have been investigating several ways to reach this goal as the following.
Firstly, we attempted to obtain transparent to dark black EC materials in a relatively simple process by spraying method. By using green and purple as complementary colors, a mixed solution of polymer was sprayed, and the functional film was obtained. Secondly, using the easy-oxidization properties of N-methyl-phenothiazine (NMP) to match the charge capacity of WO_3 thin films, we prepared a complementary EC device with good optical regulation and high stability. Thirdly, we selected benzothiadiazole viologen and triaminocyclopropene salt to prepare EC devices, which is unpublished yet.
Finally, using Ag as the functioal material, which has a good electrodeposition effect, we utilized electrodepositing Ag on PProDOT-Me_2 to fabric functional devices, which achieve excellent performance of a high optical contrast, a fast coloring speed and a strong cycle stability with colorless, blue and black three-state transition.

SYMPOSIUM

April 12 - April 26, 2023

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Linn Leppert, University of Twente
Sebastian Reyes-Lillo, Universidad Andres Bello
Carolin Sutter-Fella, Lawrence Berkeley National Laboratory

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* Invited Paper
\+ Distinguished Invited

SESSION EL04.01: Metal Halide Perovskites for Applications Beyond Solar I
Session Chairs: Bruno Ehrler and Carolin Sutter-Fella
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3004

8:30 AM *EL04.01.01
Ions and Electrons in Halide Perovskites—Bulk vs Interfaces Joachim Maier; Max Planck Institute for Solid State Research, Germany

The first part of the presentation summarizes parts of our work on bulk ion conductivity in halide perovskites. It deals with identifying the respective ionic and electronic charge carriers, discusses the adjusting screws for changing their concentrations as well as the relevance for polarization phenomena and stability. The surprising finding that light enhances the ion conductivity in the iodides [1] but not in the bromides, offers a simple explanation for the light induced demixing [2]. In the context of stability recent work on ion conduction in "hollow perovskites" [3] and "2D perovskites" [4] will be touched upon. The second part of the presentation refers to interfaces. It is shown that mobility of ions and the significant fraction of ionic charge carriers gives rise to ionically dominated built-in potentials, a point that had not been addressed in the photovoltaic literature and might lead to a paradigm change in the understanding of photoactive interfaces [4,5]. This ionic interaction "enslaves" the electronic redistribution, such that the electrons undergo a "fellow traveler effect".

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9:00 AM EL04.01.02
Molecular Relays in Nanometer Scale Alumina—Effective Protection Layers for Water-Submersed Halide Perovskite Photocathodes Yuval Harari, Chandra Pathak and Eran Edri; Ben-Gurion University of the Negev, Israel

Halide perovskite (HaP) solar cells have an excellent voltage efficiency (>70%) and a low electron-affinity conduction band minimum, making them prospective candidates to be used as photocathodes in integrated low-cost solar fuel generators. However, halide perovskites are notoriously unstable in aqueous solutions and immediately dissolve upon exposure to liquid water. Ultrathin layers (< 10 nm) of Al_2O_3 deposited by atomic layer deposition are suitable encapsulants to prevent water ingression but are also electronically insulating. Embedding linear conjugated organic molecules ('molecular relays') that transverse the insulating layer enables selective electron transport across the insulating encapsulating layer. The electronic functionality of the embedded molecular relays is verified by conductive probe atomic force microscopy and photo-electrodeposition of metal particles (Pt and Ag) from ethanolic solutions. Lastly, the encapsulated HaP photoelectrodes were submersed in a CO_2-saturated aqueous electrolyte and a photocurrent of ~100 $\mu A/cm^2$ (at ~ -0.32 V vs. Ag/AgCl) was measured. This work demonstrates a way for stabilizing semiconductors in polar and protonic electrolytes as photoelectrodes for the generation of solar fuels.

9:15 AM EL04.01.03
Lead-free Bismuth Based Perovskites for Integrated Electrochemical Storage and Generation Jonathan E. Halpert and Neha Tewari; Hong Kong University of Science & Technology, Hong Kong

The demand for sustainable energy has driven a recent burst of interest in solar storage devices. One such device, the photo-battery (PHBAT), is capable of providing both energy storage and generation from a single device architecture. This idea has existed for many decades, since the first demonstration in the 70's and such a design should permit increased energy storage efficiency and energy density, while reducing packaging requirements, ohmic losses, size, weight, and cost. Unfortunately, in past years, the poor efficiency of these devices failed to improve upon the standard industry solution: a solar cell wired to an external battery. Recent advances in the literature suggest a promising new start for this technology. Here we present he first lead-free, bismuth-based, all-inorganic halide perovskite photo-rechargeable *lithium-ion* PHBAT. This device enables both energy storage and photovoltaic power generation over several tens of cycles, after which the anode must be regenerated by electrical charging. In that work, we used the favorable charge transport behavior, high defect tolerance and wide absorption range for colloidal nanocrystals of $Cs_3Bi_2I_9$ perovskites, to fabricate a photo-active electrode, and a functioning photo-battery. The champion devices were able to achieve a peak photo conversion efficiency of ~0.43 %, for the first charge and an average efficiency of ~ 0.10 % for subsequent cycles. Devices showed good performance as batteries over the first ten cycles with capacity >300 mAh/g, but performance declined over the first 100 cycles. Under 1 sun and at low current, the battery could be operated with arbitrarily large *effective* capacity, demonstrated up to 900 mAh/g by essentially using the battery as a solar cell. These results compared favorably with other photo-battery devices using other materials as the active layers. We found that during the charge-discharge cycle, the lithium first intercalated into the bismuth perovskite, and, later, as the voltage decreased, formed reduced Li_xBi compounds. In addition we have found similar results are possible using Cs_2NaBiI_6 nanocrystals and 2D PEA3Bi2I9. We present these results, with high capacity and PCE of up to 0.27% and good stability. Mechanistic studies on these materials suggest future improvements are possible and give a general strategy for improving performance by perovskite engineering.

9:30 AM EL04.01.04
Dynamic Structural Fluctuations from Strongly Anharmonic Phonons in Metal Halide Perovskites Olivier Delaire[1], Xing He[1], Chengjie Mao[1], Tyson Lanigan-Atkins[1], Mercouri G. Kanatzidis[2], Matthew Krogstad[3], Stephan Rosenkranz[3], Raymond Osborn[3], Daniel Pajerowski[4] and Tao Hong[4]; [1]Duke University, United States; [2]Northwestern University, United States; [3]Argonne National Laboratory, United States; [4]Oak Ridge National Laboratory, United States

Besides their photovoltaic performance metal halide perovskites (MHPs) are attracting increased interest for their excellent performance in optoelectronic and radiation detection, as well as thermoelectric conversion applications. MHPs are known to exhibit a soft lattice with large-amplitude atomic fluctuations. While crucial to understand electron-phonon and phonon-phonon couplings, the spatiotemporal correlations of these fluctuations remain largely unknown. We discuss these correlations based on comprehensive neutron and x-ray scattering measurements, complemented with first-principles simulations augmented with machine learning. Our measurements and simulations reveal complex potential energy surfaces, resulting in multiple soft competing phonons that dynamically distort the lattice at finite temperature. These result in 2D dynamic fluctuations of cooperative halide octahedra tilts, as revealed by characteristic diffuse scattering rods. The short-ranged correlations are not static, and their dynamics are probed with inelastic measurements, revealing pervasive overdamped phonon spectra and quasielastic signatures. These results provide new insights into the atomic structure and fluctuations in MHPs, critical to understand their unusual electron-phonon and phonon-phonon couplings, underlying their optoelectronic, thermal transport and thermodynamic properties.

9:45 AM EL04.01.05
Ultrafast Spatiotemporal Dynamics of Room-Temperature Exciton Spins in a Two-Dimensional Layered Halide Perovskite Go Yumoto, Fumiya Sekiguchi, Ruito Hashimoto, Tomoya Nakamura, Atsushi Wakamiya and Yoshihiko Kanemitsu; Institute for Chemical Research, Kyoto University, Japan

Spin-polarized excitons in atomically thin two-dimensional (2D) semiconductors have attracted great interest for spin-optoelectronic applications because of their large exciton binding energies and unique spin-dependent characters. Spatially resolved optical measurements have revealed the formation of spatial patterns and long-range transport of the exciton spins in 2D transition metal dichalcogenides [1-3]. This spatial controllability of the exciton spins shows the potential of 2D semiconductors for exciton-based spin-optoelectronic applications. However, observations of such spatial dynamics have been restricted to cryogenic temperatures because the short exciton spin relaxation times at room temperature prevent formation of a spatial pattern and transport of the exciton spins. The absence of spatial evolution of spin-polarized excitons at room temperature limits the potential for applications such as information and signal processing and chiral nanophotonics.

This limitation could be overcome by utilizing exciton-exciton exchange interactions, where the repulsive force between excitons with the same spin drives fast expansion of a spatial profile of spin-polarized excitons. From this point of view, 2D Ruddlesden-Popper lead halide perovskites (RPPs) are promising candidates for demonstrating spatial evolution of exciton spins at room temperature. This is because 2D RPPs have stable excitons characterized by a total exciton angular momentum projection of ±1 [4-9] and exhibit substantial exciton-exciton interactions [10] and relatively long exciton spin relaxation times at room temperature [11]. We synthesized phase-pure 2D RPP single crystals of $(C_4H_9NH_3)_2(CH_3NH_3)_3Pb_4I_{13}$, and mechanically exfoliated the crystal flakes and transferred them onto a glass substrate.

To investigate the spatial and temporal dynamics of the exciton spins in 2D RPPs at room temperature, we developed polarization-resolved pump-probe microscopy with millidegree, submicrometer, and subpicosecond resolutions [12]. Because the pump-induced Faraday rotation angle is proportional to the spin-polarized exciton population, we measured the images of the time-resolved Faraday rotation angle. At low pump intensity, the spin-polarized exciton population decays keeping its isotropic Gaussian spatial profile, which reflects the pump beam profile. In contrast, at high pump intensity, we observed that the spatial profile of the spin-polarized exciton population evolves into a halo-like spatial pattern with increasing pump-probe delay time and ultrafast exciton spin transport occurs [12]. We found that the rapidly expanding halo-like spatial profile is caused by density-dependent nonlinear relaxation and repulsive interaction between excitons with the same spin, both of which are induced by exciton-exciton exchange interactions. Our findings reveal the impact of the exciton-exciton interactions on the spatiotemporal dynamics of exciton spins at room temperature and suggest the potential of 2D RPPs for spin-optoelectronic applications.

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10:00 AM BREAK

SESSION EL04.02: Metal Halide Perovskites for Applications Beyond Solar II
Session Chairs: Felix Deschler and Linn Leppert
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3004

10:30 AM *EL04.02.01
Excitons, Phonons and Symmetry Breaking in Complex Metal Halide Perovskites from First Principles Jeffrey B. Neaton[1,2,3]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Kavli Energy NanoScience Institute, United States

The ability to synthesize and probe a diversity of metal halide perovskites has driven the need for new intuition to interpret and predict their structural, electronic, and optical properties and how they vary with composition, dimensionality, temperature, and pressure. Here, I will discuss recent examples of first-principles calculations – based on density functional theory and ab initio many-body perturbation theory – of the structural, electronic and optical properties of complex metal halide perovskites, drawing on recent advances in non-empirically tuned hybrid functionals and our ability to compute electron-phonon and exciton-phonon interactions. I will focus on recent studies of lead halide perovskites, and of novel lead-free double and mixed-valence perovskites. I will highlight new understanding of their phase behavior, electronic structure and photoexcited states, and discuss how these properties are influenced by phonons, composition, organic cations, dimensionality, and pressure, comparing with experiments where possible and emphasizing new intuition that emerges from our calculations. Portions of this work are supported by the Theory of Materials program and Center for Computational Study of Excited-State Phenomena in Energy Materials (C2SEPEM) at the Lawrence Berkeley National Laboratory, funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, under Contract No. DE-C02-05CH11231, and by the U.S.-Israel NSF–Binational Science Foundation under Grant No. DMR-2015991. Computational resources provided by NERSC at LBNL and XSEDE at TACC.

11:00 AM EL04.02.02
Machine-Learning-Assisted Characterization of Hybrid Perovskites' Optical Properties Abigail Hering[1], Meghna Srivastava[1], Juan Pablo Correa Baena[2] and Marina S. Leite[1]; [1]University of California, Davis, United States; [2]Georgia Institute of Technology, United States

The compositional tuning of the A- and X-sites in $Cs_yFA_{1-y}Pb(Br_xI_{1-x})_3$ (Cs-FA) hybrid perovskites allows bandgap engineering, relevant for light-emitting and -absorbing optoelectronic devices. However, the relationship between chemical composition and the effects of environmental stressors (light, bias, oxygen, temperature, and humidity) is currently not well understood. Thus, we use high-throughput, environmental photoluminescence (PL) to elucidate how the optical response of Cs-FA thin films with variable cation and anion concentrations changes upon materials' exposure to relative humidity (rH) cycles that emulate accelerated day-night weather variations based on summer days in Northern California. We use machine learning (ML) models to forecast the PL response of the samples. As expected, all samples present PL enhancement with increasing rH, as a direct result of trap states' occupation. We implement Linear Regression (LR), Echo State Network (ESN), and Seasonal Auto-Regressive Integrated Moving Average with eXogenous Regressors (SARIMAX) algorithms upon splitting the data into 50%-50% for training and testing. The latter algorithm is very suitable for predicting non-linear responses, achieving an average normalized root mean square error (NRMSE) of only 8% over a 50-hour window. Summarizing, our proof-of-concept accurate time series predictions demonstrate how ML can be realized for analyzing large sets of experimental data that can be used in a holistic approach for the further development of stable hybrid perovskites.

11:15 AM EL04.02.03
Equivalent Circuit and Defect Chemical Models of Hybrid Perovskite Devices Davide Moia, Mina Jung, Ya-Ru Wang and Joachim Maier; Max Planck Institute for Solid State Research, Germany

The design of models that successfully encapsulate the chemical and electrostatic effects of mobile ionic defects in hybrid perovskite solar cells is one of the most important research directions in the field. [1] This relies on the development of experimental methods able to probe the defect situation in these materials and to elucidate the influence of ionic defects on electronic processes.
In this contribution, we address the description of charge carrier behavior in hybrid perovskites for both the equilibrium and the out-of-equilibrium situations. First, we present a systematic study of mixed conduction in methylammonium lead iodide (MAPI) thin films in horizontal structures with ion

blocking contacts. The results highlight the importance of interfacial charging in the long time scale polarization behavior of MAPI devices, also allowing us to estimate values of the Debye length. This interpretation is consistent with the dynamics of electric field screening in MAPI devices probed with spectroscopic and optoelectronic methods. [2]
Secondly, starting from the description of the key disorder reactions expected for MAPI, we develop a defect chemical model that considers the electronic and ionic charge carrier situation when a perturbation term is included. Our investigation emphasizes the importance of the coupling between the ionic sublattices and the electronic charge carriers in the definition of the component (e.g., iodine for MAPI) chemical potential, and its implications in terms of light-induced stoichiometry variations and stability of the perovskite. We conclude by discussing the analysis of the experimental electrical response of hybrid perovskite devices under bias, and establish connections between the previously developed interfacial-transistor equivalent circuit model, which can reproduce much of the optoelectronic behavior of hybrid perovskite devices, [3] and the ionic and electronic disorder described in our model.

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11:30 AM *EL04.02.04
Metal Halide Perovskites for Ultralow Energy Computation Bruno Ehrler; AMOLF, Netherlands

Metal halide perovskites are now used for solar cell, lighting and sensor applications. However, the materials are still suffering from stability issues, in part attributed to the motion of mobile ions. These ions move by voltage or light stimulus, or even by thermal activation at room temperature, demonstrating how little energy is required to move ions. Here we use these efficient ion conductors to built a memristor device which uses little energy to change its conductive state. A memristor can be used in an analog computation to store and process information at the same location, overcoming the Von-Neumann bottleneck. This energy efficient computation is achieved by chosing a perovskite that is an efficient ion conductor, and by miniaturizing the device dimensions. We achieve devices with a size $< 1\ \mu m^2$ and an energy consumption approaching the femtojoule regime. We will show the promise and limitations of this approach for perovskite-based computational devices.

SESSION EL04.03: Metal Halide Perovskites for Applications Beyond Solar III
Session Chairs: Joachim Maier and Eva Unger
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3004

1:45 PM *EL04.03.01
Frenkel Excitons in Vacancy-Ordered Titanium Halide Perovskites (Cs_2TiX_6) Seán R. Kavanagh[1,2], Christopher Savory[1], Shanti Liga[3], Gerasimos Konstantatos[3], Aron Walsh[2] and David O. Scanlon[1]; [1]University College London, United Kingdom; [2]Imperial College London, United Kingdom; [3]The Barcelona Institute of Science and Technology, Spain

Low-cost, non-toxic and earth-abundant materials are a long-sought after target in the thermoelectrics research community. "Perovskite-inspired" materials have emerged as promising candidates for thermoelectric applications due to their semiconducting nature and low lattice thermal conductivities.[1,2] Researchers commonly employ materials design strategies including structural, dimensional and compositional transformations to avoid the use of rare and toxic elemental constituents, while attempting to maintain the excellent electronic structure features of their Pb-containing counterparts. These strategies have recently been invoked to propose vacancy-ordered halide perovskites (A_2BX_6; **A** = Cs, Rb, K; **B** = Sn, Ti; **X** = I, Br, Cl) for thermoelectric applications. [3,4]

Theoretical investigations of the electronic structure of the Ti based systems, however, consistently overestimate the energy band gaps, which makes understanding dopability very difficult. In this work, we reveal strong excitonic effects as the origin of this discrepancy between theory and experiment; a consequence of both low structural dimensionality and band localization.[5]

These findings have vital implications for the optoelectronic and thermoelectric application of these compounds, while also highlighting the crucial importance of frontier-orbital character for chemical substitution materials design strategies.

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2:15 PM EL04.03.03
Towards Low-Energy Consumption Artificial Synapses from Lead Halide Perovskite Jeroen J. de Boer and Bruno Ehrler; AMOLF, Netherlands

Lead halide perovskites are highly promising materials for a wide range of optoelectronic applications, such as photovoltaics and LEDs. However, perovskite optoelectronic devices typically display large hysteresis effects under mild operating conditions, which is unwanted for these applications. At the same time these large hysteresis effects under mild conditions are highly desirable for artificial synapses, which exploit hysteresis to change the conductivity of the device.
Artificial synapses based on lead halide perovskite have been demonstrated before[1]. Low energy consumptions were possible for these synapses made of methylammonium lead iodide ($MAPbI_3$), due to the diode behavior of the synapse and the low voltages at which hysteresis occurred. We estimate that downscaling devices based on $MAPbI_3$ to device areas of $1\ \mu m^2$ could already bring the energy consumption of switching events of the synapse to values as low as 1 to 100 fJ, the same range as that of biological synapses. However, the poor chemical stability of $MAPbI_3$, and lead halide perovskites in

general, makes downscaling of the device with standard lithography techniques difficult. Here, we investigate photolithography procedures that are compatible with halide perovskites to prepare artificial synapses with device areas down to the nanoscale. We show that downscaling of the synapse with these methods is indeed a viable strategy to reduce the energy consumption of the device. The goal is to further develop lead halide perovskite artificial synapses with the same energy consumption as biological synapses for ultra-low power physical computing systems.

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2:30 PM EL04.03.04
Stable Poisson-Statistics-Limited X-Ray Imaging with Solution-Grown Perovskite Single-Crystal Detectors Kostiantyn Sakhatskyi[1,2], Sergii Yakunin[1,2], Gebhard Matt[1,2], Bekir Turedi[1,2] and Maksym V. Kovalenko[1,2]; [1]ETH Zurich, Switzerland; [2]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

One of the main thrusts of medical X-ray imaging is to minimize the X-ray dose acquired by the patient, down to the fundamental limit set by the Poisson photon statistics. Such low-dose X-ray detection characteristics have been demonstrated with only a few direct-detection semiconductor materials such as Si and CdTe; however, their industrial deployment in medical diagnostics is still impeded by elaborate and costly fabrication processes. Hybrid metal halide perovskites – newcomer semiconductors -– make for a viable alternative owing to their scalable, inexpensive, robust, and versatile solution growth and recent demonstrations of single gamma-photon counting under high applied bias voltages. The major hurdle with perovskites as mixed electronic-ionic conductors, however, arises from the rapid material's degradation under high electric field, thus far used in perovskite X-ray detectors. Here we discuss the negative effects of the ion migration on X-ray detection performance and demonstrate the mitigation path by utilizing the perovskite X-ray detectors in the photovoltaic mode of operation at zero-voltage bias. We show both countings of almost every single incoming photon and long-term stable performance, by employing thick and uniform methylammonium lead iodide single crystal films, solution-grown directly on hole-transporting electrodes The operational device stability is equivalent to the intrinsic chemical shelf lifetime of $MAPbI_3$, being at least one year in the studied case. Furthermore, direct readout array integration of detectors is demonstrated as well. A high spatial resolution of 11 lp mm^{-1} is obtained with a linear detector array. We also comment the lack of a clear commonly accepted X-ray detection characterization, approach, particularly in the material research community, often leads to a misguiding assessment of performance. We propose the guidelines for the determination of figures of merit for the low-dose X-ray imagers. These findings pave the path for the implementation of hybrid perovskites in low-cost and low-dose commercial detector arrays for X-ray imaging.

2:45 PM EL04.03.05
Room-temperature Substrate Integration of Thick Halide Perovskite Single Crystal for X-ray Detection Min Kyu Kim, Youngseung Choi and Byungha Shin; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Halide perovskite has optoelectrical properties that are very suitable for direct X-ray detector application such as high stopping power against X-ray, tunable bandgap, high resistivity, large mobility-lifetime product and cheap fabrication cost. Halide perovskite as a photon-absorber in X-ray detector can be prepared in three different forms—polycrystalline thin film, polycrystalline wafer and single crystal. For hard X-ray imaging such as medical computed tomography (CT), the thickness of an X-ray photo-absorber needs to be in the range of several hundreds of µm's to several mm's. Halide perovskite thin films can be readily prepared with a solution process, however, their thickness is limited to several microns at maximum. A thick polycrystalline wafer can be fabricated but a strong electric field (> 100 V/mm) is often required for the operation owing to the presence of grain boundaries, which raises current noise. Halide perovskite single crystal (PSC) possesses a high potential as X-ray absorbing layer because it can be easily fabricated to a millimeter thick layer while maintaining a superior mobility-lifetime product due to the absence of grain boundaries.
Most of PSCs grown by a solution process have free-standing (substrate-free) form because a substrate provides nucleation sites and results in the growth of polycrystalline perovskite. As a target dimension of an X-ray absorber increases, it becomes more difficult to monolithically grow a single crystal on a substrate. A millimeter scale free-standing single crystal can be directly applied to either a lateral-structure detector where both anode and cathode locate on same plane or a vertical-structure detector where anode and cathode are formed on both sides of the crystal. For high resolution pixelated imaging, however, thin-film transistor (TFT) arrays must be integrated with the photo-absorber. In other words, the free-standing PSC should be attached to a TFT array substrate.
In this study, we have adopted an ionic liquid, methylammonium acetate (MAAc) to integrate inverse-temperature crystallized PSC onto an indium-tin-oxide (ITO) substrate. Hydrated MAAc, which exists as liquid at room temperature, chemically dissolves the interfacial part of methylammonium lead bromide ($MAPbBr_3$) into liquid and provides a strongly bonding between PSC and ITO after the solidification of the melted interfacial $MAPbBr_3$. The integration via MAAc is conducted at room temperature and therefore induced no crack during the process, unlike the integration using a low melting temperature metal (such as Gallium alloy) which involves heating over the melting temperature of the metal and cooling. PSC/ITO bonded by MAAc showed an adhesion force of 164 kPa which can hold a weight of 1.67 kg per 1 cm^2. This is the first quantitative measured adhesion force of PSC on any substrate. The PSC/ITO interface showed excellent ohmic contact which verifies that the interface is not only mechanically integrated but also electrically well-connected. A single pixel detector with 2 cm x 2 cm PSC integrated with MAAc showed a superior sensitivity of 9×10^4 µC $Gy_{air}^{-1}cm^{-2}$ which is the highest value among substrate-integrated direct X-ray detectors. Multiple PSCs are integrated onto a TFT panel for array imaging forming active area of 8 cm x 8 cm (~$10^3 \times 10^3$ pixel), which is the largest area ever reported for X-ray detector based on PSC. In addition, the MAAc integration effectively preserved electrical pixelation of the TFT due to its resistive nature unlike metallic integration. This study provided a strategy for integrating millimeter thick, large area (> 64 cm^2) PSC onto various substrates with the demonstration of high performance devices, which is essential towards the commercialization of halide perovskite radiation detectors.

3:00 PM BREAK

SESSION EL04.04: Metal Halide Perovskites for Applications Beyond Solar IV
Session Chairs: David Cahen and Mriganka Singh
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3004

3:30 PM *EL04.04.01
Gold Perovskites Kurt Lindquist[1], Armin Eghdami[2], Christina Deschene[1], Alexander Heyer[1], Jiajia Wen[1], Alexander Smith[2], Edward Solomon[1], Young Lee[1], Jeffrey B. Neaton[2], Dominic Ryan[3] and Hemamala Karunadasa[1]; [1]Stanford University, United States; [2]University of California, Berkeley, United States; [3]McGill University, Canada

Halide perovskites play an important role in the history of gold chemistry. In fact, some of the earliest examples of halide perovskites contain gold. The mixed-valence Au(I)/Au(III) double perovskites have been studied since the 1920s. We have recently expanded gold perovskites to new architectures, which stabilize unexpected oxidation states. I will describe the physical and electronic structures and the properties of these new perovskites. I will also discuss how relativistic effects play a dominant role in the chemistry of gold perovskites, engendering unusual properties not seen in their lighter analogs.

4:00 PM EL04.04.02
Synthetic Control of the Structural, Electronic and Optical Properties of Lead-Free Two-Dimensional Double Perovskites Rik Hooijer[1], Andreas Weis[1], Alexander Biewald[1], Maximilian Sirtl[1], Julian Malburg[1], Rico Holfeuer[1], Simon Thamm[1], Amir Abbas Yousefi Amin[1], Marcello Righetto[2], Melina Armer[3], Firouzeh Ebadi[4], Mahdi Mohammadi[4], Clément Maheu[5], Bas T. van Gorkom[6], Sebastian Häringer[1], Rene A. Janssen[6], Thomas Mayer[5], Vladimir Dyakonov[3], Wolfgang Tress[4], Achim Hartschuh[1], Laura Herz[2,7] and Thomas Bein[1]; [1]LMU München, Germany; [2]University of Oxford, United Kingdom; [3]Julius-Maximilians-Universität Würzburg, Germany; [4]ZHAW School of Engineering, Switzerland; [5]Technische Universität Darmstadt, Germany; [6]Technische Universiteit Eindhoven, Netherlands; [7]Technische Universität München, Germany

Hybrid halide perovskites have attracted enormous interest in the context of developing energy conversion processes towards a green, zero-carbon energy future. The structural exploration of this class of materials (three-dimensional (3D) perovskites) evolved from mainly lead- and tin-based perovskites to lead-free perovskites, double perovskites and low-dimensional substructures such as two-dimensional (2D) perovskites.

2D hybrid double perovskites are a promising emerging class of materials, possessing an even greater structural diversity and tunability than their three-dimensional (3D) parent structures. They are formed through a chemically introduced dimensional reduction of the 3D structure, where suitable organic cations intercalate between the inorganic perovskite layers. This offers access to a large compositional diversity of the inorganic and organic building units, while resulting in a naturally formed, crystallographically defined quantum well electronic structure.
We have employed different synthetic strategies to alter key properties of these 2D structures such as: i) the type of layered structure and their interlayer connectivity (i.e. Ruddlesden-Popper vs. Dion-Jacobson structures), ii) the electronic properties of the organic cations, and iii) the perovskite orientation in thin-film form, which impacts potential applications in different device architectures due to the anisotropic properties of 2D systems.
Starting from the $Cs_2AgBiBr_6$ double perovskite, we have expanded this system to Ag-Bi and Cu-Bi based 2D double perovskites with the halides chloride, bromide and iodide. We have designed different organic layers employing mono- or divalent organic cations of different size, as well as different central functional groups based on cyclohexane, phenyl, naphthalene, pyrene and perylene systems.
The resulting highly crystalline materials were characterized in bulk and thin film form and investigated with standard X-ray techniques as well as grazing incidence wide angle X-ray scattering (GIWAXS), revealing a strong dependence of morphology on substrate choice and synthesis parameters. First-principles calculations give insights into the tunability of the band gap and its nature and show the typical variations of the band alignment for these quantum well structures. Optical characterization techniques, temperature-dependent photoluminescence, and optical-pump terahertz-probe spectroscopy reveal the absorption and emissive behavior of these materials as well as their charge-carrier dynamics. Overall, we develop a comprehensive picture of the electronic and emissive properties of these intriguing materials, dominated by phonon-coupled and defect-mediated polaronic states.
Finally, we address some of the challenges for the pure 2D double perovskites, such as taking advantage of the anisotropic properties and the design and modulation of composition and synthesis towards their incorporation into different optoelectronic devices, while also demonstrating the synergy in 3D/2D heterostructures to improve the photovoltaic performance of $Cs_2AgBiBr_6$ solar cells.

4:15 PM EL04.04.03
Local Structure of Metal Halide Perovskite Glassy-Crystalline Phase Switching Damara G. Dayton[1], Julian Mars[1], Michael Toney[1], David B. Mitzi[2] and Akash Singh[2]; [1]University of Colorado Boulder, United States; [2]Duke University, United States

Amorphous metal halide perovskites (MHP) are a novel materials class with promising potential to broaden the MHP application space to include neuromorphic computing and switchable spintronics. We present a fundamental structural study of the first stable glassy MHP, [(S-(-)-1-(1- naphthyl) ethylammonium]$_2$PbBr$_4$ or "S-NPB", which demonstrates facile amorphous-crystalline phase switching with moderate cooling rates under ambient conditions. [1] Over the past several years, chiral 2D MHPs have garnered substantial research interest due to their chirality-induced Rashba-Dresselhaus spin splitting. Research interest is continually growing, but existing work is heavily focused on crystalline chiral MHPs for spintronic and optoelectronic applications. [2] Though crystallinity offers numerous advantages, we demonstrate further exploitation of the structural chirality transfer to induce glass formation and extend the associated MHP structure-property paradigm. The inherent tunability of MHPs is further enhanced through the inclusion of amorphous phases that offer unique physical properties. We present a comprehensive multimodal characterization strategy to interrogate the complex structure of the amorphous MHP phase and the inorganic-organic interfacial dynamics, addressing significant knowledge gaps within the community. This fundamental understanding of chiral MHP crystallization dynamics pioneers a new class of MHPs with promising potential for phase-change random access memory (PCRAM) neuromorphic computing architectures, and to replace high thermal-budget chalcogenides for optical storage applications.

Upon crystallization, the chirality originating in the chiral cation bilayer of the organic sublattice is transferred to the inorganic sublattice as in-plane angular octahedral distortions, inducing the high melt viscosity and melting depression that enable glass stabilization along with unprecedented thermal stability. [3] Due to S-NPB's inherent structural complexity, insightful structural analysis requires the development of a multimodal analysis strategy probing the local atomic order, thin film confinement effects, and inorganic-organic lattice coupling and interfacial dynamics. In our analysis, we employed several complex structural characterization techniques to probe the intrinsic phenomena over various length and time scales, namely Pair Distribution Function (PDF), polarization-dependent Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy, Raman Spectroscopy, Nuclear Magnetic Resonance (NMR), Quasi-elastic Neutron Scattering (QENS), and Grazing Incidence Wide Angle X-ray Scattering (GIWAXS). We conducted *in-situ* total scattering PDF studies supported with Reverse Monte-Carlo modeling, determining that the corner-sharing 6-fold octahedral coordination is largely maintained in the melt and glass, but disordered beyond the first coordination shell due to octahedral lattice distortions. The structure of the organic sublattice was informed with NEXAFS to selectively probe the chiral cation local coordination and orientation. To study the interfacial organic-inorganic dynamics, in-situ NMR and QENS were employed to identify the molecular motions facilitating the structural chirality transfer, attributed to H-bonding interactions with the terminal octahedral halide atoms. We conducted *in-situ* GIWAXS studies under various annealing conditions and temperature ramping rates to investigate and control S-NPB's morphological evolution and determine the rate-dependance of crystallization dynamics and enable the critical manipulation of crystal nucleation and growth to obtain preferred orientations. This multimodal approach establishes a comprehensive fundamental understanding of amorphous MHP structural dynamics, and presents the processing-structure-property relationships required to propose S-NPB as a promising candidate for PCRAM neuromorphic computing. [4]
Ref: A. Singh (2020),Q. Xiang (2018),M. Jana (2020),L. Wang (2020)

4:30 PM EL04.04.04
Photo-stable Lead Halide Wide Bandgap Perovskite Solar Cells through Frustration of Bromide Mediated I_2 Self-redox Yang Zhou[1], Simone V. Laar[2], Samuele Martani[1], Jia-Yong Heng[3], Kunal Datta[2], Jesús Jiménez-López[1], Feng Wang[4], E Laine Wong[1], Isabella Poli[1], Antonella Treglia[1], Daniele Cortecchia[1], Mirko Prato[1], Libor Kobera[5], Feng Gao[4], Ni Zhao[3], Rene A. Janssen[2], Annamaria Petrozza[1] and Giulia Folpini[1]; [1]Istituto Italiano di

Tecnologia, Italy; [2]Eindhoven University of Technology, Netherlands; [3]Chinese University of Hong Kong, Hong Kong; [4]Linköping University, Sweden; [5]Czech Academy of Sciences, Czechia

Bandgap tunability of metal-halide perovskites is a crucial characteristic for versatile optoelectronic applications. Nevertheless, halide photo-segregation in lead halide compounds impedes their exploitation when bandgaps larger than 1.65 eV are needed such as in perovskite/silicon and perovskite/perovskite tandem solar cells. Here, we show how the generation of I_2 in mixed-halide perovskites under illumination has a crucial role in halide segregation. In fact, I_2 reacts with bromide (Br^-) in the lattice to form a trihalide ion I_2Br^- (I^{d-}-I^{d+}-Br^{d-}), which mediates a Br^-/I^- ion exchange reaction and the formation of an I-rich phase. Importantly, we observe that the efficiency of the process is highly dependent on the binding strength of the bromide within the crystalline structure. Based on this, we propose a general paradigm where an iodine redox based model rationalizes the initiation and growth of halide photo-segregation. Thus, we show how the design of the chemical composition of the metal-halide perovskite crystalline unit can stabilize the semiconductor bandgap, and eventually the performance of related solar cells, not only acting on the reduction of the density of native defects, but stabilizing the elemental composition of the perovskite crystalline unit.

4:45 PM EL04.04.05
Optical Retardation in 2D Hybrid Copper Halides Lina Quan; Virginia Tech, United States

Light polarization and manipulation are important properties in many applications such as optical modulators, waveplates and also can generate qubits for quantum information technologies. To control the polarization, materials need to be response under polarized light due to either dichroism or birefringence. Although there are many candidate materials to perform the optical polarization effect, however, to achieve a broad range of wavelengths with homogeneous polarization is challenging. In this talk, I will present a new optical retardation material based on low-cost, non-toxic, organic-inorganic hybrid copper halide systems that exhibit strong optical anisotropy across a broad wavelength range. Such a broad degree of polarization control in hybrid copper halides offers new opportunities in polarization detectors and related applications.

SESSION EL04.05: Metal Halide Perovskites for Applications Beyond Solar V
Session Chairs: Virgil Andrei and Yoshihiko Kanemitsu
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3004

8:30 AM *EL04.05.01
Defect Tolerance in Halide Perovskites—A First-Principles Perspective Chris G. Van de Walle; University of California, Santa Barbara, United States

In recent years, the impressive photovoltaic performance of halide perovskites has been commonly attributed to their defect tolerance. This attribution seems intuitive and has been widely promoted in the field, but it has not been rigorously assessed. I will critically discuss the proposition of defect tolerance in halide perovskites based on state-of-the-art first-principles calculations. Rigorous assessments of defect formation energies and recombination rates demonstrate that halide perovskites actually *do* suffer from defect-assisted nonradiative recombination, i.e., they are *not* defect tolerant [1]. The nonradiative recombination rates in halide perovskites are comparable to or even greater than those in conventional semiconductors. We therefore conclude it is incorrect to call the halide perovskites “defect tolerant”. A more relevant distinction, compared to conventional semiconductors, is that halide perovskites with modest defect densities can be grown using low-cost deposition techniques; however, defect engineering is still key to improving the efficiency of perovskite solar cells.
For the prototypical hybrid perovskite $MAPbI_3$ [MA=(CH_3NH_3)] our results indicate that iodine interstitials are most harmful, and hence iodine-rich synthesis conditions should be avoided [2]. Experimental reports have indicated, however, that iodine-poor conditions are also detrimental. We explain this puzzle by demonstrating that iodine-poor conditions lead to formation of hydrogen vacancies on the MA molecule, which act as very efficient nonradiative recombination centers [3]. By contrast, hydrogen vacancies are not a problem in $FAPbI_3$ [FA=$CH(NH_2)_2$], rationalizing why FA is essential for realizing high efficiency in hybrid perovskites. Our findings also indicate the advantages of avoiding the organic cation altogether [4]. We show that the common belief that the organic cation suppresses defect-assisted nonradiative recombination is unfounded. Our study suggests that all-inorganic halide perovskites hold great promise for high-efficiency optoelectronic applications.

Work performed in collaboration with X. Zhang, M. Turiansky, and J.-X. Shen, and supported by DOE.

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9:00 AM EL04.05.02
Symmetry-Breaking and Reconstruction at Point Defects in Perovskite Semiconductors Seán R. Kavanagh[1,2], Irea Mosquera-Lois[2], Aron Walsh[2] and David O. Scanlon[1]; [1]University College London, United Kingdom; [2]Imperial College London, United Kingdom

Point defects are a universal feature of crystalline materials, dictating the functional performance of materials across a wide range of applications (transistors, thermoelectrics, LEDs, power electronics, transparent conductors, photovoltaics…). The standard approach of simulating defects is, however, prone to miss the ground state atomic configurations associated with energy-lowering reconstructions from the high-symmetry crystal environment.[1–5] By yielding both incorrect energies and structures, this failing of current defect calculation approaches compromises the accuracy of calculated properties and behaviour of defects in semiconductors.

To address this issue, we report an approach to efficiently navigate the defect configurational landscape using targeted bond distortions and rattling.[6] Application of our workflow to a range of materials (ranging from perovskites to conventional semiconductors) reveals symmetry breaking in each material that is not found via conventional local minimization techniques. We demonstrate the impact of these reconstructions on derived properties, including formation energies, concentrations and charge transition levels of defects in perovskite materials and beyond.

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4. Kavanagh, S. R., Walsh, A. & Scanlon, D. O. Rapid Recombination by Cadmium Vacancies in CdTe. *ACS Energy Lett.* **6**, 1392–1398 (2021).
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7. Mosquera-Lois, I., Kavanagh, S. R., Walsh, A., Scanlon, D. O. ShakeNBreak: Efficiently navigating the defect configurational landscape. *J Open Source Software* (In submission; https://github.com/SMTG-UCL/ShakeNBreak)

9:15 AM EL04.05.03
Studying Defect Density Distributions in Mixed Perovskites Mriganka Singh, Michel D. Keersmaecker and Erin L. Ratcliff; University of Arizona, United States

The immoderate distribution of defects at grain boundaries (GBs), interfaces, and surfaces are dominant factors for highly efficient and stable perovskite solar cells. Here, we introduced an effective way to suppress interfacial defect densities using ionic liquids (ILs; 1-methyl-3-octylimidazolium tetrafluoroborate: $C_{12}H_{23}BF_4N_2$) as the surface passivation which accelerates the perovskite crystallization via two-step spin coating formed metal halide mixed perovskites without solvent engineering. Using a solid-state electrochemical approach [Ref 1], we measure defect densities for SnO_2/perovskite stacks with or without doping of ILs. To study defect density distributions of passivated and unpassivated SnO_2/perovskite films, the carrier recombination velocities of individual GBs are measured at the microscope scale by mapping the photoluminescence pattern in which changes in nonradiative recombination of carriers at GBs are captured.

Keywords: *Operando characterization, Electrochemistry, Mixed perovskite, Surface passivation, solar cells.*

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9:30 AM EL04.05.04
Controlled Passivation by Lead Halides of Interfacial Defects of Perovskite Films for Emerging Electronic Applications Jihyun Kim, William Jo and Seho Yi; Ewha Womans University, Korea (the Republic of)

In mixed organic–inorganic lead halide perovskites $APbX_3$ (A = methylammonium (MA) or formamidinium (FA); X is Cl, Br or I), the formation of secondary-phase excess lead iodide (PbI_2) has some positive effects as a grain-boundary passivation on interstitial defects but can be detrimental to device stability and lead to large hysteresis effects in voltage sweeps. We converted PbI_2 into an inactive (NH_4^+)-PbI_2 compound via pre-extracted NH_4+/SnO_2 by NH_4Cl passivator [1], which effectively stabilizes the perovskite crystalline phase. These effects were discussed with density functional theory (DFT) and shown to grain voltage sweep measurement by conductive atomic force microscopy (C-AFM) and surface photo-voltage by illuminated Kelvin probe force microscopy. We compared the current and voltage properties for insulating domains of PbI2, (Cl)-PbI_2, and (NH_4^+)-PbI_2 in-situ perovskite films. The ferro-electric properties were discovered on PbI_2 and (Cl)-PbI_2, on the other hand (NH_4^+)-PbI_2 show no ion migration. This means that inactive (NH_4^+)-PbI_2 effects can be stabilized the indiscriminate ion movements on the perovskite-based optoelectronics. As a result, the perovskite solar cells (PSCs) achieve an average efficiency of 21.57 ± 0.45 % and best efficiency of 22.25 % [2] due to the dramatically enhanced open circuit voltage by 1.180 V, which is the main effect of efficiency improvement, and increase the operational device stability over 50 days in ambient conditions with ~50 % of relative humidity. It is very curious that the results also show passivated interface is an effective way to modify bifacial defects and electronic structures improving charge configuration with high resistant / low resistant states and its transfer and extraction, and eventually it is leading to new emergent electronic devices.
[1] J. H. Kim, Y. S. Kim, H. R. Jung, and W. Jo, "Chlorine-passivation of the ozone-treated SnO_2 thin films: occurrence of oxygen vacancies for manipulation of conducting states and bipolarities in resistive switching", Applied Surface Science 555, 149625 (2021).
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9:45 AM EL04.05.05
Degenerate Lattice Instability-Driven Amorphization under Compression in Metal Halide Perovskite $CsPbI_3$ Jung-Hoon Lee and Seho Yi; Korea Institute of Science and Technology, Korea (the Republic of)

Due to their good optoelectronic properties and inexpensive cost, halide perovskites have been intensively investigated for photovoltaic applications. Different high-pressure experiments report that they generally undergo the reversible phase transitions between different crystalline phases and between crystalline and amorphous phases under an external pressure. Herein, using first-principles density-functional theory (DFT) and ab-initio molecular dynamics (AIMD) calculations, we investigate the origin of the pressure-induced amorphization in halide perovskite $CsPbI_3$. We find that the amorphous-like structures obtained from AIMD calculations become more stable than the orthorhombic *Pbnm* phase above 6.66 GPa, in good agreement with the experimental value (4.44 GPa). Intriguingly, we further find that an imaginary flat band appears in the phonon dispersion of the orthorhombic $CsPbI_3$ phase across the Brillouin zone at 10 GPa, leading to degenerate lattice instabilities. We demonstrate that these energetically degenerated phonon modes are related to PbI_6 octahedral tilting modes and provide random local distortions, leading to amorphization. Our findings contribute to a greater comprehension of the mechanism behind the pressure-induced amorphization in halide perovskites.

10:00 AM BREAK

SESSION EL04.06: Metal Halide Perovskites for Applications Beyond Solar VI
Session Chairs: Mriganka Singh and Chris Van de Walle
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3004

10:30 AM *EL04.06.01
Mixing and Matching Organic Cations in 2D Perovskites Rand L. Kingsford and Connor G. Bischak; The University of Utah, United States

Two-dimensional Ruddlesden-Popper perovskite quantum wells have an incredible degree of synthetic flexibility, as their optoelectronic and physical properties can be tuned by changing the halide or the organic cation spacer molecules. Mixing organic cations is a promising, yet underexplored, way to tune the properties of 2D perovskites. The underlying thermodynamics of whether organic cations will mix or phase separate is not well understood. Here, we investigate organic cation mixing in 2D perovskites and demonstrate that whether cations mix or demix depends on their chemical properties and length. We find that we can tune the phase transition temperature of organic cations in the 2D perovskites by blending alkylammonium cations of different length. We also show that cations with distinctly different chemical properties phase separate and we investigate the nanoscale ordering if these phase-separated perovskite domains using nanoscale infrared imaging with photoinduced force microscopy (PiFM). Our results demonstrate that cation mixing is a powerful way to tune thermodynamic properties of 2D perovskites and template these materials at the nanoscale.

11:00 AM EL04.06.02
Lightweight, Floating Perovskite-BiVO$_4$ Tandem Devices for Scalable Artificial Photosynthesis Virgil Andrei[1,1], Geani M. Ucoski[1], Robert Jagt[1], Chanon Pornrungroj[1], Demetra S. Achilleos[1], Katarzyna Sokol[1], Judith MacManus-Driscoll[1], Robert Hoye[2], Richard Friend[1] and Erwin Reisner[1]; [1]University of Cambridge, United Kingdom; [2]Imperial College London, United Kingdom

Photoelectrochemical (PEC) artificial leaves hold the potential to lower the costs of sustainable solar fuel production by integrating light harvesting and catalysis within one compact device. However, current deposition techniques limit their scalability, while fragile and heavy bulk materials can affect their transport and deployment. Here, we demonstrate the fabrication of lightweight artificial leaves by employing thin, flexible substrates and carbonaceous protection layers.[1] Lead halide perovskite photocathodes deposited onto indium tin oxide coated polyethylene terephthalate achieve an activity of 4266 μmol H_2 g^{-1} h^{-1} using a platinum catalyst, whereas photocathodes with a molecular Co catalyst for CO_2 reduction attain a high CO:H_2 selectivity of 7.2 under a lower 0.1 sun irradiation. The corresponding lightweight perovskite-BiVO$_4$ PEC devices display unassisted solar-to-fuel efficiencies of 0.58% (H_2) and 0.053% (CO),respectively. Their potential for scalability is demonstrated by 100 cm^2 standalone artificial leaves, which sustain a comparable performance and stability of ≈24 h to their 1.7 cm^2 counterparts. Bubbles formed under operation further enable the 30-100 mg cm^{-2} devices to float, while lightweight reactors facilitate gas collection during outdoor testing on a river. The leaf-like PEC device bridges the gulf in weight between traditional solar fuel approaches, showcasing activities per gram comparable to photocatalytic suspensions and plant leaves.[1] The presented lightweight, floating systems are compatible with modern fabrication techniques,[2] and may enable open water applications, while avoiding competition with land use.

[1] Andrei, V.; Ucoski, G. M.; Pornrungroj, C.; Uswachoke, C.; Wang, Q.; Achilleos, D. S.; Kasap, H.; Sokol, K. P.; Jagt, R. A.; Lu, H.; Lawson, T.; Wagner, A.; Pike, S. D.; Wright, D. S.; Hoye, R. L. Z.; MacManus-Driscoll, J. L.; Joyce, H. J.; Friend, R. H.; Reisner, E., Nature 2022, 608, 518–522.
[2] Sokol, K. P.; Andrei, V. Nat. Rev. Mater. 2022, 7, 251–253.

11:15 AM EL04.06.03
Perovskite Grain Wrapping by Converting Interfaces and Grain Boundaries into Robust and Water-Insoluble Low Dimensional Perovskites Haoyang Jiao; University of North Carolina at Chapel Hill, United States

Stabilizing perovskite solar cells need to consider all defective sites in the devices. Significant efforts have been devoted to stabilizing interfaces, while stabilization of grain boundaries received less attention. Here we report a molecule tributyl(methyl)phosphonium iodide (TPI), which can convert perovskite into a wide bandgap one-dimensional (1D) perovskite that is mechanically robust, water-insoluble. Adding TPI into perovskite precursor results in a wrapping of perovskite grains with both grain surfaces and grain boundaries converted into several nanometer-thick 1D perovskites during the grain-formation process as observed by direct mapping of it. The grain wrapping passivates the grain boundaries, enhances their resistance to moisture, and reduces the iodine released during light soaking. The perovskite films with wrapped grains are more stable under heat and light. The best device with wrapped grains maintained 92.2% of its highest efficiency after light soaking under one sun illumination for 1900 hours at 55 °C open circuit condition.

11:30 AM *EL04.06.04
Halide Perovskite Thin-Film Growth Control via Pulsed Laser Deposition—A Single-Source, Dry, Vapor Deposition Approach Monica Morales-Masis; University of Twente, Netherlands

The adoption of new semiconductor materials in high-end technologies, such as multi-junction devices, integrated circuits and other, demands fabrication processes that allow a high level of control over film properties such as composition, microstructure, thickness and conformality. The ability to control the film formation of semiconductors like indium phosphide, gallium arsenide, and several metal oxides and nitrides, opened the way for applications such as light emitting devices, high-efficiency photovoltaics and integrated electronics and photonics. Halide perovskites have demonstrated a huge potential in optoelectronic applications, and as the understanding and compositional landscape increases for this family of materials, interesting properties for applications beyond optoelectronics are being investigated. The ability to control the growth of these new perovskites in thin film form, with flexibility for composition exploration and full control on polymorph and thickness will aid the experimental validation of new physical phenomena as well as the exploration on various applications. In this presentation, we will discuss how we leverage pulsed laser deposition (PLD) as a unique single-source vapor deposition method allowing near-stoichiometric transfer of multi-compounds from a single solid target to a thin film. We demonstrate PLD of a variety of compounds from multi-organic cation perovskites, to inorganic halide perovskites and chalco-halide perovskites. The critical role of the PLD parameters to control deposition rate and microstructure from polycrystalline up to epitaxial formation will be discussed. In addition to growth control, PLD allows for heterostructure formation, conformal deposition and patterning, all important steps for integration in various device platforms. This work proposes strategies for growth control, versatile film deposition and the possibility of complex device integration of a large variety of halide perovskite compositions.

SESSION EL04.07: Metal Halide Perovskites for Applications Beyond Solar VII
Session Chairs: Virgil Andrei and Jeffrey Neaton
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3004

1:30 PM *EL04.07.01
Exciton Photophysics of Halide Perovskites for Novel Applications Yoshihiko Kanemitsu and Go Yumoto; Kyoto University, Japan

Halide perovskite semiconductors exhibit unique optical, transport, and thermal properties even at room temperature. High-quality perovskite samples show no light scattering losses, high optical transparency in the visible and near-infrared regions, and efficient photoluminescence with no essential Stokes shift. Therefore, the dynamics of charge carriers, excitons, and spins can be studied using optical spectroscopy. We studied the exciton properties of halide perovskites using nonlinear optical spectroscopy, single dot spectroscopy, and terahertz spectroscopy [1-7]. In this talk, we discuss the exciton-phonon interactions, exciton-exciton interactions, and higher harmonic generation for optical refrigeration, spintronics, and light source applications.

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[4] G. Yumoto *et al*., *Nature Commun.* **12**, 3026 (2021).
[5] F. Sekiguchi *et al*., *Phys. Rev. Lett.* **126**, 077401 (2021).
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[7] Y. Sanari *et al*., *Phys. Rev. B* **102**, 041125(R) (2020).

2:00 PM EL04.07.02
Leveraging *Operando* Methodologies to Reveal Chemical Mechanisms for Perovskite Degradation Michel De Keersmaecker, Neal R. Armstrong and Erin L. Ratcliff; The University of Arizona, United States

To control lead halide perovskite degradation, characterization strategies have mostly counted on researcher dependent models that try to understand mechanisms by indirectly measuring defects, but rarely their chemical makeup and reactivity under stress are considered part of the long-term stability problem. To probe reactive defects and correlate their chemical composition to ultimately comprehend degradation mechanisms, the community will need to move towards powerful and advanced characterization tools that measure the chemical, electronic and physical evolution under real-time operation. Here, we demonstrate *operando* methodologies based on an innovative electrochemical approach that starts from a “peel and stick” electrochemical half-cell device stack that uses a solid elecrolyte top contact. Systematic potential modulation polarizes any chosen interface of any type of device stack to measure defect concentrations and their electrochemical activity. By integrating this probe into an environmental chamber, we reveal the evolution of defect concentrations and structural data under relevant bias and specifically chosen accelerated aging conditions. With the help of a near-ambient pressure X-ray photoelectron spectroscopy approach, we have recently discovered a realistic mechanism for the environmental degradation of lead halide perovskites linking both experimental and theoretical efforts in this field.
In conclusion, this electrochemical probe and its combination with complementary methods is shown to promote *operando* analysis of thin film perovskites, but potentially also (in)organic semiconductors, quantum dots, material blends and device stacks, where the removable electrolyte functions as a removable top contact. This type of advanced characterization platform will prove to be crucial for the improvement of perovskite stability and durability to close the gap towards an industry-scalable perovskite-based technology in the field of photovoltaics, spintronics, electrochemical charge storage systems, photoelectrochemical cells, etc.

2:15 PM EL04.07.03
Hidden Spin-Splitting in Globally Centrosymmetric 2D Ruddlesden-Popper Halide Perovskites Willa Mihalyi-Koch[1], Dongxu Pan[1], Zhenbang Dai[2], David P. Lafayette[1], Kyana M. Sanders[1], Simon Teat[3], Ilia A. Guzei[1], John C. Wright[1], Andrew M. Rappe[2] and Song Jin[1]; [1]University of Wisconsin–Madison, United States; [2]University of Pennsylvania, United States; [3]Lawrence Berkeley National Laboratory, United States

2D hybrid lead halide perovskites have emerged as promising materials for spintronic applications due to the observation of spin splitting effects when the inversion symmetry of the crystal structure is broken. The organic cations incorporated into the 2D structure template the lead iodide octahedral network, often dictating the resulting crystal symmetry. Unlike 3D perovskites, 2D Ruddlesden-Popper (RP) perovskites can host larger, oversized A-cations in the perovskite cage formed by corner-sharing lead iodide octahedra. Here we report crystal structures for a series of 2D lead iodide perovskites containing a set of six different A-site cations of varying size for the first time. The resulting library of 2D RP perovskites exhibit varying levels of symmetry breaking at the octahedral, layer, and unit cell levels. Second harmonic generation is used to experimentally investigate such complex scenarios of symmetry breaking. Several globally centrosymmetric structures exhibit polar layer symmetry, leading to calculated hidden spin polarization effects analogous to inorganic 2D materials such as MoS_2. This work suggests the existence of a large hidden class of centrosymmetric 2D RP perovskites that can be utilized for spintronic applications through perturbation of the compensated symmetry.

2:30 PM BREAK

SESSION EL04.08: Metal Halide Perovskites for Applications Beyond Solar VIII
Session Chairs: Linn Leppert and Carolin Sutter-Fella
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3004

3:30 PM EL04.08.01
Molecular Doping Strategy in Low Dimensional Perovskites by Dopant Intercalation Keehoon Kang[1], Jonghoon Lee[1], Kyeong-Yoon Baek[1], Henning Sirringhaus[2], Jeongjae Lee[1] and Takhee Lee[1]; [1]Seoul National University, Korea (the Republic of); [2]University of Cambridge, United Kingdom

Doping has been one of the most essential methods to control charge carrier concentration in semiconductors. In metal halide perovskite, which have revolutionized the field of solar cells and light-emitting diodes due to their favorable optoelectrical properties, extensive doping via atomic substitution still remains challenging due to their structural stability limited by tolerance factor and compensation of intentionally introduced defects by mobile halide ions. As an alternative non-invasive approach for, concepts utilizing molecular dopants for surface charge transfer doping have been previously reported for tuning the conductivity of metal-halide perovskite. However, most of the reports have been focused on charge transfer effects at the interface or grain boundaries which have limited the range of doping attainable. In this work, we use strong molecular p-dopant, tris(4-bromophenyl)ammoniumyl hexachloroantimonate (magic blue), for significantly improving the electrical conductivity of low-dimensional perovskite films. We identify that dopant incorporation into the bulk of the film as the structural origin of the improved conductivity and propose the solvent selection criteria for achieving effective molecular doping, which can potentially open up a controllable route towards tuning electronic structure for optimizing perovskite-based devices.

3:45 PM EL04.08.02
Anisotropy of Phonon Transition Dipole Moments and Hints of Anisotropy in the Photoconductivity of Single-Crystalline Two-Dimensional Lead-Halide Perovskites Jaco Geuchies[1], Johan Klarbring[2], Shuai Fu[1], Lucia Di Virgilio[1], Sheng Qu[1], Hai Wang[1], Maksim Grechko[1], Jarvist M. Frost[2], Aron Walsh[2], Mischa Bonn[1] and Heejae Kim[1]; [1]Max Planck Institute for Polymer Research, Germany; [2]Imperial College London, United Kingdom

The lattice of hybrid organic-inorganic metal halide perovskites is both soft and ionic. The particular combination gives rise to interesting molecular physics: electrons in these materials are strongly coupled to vibrations and phonons. Analogous to the solvation of ions in water, when the coupling between vibrations and charge carriers is strong enough, it leads to the formation of polarons, where the charge carrier and lattice vibration cannot be disentangled into two separate entities anymore. Here, we study single crystals of butylammonium lead iodide (BAPI), a two-dimensional perovskite structure, with different, but well defined, thicknesses of the inorganic lattice. We measured angle-and-polarization dependent THz transmission through the samples to study the directionality of the transition dipole moments (TDMs) of vibrational modes between 0.3 – 3 THz; the vibrations in the inorganic planes inside the lattice. Next to this, we use optical-pump/THz probe spectroscopy to measure the materials' photoconductivity along different crystallographic directions. We find signatures of higher photoconductivity in the direction perpendicular to the 1 THz TDMs compared to parallel to it, and discuss possible origins of this phenomenon by comparison to theory.

4:00 PM *EL04.08.03
Excitons in Quasi-Two Dimensional Metal Halide Perovskites from First Principles Computational Modeling Marina Filip; University of Oxford, United Kingdom

Quasi-two dimensional organic-inorganic metal-halide perovskites are a family of solutionprocessable semiconductors of unparalleled chemical and structural heterogeneity. Starting from prototypical 3D perovskites, organic cations of different sizes, shapes and charges can be used to "carve" out inorganic metal-halide layers of different thicknesses, shapes and alignments in a controlled way, leading to so-called Ruddlesden-Popper or Dion-Jacobson type perovskites, as well as other more complex structures, including perovskite-intergrowth hetero-structures [1,2]. These quasi-low dimensional systems combine the tunability of the optoelectronic properties of 3D perovskites, with quantum- and dielectric-confinement, and give rise to a wide range of excited state phenomena. In this talk I will present our study of the photophysical properties of Ruddlesden- Popper and Dion-Jacobson layered perovskites, using Green's functions based first principles
methods within the GW approximation [3] and the Bethe-Salpeter equation [4]. I will discuss the dielectric properties of layered perovskites, and present how the A-site cation takes a central role in the screening of excitons in layered perovskites [5]. Furthermore, I will present recent results on understanding the effect of layer alignment and interlayer distance on the photophysical properties of quasi-2D halide perovskites.
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We acknowledge funding by the UK-EPSRC and computational resources from Archer (through the MCC consortium), NERSC (via the Molecular Foundry User Program), TACC (via the NSFXSEDE program), Summit (via the DOE-INCITE program) and Marconi100 (via the PRACE program).

4:30 PM EL04.08.04
Photo-Induced Spin-Spin Coupling in Doped Organic-Inorganic Hybrid Perovskites Tao Xu; Northern Illinois University, United States

The fundamental understanding of light-matter interaction can provide mechanistic guidance to enhance the carrier generation and transport efficiency in photovoltaic materials. We will present a set of intriguing photo-induced spin-spin interaction between photoelectrons and dopants in organic-inorganic hybrid perovskites provides. We show that at cryogenic temperature, the spin impurity dopants and the light-induced photoelectrons exhibits strong spin coupling via exchange interaction which can further be modulated.

4:45 PM EL04.08.05
Manipulating Thermal Transport in Two-Dimensional Organic–Inorganic Perovskites Rahil Ukani[1], Alexander Christodoulides[2], Qichen Song[1], Ryan McGillicuddy[1], Yukyung Moon[1], Hong Ki Kim[1], Jinyoung Seo[1], Jonathan A. Malen[2] and Jarad A. Mason[1]; [1]Harvard University, United States; [2]Carnegie Mellon University, United States

Two-dimensional (2-D) organic–inorganic perovskites containing first-row transition metals and long-chain organic cations have recently been explored for thermal applications, including thermal energy storage and solid-state barocaloric cooling. Controlling the thermal conductivity of these materials is essential to capturing their value in practical systems, yet few studies have examined the transport mechanisms of these structures. Most importantly, much remains to be understood about the chemical and structural factors that regulate thermal transport at a molecular level. We report systematic investigations into the thermal conductivity of 2-D perovskites, seeking to understand the role of chemical interactions at the organic–organic interface in dictating thermal transport. Variable temperature frequency-domain thermoreflectance and nanomechanical indentation measurements were performed on a library of 2-D Mn–Cl perovskites to probe the relationship between structural features and the character of thermal vibrations. These measurements were carried out across their order–disorder phase transitions to evaluate the effects of structural disorder on thermal transport. Additionally, 2-D perovskites whose organic bilayers feature an array of chain flexibilities and chemical interaction networks have been explored in the context of tuning thermal conductivity *via* interlayer adhesion strengths.

SESSION EL04.09: Poster Session: Metal Halide Perovskites for Applications Beyond Solar
Session Chairs: Sebastian Reyes-Lillo and Carolin Sutter-Fella
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL04.09.01
Integrated Photoelectrochemical Devices for Solar Water-Splitting with Silicon-Perovskite Tandems at >21% STH Austin Fehr[1], Ayush Agrawal[1], Faiz Mandani[1], Chris Conrad[1], Qi Jiang[2], Soyeon Park[2], Olivia J. Alley[3], Bor Li[4], Siraj Sidhik[1], Isaac Metcalf[1], Chris Botello[1], James Young[2], Jacky Even[5], Jean-Christophe Blancon[1], Todd G. Deutsch[2], Kai Zhu[2], Steve Albrecht[4], Francesca Maria Toma[3], Michael Wong[1] and Aditya D. Mohite[1]; [1]Rice

University, United States; [2]National Renewable Energy Laboratory, United States; [3]Lawrence Berkeley National Laboratory, United States; [4]Helmholtz-Zentrum Berlin, Germany; [5]Institut national des sciences appliquées de Rennes, France

Low-cost green hydrogen is a critical objective for the renewabilization of chemical manufacturing and as an energy carrier for a clean energy economy. Integrated photoelectrochemical cells (PECs) directly couple the photoabsorber, anticorrosion barriers, and electrocatalysts to the electrolyte so that photogenerated carriers carry out electrochemistry on the device surface, resulting in lower costs and improved performance. State-of-the-art PECs have used III-V panel photoabsorbers and are limited by high cost. Alternative absorbers like Si have insufficient voltage, and particle photocatalysts, while stable, are inefficient. Halide perovskites are promising next-generation semiconductors which offer impressive photovoltaic performance at low cost.

Here, we demonstrate a high-efficiency halide perovskite-based photoelectrochemical device with solar-to-hydrogen efficiency. The HaP-PEC is enabled by the development of a high-performance anticorrosion barrier technology which is modular, scalable, low-cost, and importantly introduces no observable losses through series resistance or cell damage on deposition. This means that the photovoltaic efficiency is perfectly delivered to the catalyst active site. Using this approach, we demonstrate perfect preservation of photovoltaic efficiency for single and multijunction perovskite PECs, and a tandem silicon-perovskite photoanode with STH = 21.5% and t_{60} lifetime = 102 hours, which to the best of our knowledge is a record efficiency and state-of-the-art stability across all published PEC demonstrations. These figures of merit represent the first demonstration of high PEC efficiency coupled with low-cost photoabsorbers and pave a path to a surprising commercial pathway for halide perovskite devices producing solar fuels.

5:00 PM EL04.09.02

Impact of the Layer Number on the Biexciton Binding Energy in 2D Perovskite Series $[CH_3(CH_2)_3NH_3]_2(CH_3NH_3)_{n-1}Pb_nBr_{3n+1}$ (n = 1–3) Jun Sang Cho[1], Hyun Kyung So[1], Eugenia S. Vasileiadou[2], Mercouri G. Kanatzidis[2], Myung Hwa Jung[1] and Joon Ik Jang[1]; [1]Sogang University, Korea (the Republic of); [2]Northwestern University, United States

The Ruddlesden-Popper (R-P) series of metal organic halide perovskites can host tightly bound excitons even at room temperature due to strong quantum confinement. [1] This implies that two-dimensional (2D) confinement can also enhance the stability of their Coulomb bound state, the so-called biexciton. This confinement effect is supposed to increase when decreasing the perovskite layer number (n) in the Br-based R-P perovskite series, $(BA)_2(MA)_{n-1}Pb_nBr_{3n+1}$ ($BA = CH_3(CH_2)_3NH_3$, $MA = CH_3NH_3$, n = 1–3). Recently, it was shown that biexcitons are formed by binding of two dark excitons, which are stable up to around 100 K in $(BA)_2PbBr_4$ (n = 1). [2] However, there is no comprehensive study on the stability of biexcitons upon tuning the confinement effect by varying the layer number in the R-P series. Herein, we investigate the impact of quantum confinement on the biexciton binding energy as a function of n = 1–3 by employing precision photoluminescence (PL) spectroscopy and second harmonic generation (SHG) measurement. Based on the series of PL spectra obtained as a function of excitation intensity, polarization, and temperature, the biexciton binding energies are precisely determined to be 18.7, 25.5, and 12.0 meV at 10 K for n = 1, 2, and 3, respectively. Therefore, our results unexpectedly indicate that the quantum confinement effect seems to be strongest at n = 2, not n = 1. However. we show that this anomaly arises basically from the unusually small exchange interaction at n = 2, which is 6.9 meV. This value is much smaller than 21.8 meV (n = 1) and 12.6 meV (n = 3). Temperature-dependent SHG and PL spectra clearly demonstrate that this small dark-bright splitting energy of 6.9 meV is associated with a newly discovered structural phase transition near 100 K, occurring only in the n = 2 perovskite. We will discuss the nature of the structural phase transition and its impact on the dark-bright splitting that directly affects the biexciton binding energies of the series. Our study will deepen the understanding of the excitonic fine structure and structural phase transition as a function of layer number in these important materials and potentially pave a way toward 2D excitonics.

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5:00 PM EL04.09.03

Carrier Multiplication in Perovskite Solar Cells Yue Wang, Senyun Ye, Jia Wei Melvin Lim, David Giovanni, Minjun Feng, Jianhui Fu, Harish N. Krishnamoorthy, Qiannan Zhang and Tze Chien Sum; Nanyang Technological University, Singapore

Harnessing solar energy is one of the sustainable methods for addressing the deepening energy crisis. Perovskite solar cells (PSC) emerged as a rising star due to their outstanding power conversion efficiency (PCE) which increased to more than 25% over a decade of development.[1] However, the theoretical maximum efficiency of single junction solar cells, which is also known as the Shockley-Queisser (SQ) limit, is around 33%.[2] One of the main loss pathways is the dissipation of excess energies of hot carriers into heat through lattice vibration.[3] Carrier multiplication (CM) or multiple exciton generation (MEG), generating multiple carriers or electron-hole pairs from the absorption of a single high-energy photon, is hailed as one of the advanced photovoltaic concepts to break the SQ limit.[4] Although CM/MEG effects in halide perovskites have been extensively studied primarily using ultrafast transient absorption (TA) spectroscopy on bare perovskite films, there remain several open questions on whether CM would (i) manifest in an actual PSC device operating under solar illumination; and whether it could (ii) contribute to performance enhancements. Here, we combine both the spectroscopic techniques and solar cell device performance studies to carefully assess the contributions from CM to the overall performance. Our findings provide new insights into the intricate interplay of numerous parameters that may negate the contribution of CM on PSC performance. I will also discuss about the challenges and opportunities to leverage this untapped potential to further enhance PSC performance using CM effects.

5:00 PM EL04.09.04

Tailoring the Thermal Conductivity of Two-Dimensional Metal Halide Perovskites Sandip Thakur and Ashutosh Giri; University of Rhode Island, United States

Proper thermal management of solar cells based on metal halide perovskites (MHPs) is key to replacing and surpassing the efficiencies attainable in the widely used silicon-based photovoltaics. In that aspect, the enhancement in thermal stability of two-dimensional (2D) MHPs with respect to their three-dimensional counterparts positions them as the next generation materials to revolutionize energy storage and conversion. However, the ultralow thermal conductivities of the 2D MHPs and the limited understanding of the heat transfer mechanisms in these materials is still a major bottleneck for their large scale incorporation in photovoltaic devices. Herein, we provide a detailed analysis of the heat transfer mechanisms in 2D MHPs through both experimental and computational approaches demonstrating a novel strategy to engineer enhanced thermal conductivities in these materials.

We use the time-domain thermoreflectance technique to measure the thermal conductivities of 0.19 ± 0.03 W m^{-1} K^{-1} and 0.18 ± 0.03 W m^{-1} K^{-1} for the Ruddlesden-Popper (RP) and Dion-Jacobson (DJ) phases of 2D MHPs (n=1) with 13.6 Å and 6.3 Å interlayer inorganic separations, respectively. Through our computational and experimental results, we find that changing the size of the organic spacers in between the 2D inorganic layers has a negligible influence in the thermal transport properties of these materials. We attribute this to coherent heat transport rather than incoherent scattering at the hybrid interfaces dictating the vibrational properties of these 2D MHPs. In contrast to conventional approaches utilized to increase thermal conductivity in layered materials (such as by decreasing interfacial scattering of phonons via reducing the interface density), we show that decreasing the distance between adjacent organic cations (by up to 40%) can lead to more than threefold increase in overall heat conduction which is mainly driven by the vibrational hardening of the organic spacers. Our experimental measurements along with our atomistic simulations provide new insights into the underlying physics and provide valuable strategies for tailor-made thermal conductivities in 2D MHPs, an emergent material for solar cell applications.

5:00 PM EL04.09.05

Exciton Quantum Coherence and Spin Relaxation in Halide Perovskite Nanocrystals Rui Cai, Indrajit Wadgaonkar, Jia Wei Melvin Lim, Stefano Forno, David Giovanni, Minjun Feng, Senyun Ye, Marco Battiato and Tze Chien Sum; Nanyang Technological University, Singapore

The recent discoveries of exciton fine structure splitting (FSS) in perovskite nanocrystals (NCs)[1, 2] suggest their great potential in optospintronics and quantum technologies. However, the coherent manipulation of these FSS states and the exciton multilevel coherence are lacking. Here, we provide new insights into the exciton and spin physics in ensembles of $CsPbBr_3$ NCs using ultrafast spectroscopy, including the observation and coherent control of exciton quantum beating and the underlying mechanisms for exciton spin decoherence.

First, the FSS multilevel coherence will be discussed with a quantum beating model. Using transient absorption (TA) spectroscopy, we observe periodically modulated TA kinetics that are sensitive to the light helicity, which enables ultrafast control of the excitonic degree of freedom. The low-temperature oscillatory dynamics allow to estimate the average FSS energies that are comparable to these measured by single-particle photoluminescence. The exciton spin relaxation mechanisms in halide perovskite NCs, which are now under intense debate will also be discussed. Combining the temperature-dependent exciton spin lifetimes with a Monte Carlo simulation, we present a full physical picture of the exciton spin depolarization processes. The dominating spin decoherence mechanism varies with both temperature and nanocrystal size, showing temperature crossovers from one mechanism to the other. The thorough understanding of exciton spin dynamics provides guidance for spin engineering in halide perovskites and their optospintronic applications.

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2. Tamarat, P. et al. *Nature Materials* **18**, 717-724 (2019).

5:00 PM EL04.09.06

Practical Demonstration of Deep-Ultraviolet Detection with Wearable and Self-Powered Halide Perovskite-Based Photodetector Thi My Huyen Nguyen[1], Shinkyu Lee[1], Sangmo Kim[2] and Chung Wung Bark[1]; [1]Gachon Univ, Korea (the Republic of); [2]Sejong University, Korea (the Republic of)

Flexible and self-powered photodetectors (PDs) have become one of the most popular topics, attracting researchers in the field of optoelectronic applications. In this study, for the first time, we demonstrate partial discharge detection in a practical environment with a prepared flexible device. Poly(vinylidene fluoride) (PVDF) is utilized as a highly transparent material in the UVC region, to create a flexible substrate with the antihumidity property. A detector that uses a mixed-halide perovskite $(FAPbI_3)_{1-x}(MAPbBr_3)_x$ as the photoactive material is constructed in a vertical structure on the as-prepared hydrophobic PVDF substrate. The fabricated device exhibits good performance with a fast response speed (and a high detectivity of 7.21×10^{10} Jones at zero bias under 254 nm UV illumination, along with superior mechanical flexibility at various bending angles. The critical parameters of our PD based on mixed-halide perovskite $(FAPbI_3)_{1-x}(MAPbBr_3)_x$ were higher than those of the PDs based on other kinds of photoactive materials such as inorganic perovskites ($CaSnO_3$, $BiFeO_3$, $BiTiO_3$, $SrTiO_3$), diamond, oxides (ZnO, TiO_2), and nitrides (GaN) reported in previous studies. Additionally, the air-exposure stability and reproducibility of the as-prepared device exhibit almost the original performance after 6 weeks of storage. For practical applications, we demonstrate a facile and sensitive detection for UVC leakage from a germicidal lamp and simulated a partial discharge system using our PD without energy consumption. As a realistic demonstration of UVC detection, the result shows a photograph of the measurement of partial discharge. The partial discharge inception at a high voltage occurs at 12 kV, and the voltage is then downregulated to 8 and 4 kV. The prepared flexible PD was hung on a holder placed 1 m from the rod-plane electrode, and data were recorded using the Keithley analyzer system. It can be observed that the current signals were generated during various partial discharges. this application confirmed that a halide perovskite-based PD can monitor and witness UV radiation leakage from insulation defects in high-voltage apparatus in the early stages to prevent unexpected damage. These results indicate that this new approach may be useful and convenient for the detection of partial discharge as well as for several practical applications.

5:00 PM EL04.09.07

Epitaxy of Halide Perovskites by Pulsed Laser Deposition (PLD)—The Case of $CsSnI_3$ and $MAPbI_3$ Junia Shelomi Solomon S. Solomon Sathiaraj[1], Yorick A Birkhölzer[1,2], Tatiana Soto-Montero[1], Wiria Soltanpoor[1] and Monica Morales-Masis[1]; [1]University of Twente, Netherlands; [2]Cornell University, United States

Halide perovskite (HP) materials have shown great promise for optoelectronic applications owing to their intrinsic material properties. However, HPs in their polycrystalline form are still limited by their environmental, thermal, and structural instability. Focusing on structural stability, here we explore the epitaxial growth of $CsSnI_3$ and $MAPbI_3$ on lattice-(mis)matched crystalline substrates using pulsed laser deposition (PLD). This allows us to monitor the polymorph stabilisation on achieving epitaxy. Additionally, it helps us understand the effect of strain and study the fundamental properties that become accessible when going from polycrystalline to single-crystalline films.

In the case of $CsSnI_3$, using reciprocal space maps we confirm the stabilisation of single orientation of the orthorhombic (γ) phase of $CsSnI_3$ on KCl substrates. Further, rocking curve measurements give insights into the mosaicity of the film and pole figure measurements confirm the film is epitaxial and not textured. Transmission electron microscopy (TEM), photoluminescence (PL) and optical absorption spectroscopy measurements were performed to confirm the epitaxial formation and its effect on the optical properties of the films.

In the case of $MAPbI_3$ films grown on KCl substrates, reciprocal space maps, rocking curve and pole figure measurements were also performed to validate epitaxial growth and stabilisation of the cubic phase at room temperature. The latter contrasts with the usually polycrystalline tetragonal phase growth of $MAPbI_3$ on typical solar cell contact layers. The highly oriented $MAPbI_3$ films on KCl showed a sharper PL peak over their polycrystalline counterparts and the band gap is also consistent with reports of cubic $MAPbI_3$ phase.

Overall, we demonstrate the successful epitaxial growth of homogeneous and dense thin films of $CsSnI_3$ and $MAPbI_3$ by PLD. This demonstrates the potential of this physical vapor deposition technique to achieve control of thin film deposition, from polycrystalline films all the way to epitaxial formation. In-depth structural analysis with different X-ray diffraction measurements was conducted to verify epitaxial growth and to understand the influence of lattice-(mis)matched strain on the stabilisation of the polymorphs. This work paves the way to further fundamental materials studies and high-end optoelectronic devices based on halide perovskite thin films.

5:00 PM EL04.09.08

Homogeneous Charge Distribution for Suppressing Charge Recombination in Perovskite Solar Cells under Low-Intensity Indoor Lights Min Jun Choi[1], Seok Woo Lee[2], Minwoo Lee[3,3], Sojeong Shin[1], Moonyong Kim[3], Geongguk Jeon[1], Sang Eun Yoon[1], Xiangyang Fan[2], Bo Ram R. Lee[2], Jan Seidel[3], Jae Sung Yun[3,4], Dong Wook Chang[2] and Jong Hyun Kim[1]; [1]Ajou University, Korea (the Republic of); [2]Pukyong National University, Korea (the Republic of); [3]University of New South Wales, Australia; [4]University of Surrey, United Kingdom

Due to the rapid advances on the Internet-of-Things (IoT) technology, the number of IoT sensors has recently explosive increased. most of wireless IoT sensors are expected to be installed in indoor environments. Instead of the using batteries that needed replacement and maintenance, Using the energy harvesting for self-powered IoT electronic devices is one of the most critical issues. Therefore, indoor photovoltaics (PVs) have been proposed as a great potential candidate for harvesting indoor light energy toward the long-term and stable operation of indoor IoT sensors.
Among the various types of light absorbers in PV cells, inorganic–organic hybrid perovskites are promising for indoor-light-harvesting applications, owing to their appealing merits such as high absorption coefficient in the visible range, high charge carrier mobility, and tunable bandgap (E_g). By exploiting these properties and through the E_g engineering of perovskites and the optimization of device architectures, perovskite solar cells (PVSCs) with high indoor power conversion efficiency (iPCE) have been developed.
Compared with 1 sun condition, indoor light has a very low intensity (200–1,000 lux). Due to the relatively small amount of carrier generation under low-intensity light environments than those under outdoor light conditions, photo-generated charge carriers can be more affected by the density of defects or trap sites, resulting in the non-radiative recombination. Therefore, frustration of the trap-mediated charge recombination is most critical issue in improving iPCEs. To suppress recombination, interface engineering is crucial for the indoor performance of devices.
In this work, we reported the effect with interfacial dipoles and uniformity of excited carrier distributions by using an interfacial dipole layer (IDL) material-quinoxaline-phosphine-oxide-based electron transporting small molecule [(2,3-diphenylquinoxaline-5,8-diyl)bis(4,1-phenylene))bis(diphenylphosphine oxide) (QDPPO)] on top of [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) electron transport layer (ETL). With high molecular electric dipole moment and efficient electron extraction properties, QDPPO induces the uniform accumulation of excited carriers on the ETLs under low-intensity illumination conditions. Electrochemical impedance spectroscopy, and transient photovoltage revealed that the homogeneous distribution of charge carriers effectively suppresses charge recombination, which result in a persistently high FF of PVSCs under low-intensity light-emitting diode (LED) condition. Furthermore, the photoluminescence (PL), time-resolved photoluminescence (TRPL), and Photo-CELIV measurement revealed that insertion of QDPPO facilitated charge extraction of PVs, resulting in high short circuit current densities.
As a result, QDPPO enabled with high indoor power density (iPD) and indoor power conversion efficiency (iPCE) of 65.63 *m*W/cm^2 and 27.49% under 800 lux LED, which were further enhanced to 36.90% by additional insertion of passivation layer. We also successfully fabricated mini-modules using QDPPO-based PVSCs exhibiting indoor power output (iPO) of up to 2.4 mW under 1,000 lux halogen light conditions, verifying the practical applicability of for operating indoor IoT sensors.
In summary, we investigated the effect of IDLs on the PV properties of the PVSCs under indoor low-intensity light conditions. The insertion of polar molecules revealed that homogeneous generation of excited charge carriers on the surface strongly affected the recombination reduction. Significantly improved uniformity of interfacial dipoles, in the QDPPO layer, effectively improved indoor PV properties while maintaining high FF under low-intensity light conditions. These results indicate that uniform charge distribution is an effective strategy to enhance PSCs performance in low light conditions.

5:00 PM EL04.09.12
Optimal Solvents for Interfacial Engineering towards Efficient Perovskite Solar Cells Wonjin Jang, Doyeon Heo and Sooyoung Kim; Korea University, Korea (the Republic of)

Perovskite solar cells (PSCs) have been attracting attention for several years due to their excellent optoelectronic properties, low processing cost, easy manufacturing process. However, improving the efficiency and long-term stability of PSCs still remains a challenge. Many methods have been studied to increase the efficiency and stability of the PSCs by controlling the perovskite manufacturing process, device structural design, compositional engineering, and interfacial modification. Among them, interfacial engineering is widely used to reduce the interfacial loss process caused by surface recombination, improve the crystallinity of the active absorption layer, the work function of the contact layer, and the intimacy of the contact at the interface, as well as help the long-term stability of the solar cell. To deposit the interfacial layer, solution process such as spin-coating or dip coating is commonly used because it is cheap and facile.
In the solution process, determining the solute is important, but determining the solvent is also important. In order to select the best solvent in the solution process, the most commonly used solvent was selected and tested, and the solvents were divided into two groups: a non-polar group and a polar group. We focused on the interfacial layer between electron transport layer (ETL) and perovskite, and checked how it affects perovskite and ETL by coating solvent between ETL and perovskite. It was confirmed that some solvents were detrimental to the efficiency of PSCs, and some solvents are effective in the efficiency of PSCs. The effects of solvents on PSCs were proved through various analyses. Among them, the best solvent used in the solution process and the solvent to be avoided were selected from the non-polar group and the polar group one by one.

5:00 PM EL04.09.14
Switchable Perovskite/Organic Dual-Band Photodetectors for Dual Optical Communication Applications Yu Gao, Zhaoming Wang, H.Y. Fu and Guodan Wei; Tsinghua-Berkeley Shenzhen Institute, China

It remains challenging to realize fast-switching speed and crosstalk-free high responsivity for visible and nearinfrared (NIR) dual-band photodetectors. Here we have carried out extensively interdisciplinary work on optoelectronic devices and their practical applications in optical communications for smart living: wavelength multiplexing and security enhancement. Herein, we report a fast switchable perovskite/organic bulk heterojunction (BHJ) dual-band PD with high selective responsivities over 100 mA/W in distinct visible (<820 nm) and near-infrared (NIR) bands (>850 nm). The dynamic dual-band response could be conveniently switched under a low-voltage modulation range from forward bias of +0.3 V for visible light to reverse bias of −0.8 V for NIR light. To note, the visible/ NIR response switching frequency has been reached as high as 1 MHz, which has been the highest values to our best knowledge for dual-band photodetectors. Due to such as switching speed, two novel optical communication applications: wavelength division multiplexing (WDM) and encryptedsecurity enhancement have been successfully established. The WDM application has been realized with a sum rate of 1.1 Mbps without any complicated circuit design and computation. The demonstrated encrypted scheme combining visible/invisible light in one channel to deceive cryptanalysts can support a data rate of 200 Kbps, where counterfeiting data are always accompanying to protect the real data. These findings demonstrate the feasibility of dual-band PDs for variety applications in the future optical communication networks.

5:00 PM EL04.09.15
Anion-Vacancy-Defect Passivation of a 2D-Layered Tin-Based Perovskite Thin-Film Transistor with Sulfur Doping Jaehyeok Cho and Myung-Gil Kim; Sungkyunkwan University, Korea (the Republic of)

Metal halide perovskites have attracted a considerable amount of research attention with significant progress made in the field of optoelectronics. Despite their outstanding electrical characteristics, structural defects impede their potential performance due to the polycrystalline nature of solution-processed perovskite films. Herein, the effective *p*-type doping and defect passivation of phenethylammonium tin iodide ($(PEA)_2SnI_4$) perovskite films using xanthate additives as a sulfur source is reported. Sulfur can be introduced to the iodine vacancies mainly at the grain boundaries of the perovskite film, passivating the electrical defects originating from the iodine vacancy and increasing the hole concentration. The Fermi-level shift toward the valence band maximum of the sulfur-doped perovskite film is confirmed using ultraviolet photoemission spectroscopy, resulting in *p*-type doping. Finally, the electrical performance improvement for the 0.2% sulfur-doped $(PEA)_2SnI_4$ thin-film transistor with a mobility of 1.45 cm^2 V^{-1} s^{-1}, an on/off ratio of 2.9×10^5 is demonstrated, and hysteresis of 10 V is reduced.

5:00 PM EL04.09.16
Optoelectronic Properties of Magnetic Halide Perovskites with Green's Function-Based Many-Body Perturbation Theory Linn Leppert and Kostas Fykouras; University of Twente, Netherlands

In the past years metal-halide perovskites with the structural formula ABX3 have emerged as promising candidates for applications ranging from photovoltaics to lighting and detectors. In these materials, the A site is a monovalent cation such as Cs+ or CH3NH3 +, the B site a divalent metal such as Pb2+ and the X site is a halide such as I−, Br−, or Cl−. Despite their facile fabrication and attractive and highly tunable optoelectonic properties, the commercialisation of these materials has been limited by the inherent toxicity associated with Pb and the fact that they are prone to degradation when exposed to a humid environment. Pb-free double perovksites with formula A2BB'X6 allow for alternating metal B sites, thereby introducing tremendous chemical and electronic diversity and the potential for new applications [1-3]. Recently, a new class of halide double perovskites featuring 3d transition metals such as Fe3+ has been reported [4]. Cs2AgFeCl6, in particular, exhibits excellent optical absorption properties with an optical band gap of around 1.6 eV [5]. However, little is known about the band structure and the excitonic properties of this material and how they are affected by the magnetic ordering of the alternating Fe sites.

Here, we use first-principles density functional theory (DFT) and Green's function-based many-body perturbation theory in the GW and Bethe-Salpeter Equation approach, to study these properties in Cs2AgFeX6 (X= Br−, Cl−) and alloys in which Fe3+ is partially replaced by Bi3+. Our results demonstrate that the band structure of these new materials considerably differs from that of previously known halide double perovskites, featuring flat conduction bands derived from Fe 3d orbitals. We show that not only the band gap energy but also the relative ordering of the lowest-energy conduction bands sensitively depends on the approximations used in the DFT and GW calculations and on the magnetic ordering of the Fe sites. Finally, we present preliminary results for the excitonic properties of this class of materials.
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SESSION EL04.10: Metal Halide Perovskites for Applications Beyond Solar IX
Session Chairs: Emmanuelle Deleporte and Sebastian Reyes-Lillo
Friday Morning, April 14, 2023
Moscone West, Level 3, Room 3004

8:30 AM *EL04.10.01
How do Halide Perovskite Dynamics Explain Lack of Defects, Sustainability and Stability? Sigalit Aharon[1] and David Cahen[2,1]; [1]Weizmann Institute of Science, Israel; [2]Bar-Ilan University, Israel

Different types of experiments have yielded results that are consistent with low to ultra-low densities of structural imperfections (that are opto-electronically active) in Pb-halide perovskite, HaP, single crystals, or polycrystalline films, prepared at or near STP from organic solvents. The leading argument for these low defect densities is that the materials are Defect Tolerant. We showed, by *simple logic*, that DT cannot be the sole cause and, if present, must include an active mechanism to repair damage[2]. Such process, Self-Healing, SH, was invoked earlier (with a different mechanism) to explain $CuInSe_2$ (àCIGS) stability[1].
For single crystals of 3D HaPs experimental evidence has been presented for SH, using PL as reporter for photodamage. SH, in inanimate matter, is explained by equilibrium thermodynamics.[3] Recovery from photodamage in 2D and 2D-3D HaP single crystals, was found, too,[4] showing the wider SH applicability.
We will report on healing on and in polycrystalline thin films of primarily Pb-iodide perovskites, which are encapsulated to prevent reaction with, and escape of degradation products into the ambient.
SH, which explains the low defect densities, is, on an atomic scale, likely connected to the lattice ***dynamics*** of the HaPs. As such the SH mechanism in HaPs appears to differ from the mechanism of repair and healing in other inorganics, esp. CIS/CIGS, or in organics.[1,5]
Still, films can also show higher (~ 10^{16} cm^{-3}) carrier densities, which we then relate to doping densities, and we will address how surface defects (@ ~ 10^{11}-10^{12} cm^{-2}) readily explain such densities. That, then begs the question of how, for other films, surface defects can be (much) lower, a crucial topic that we will discuss.
To follow the arguments and models for HaP defect, doping, and carrier densities, it is important to distinguish between static defects, of the textbook kind, familiar to, and used by us commonly for semiconductors, and ***dynamic*** ones, which might well dominate in high-quality crystals and films.[6]

* work with DR Ceratti, P Singh, S Elboher-Aharon, D. Oron, Y Sofer, G Hodes, D Egger, L Kronik, S Kumar +++.

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9:00 AM EL04.10.02
"Imperfectly perfect" Semiconductors—Static Disorder in Lead Halide Perovskites Ardalan Armin; Swansea University, United Kingdom

Perovskites are often characterised by small Urbach energies on the order of 12-14 meV. Whether this relatively small Urbach energy originates from small structural disorder or low dynamic disorder is not clear. In my talk I will discuss the static disorder in different perovskite compositions. I will show that Einstein solid model, based upon single mode harmonic oscillator, cannot describe temperature dependence of the Urbach energies of perovskites. This points towards existence of anharmonicities in perovskite lattice. Einstein's model is then modified and employed to evaluate static and dynamic disorder in single, double and triple cation perovskites. I will provide compelling evidence that static disorder in perovskites is predominantly caused by zero-point motion of phonons rather than structural imperfections. This makes us believe that such perovskites are "imperfectly perfect" which means, even though films are often poly-crystalline, each crystallite is nearly structurally perfect with its static disorder being only limited by the quantum zero point fluctuations in the lattice. This is also in accordance with multiple reports on self-healing characteristics of these material.

Zero-point-motion-limited static disorder is unusual for solution processed semiconductors but broadens the potential application of perovskites further to quantum electronics and devices operating at low temperature.

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9:15 AM EL04.10.03
Scattering toward Local Order in Hybrid Metal Halide Perovskites Dylan Ladd[1], Nicholas J. Weadock[1], Jared Fletcher[2], Mercouri G. Kanatzidis[2] and Michael Toney[1]; [1]University of Colorado Boulder, United States; [2]Northwestern University, United States

Research activity in hybrid metal halide perovskites for photvoltaics materials has brought a surge of interest in their "2D" layered and colloidal nanocrystal analogues. Countless organic molecules may serve to separate slabs of metal halide octahedra or terminate nanocrystal surfaces, and their chemical structure has significant impact on orientation and distortion of the corner sharing lead halide octahedra. The design freedom here has produced MHP systems with emergent properties of interest for spintronics, lasing, and beyond.[1,2] To date however, lattice dynamics of the inorganic constituents, structural constraints imposed by ammonium cations, and correlations between the two have not been well established. To achieve a better understanding of MHP systems overall, characterization methods that probe the structural local order are required.

Recent advances in X-ray beam probes now enable study of the local order to reveal static and dynamic lattice distortions, defects, and critical information otherwise hidden under the average crystal structure assigned by conventional crystallography. Preceding studies of local order by our group have established the presence of a dynamic lower symmetry phase in the globally higher symmetry cubic structure of the bulk 3D MHP and raise the question whether similar dynamics are driving optoelectronic properties in other MHP systems.[3] Here we present a study of the local order in hybrid MHP using synchrotron X-ray diffuse scattering which reveals significant deviation from a perfectly periodic crystal structure. Analysis of oriented three-dimensional reciprocal space from scattering of single crystals provides spatial understanding of dimensionally correlated disorder in the inorganic sublattice. Ready comparison across systems highlights the dependence of octahedral distortions on cation species. The unique local order revealed in MHP provides unique structural information to toward explaining emergent properties otherwise ill-explained by the crystallographic space group. Establishing structure-property relationships in this material class helps enable the intentional design of new MHP systems for application in topological materials, ferroelectrics, phase-change memory, and engineered heterostructures for improved environmental stability of photovoltaics.

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9:30 AM EL04.10.04
Controlling Halide Segregation in Mixed-Halide Perovskites Asaph Widmer-Cooper; The University of Sydney, Australia

Metal halide perovskites (MHPs) are a promising class of materials for optoelectronic and other applications that are energy efficient, printable, low-cost and solution processable. A key requirement for many MHP applications, including tandem solar cells, LEDs, photodetectors and lasers, is the ability to tune the material bandgap by varying the halide composition, i.e. the ratio of I^-, Br^- and Cl^-. This can be well controlled at the manufacturing stage by changing the relative amounts of halide precursors in solution. However, in practice, the performance of devices made using mixed-halide perovskites has been limited by poor material stability as the halides phase segregate upon light exposure. This leads to localized changes in the material bandgap which in turn affect the optoelectronic properties. This effect is known as photoinduced halide-ion segregation (PHS). Understanding its origin and how to reverse it, is therefore vital to develop stable MHP devices and to promote their adoption into the market.

In this work [1] we present a method by which PHS can be reversed *in situ,* effectively controlling the amount of homogeneous (mixed) and inhomogeneous (phase-segregated) halide domains. This is achieved using light alone and demonstrated experimentally. To understand the fundamental process underlying the observed photoinduced remixing, we developed a lattice model based on the Ising spin theory and on the hypothesis of polaron mediated segregation. In the model, halide ions are represented as nodes on a 2D lattice that can exchange position with neighboring ions. The exchange depends on the interaction felt with neighbors and with polarons. Simulations of photoinduced halide migration within single crystals have been performed using a Monte Carlo (MC) algorithm which, akin to Kinetic MC, allows the simulation to resemble the time evolution of an actual phase space trajectory as the system approaches equilibrium. These simulations show excellent agreement with the experimental results.

Our results add to the ongoing debate about what mechanism is ultimately responsible for PHS and proposes a solution to the problem of PHS of MHPs, with potential new applications for mixed halide perovskites.

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9:45 AM EL04.10.05
Photo De-Mixing and Ion Transport in Two-Dimensional Dion-Jacobson Mixed Halide Perovskites Ya-Ru Wang[1], Marko Mladenović[2], Ursula Roethlisberger[2], Jovana V. Milic[3], Davide Moia[1], Michael Grätzel[2] and Joachim Maier[1]; [1]Max Planck Institute for Solid State Research, Germany; [2]EPFL, Switzerland; [3]University of Fribourg, Switzerland

Using mixtures of iodide and bromide in 2D halide perovskites has proved to be a powerful tool for tunable optoelectronic material design. However such mixtures suffer from photo-induced phase segregation when exposed to light(photo de-mixing), similarly to their 3D counterparts[1]. While the process is reversible (two phases remix back in the dark to the pristine state, dark re-mixing),[2] this phase instability can potentially lead to unstable optoelectronic properties and device performance, making its understanding essential to progress the field of halide perovskites. Since the observed light-induced evolution of different phases involves significant ion transport, clarifying the underlying defect chemical mechanisms involved in photo de-mixing is critical.
Here, we study thin films of 2D Dion-Jacobson mixed halide perovskites (PDMA)Pb(Br0$_{.5}$I$_{0.5}$)$_4$ (PDMA: 1,4-phenylenedimethanammonium spacer) as model material to investigate their phase behavior both under light and in the dark using a wide range of experimental techniques. First, we are able to track the compositional evolution in the films during de-mixing and re-mixing by analyzing their time-dependent in-situ optical absorption properties. We simultaneously monitor the electrical conductivity of the sample, which provides a probe of defect concentration in and ion transport through the de-mixed phases. We furthermore take advantage of SEM and TEM to investigate the morphological changes and the nature of the iodide-rich and bromide-rich phases resulting from phase segregation. Lastly, we propose a model that considers possible opto-ionic effects, which can contribute to the driving force of de-mixing[3] and should therefore be considered in the overall energy balance of the process, together with the electronic effects discussed in the literature.[4]

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10:00 AM BREAK

SESSION EL04.11: Metal Halide Perovskites for Applications Beyond Solar X
Session Chairs: Connor Bischak and Markus Heindl
Friday Morning, April 14, 2023
Moscone West, Level 3, Room 3004

10:30 AM *EL04.11.01
Halide Perovskites Application Toolkit Tze Chien Sum; Nanyang Technological University, Singapore

Halide perovskites have firmly established themselves as the forerunners in next generation photovoltaics and light-emitting devices. Underpinning this spectacular rise are their exceptional properties such as large absorption cross-sections, defect tolerance, large spin-orbit coupling, long balanced charge diffusion lengths, slow hot carrier cooling, ion migration, radiation tolerance etc. Hence, there has been a rapid proliferation of their applications beyond conventional optoelectronics to fields such as spintronics, radiation detectors, memristors, bioimaging *etc*. Cutting across the boundaries of these emerging perovskite applications, artificial intelligence (AI) and machine learning are key enablers advancing the state-of-the-art in perovskite materials discovery optimized for each niche area. In this talk, I will examine some of our studies in these unconventional applications ranging from advanced photovoltaics concepts of hot carriers (Li et al., 2017) and multiple exciton generation (Li et al., 2018); high order multi-photon spectroscopy(Chen et al., 2017); spintronics (Giovanni et al., 2019); strain engineering and structural dynamics(Fu et al., 2022); as well as our latest foray into perovskite materials design and discovery leveraging fresh Mathematical AI methods based on topology and geometry (Anand et al., 2022).

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11:00 AM EL04.11.02
Manipulating the Cooling Bottleneck Through Quantum Confinement in Halide Perovskite Nanocrystals Jia Wei Melvin Lim, Yuanyuan Guo, Minjun Feng and Tze Chien Sum; Nanyang Technological University, Singapore

Halide perovskites have recently been cast into the limelight for their potential in next-generation photovoltaic concepts such as hot carrier solar cells (HCSCs) [1]. The strong phonon bottleneck and high carrier temperatures in these materials make them excellent candidates for HCSCs. One way to further enhance these properties is through quantum confinement in halide perovskite nanocrystals or quantum dots, where an intrinsic cooling bottleneck can be induced due to the discretization of energy levels [2]. However, reports on the size dependence of the intrinsic cooling bottleneck in halide perovskite nanocrystals are still divergent. With advancements in methods to synthesize strongly confined perovskite nanocrystals recently, it is worthwhile to re-examine this effect [3]. In this talk, we attempt to rationalize these divergent observations. The size, shape, and composition effects on the cooling bottleneck will be discussed. Through independent ultrafast spectroscopy measurements, we show that the nature of the cooling bottleneck in halide perovskite nanocrystals can be tuned. Ultimately, we wish to provide a broad overview of the quantum confinement effects on this cooling bottleneck to resolve the existing controversy.

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11:15 AM EL04.11.04

Utilizing Transient Absorption Spesctroscopy to Characterize the Anionic Composition of Perovskite Films Rebecca Scheidt, Matthew C. Beard, Kai Zhu and Qi Jiang; National Renewable Energy Laboratory, United States

Tandem solar cells require the development of efficient and stable wide band gap perovskites to be used at the top absorbing layer. This necessitates the need for mixed halide (i.e. mixed bromide and iodide perovskites) in order to obtain the optimum band gap needed for tandem applications. However, mixed halide perovskites often suffer from phase segregation under operating conditions. In order to combat this issue, we have recently developed a technique to create stable wide band gap perovskites with a variable band gap that contains both bromide and iodide. This variable band gap perovskite has an anion composition that shifts from low iodide concentration at the surface to high iodide concentration deeper into the film.

The variable band gap perovskites we have developed have a complex anionic composition that cannot be characterized using traditional methods, such as TOF-SIMS, due to the short length scales the halide gradient develops on. Using transient absorption optical spectroscopy, we have developed a model that allows us to fit transient absorption spectra taken at varying pump excitation energies to elucidate the physical composition of the perovskite. We are able to characterize the films and ascertain the composition of the films at different depths, more precisely than other characterization techniques are able to at the length scales of interest. With this model, we are also able to understand the movement of photogenerated charge carriers throughout the film as well as the implications this movement on operational solar cells.

SESSION EL04.12: Metal Halide Perovskites for Applications Beyond Solar XI
Session Chairs: Linn Leppert and Julian Vigil
Friday Afternoon, April 14, 2023
Moscone West, Level 3, Room 3004

1:30 PM *EL04.12.01

Study of the Formation Mechanism of 2D/3D Hybrid Halide Perovskite Heterostructures Using Phenylethylammonium Amino-Aroups
Emmanuelle Deleporte; ENS Paris-Saclay, France

Halide perovskites have proven recently to be excellent materials for optoelectronics, showing relevant properties both in the photovoltaic and light emitting devices context. In particular, perovskite-based solar cells, using three-dimensional (3D) perovskites, have reached power conversion efficiencies (PCE) up to 25.7%, close to silicon technology. However, it is still limited for commercialization by the instability of the 3D perovskites when exposed to light, temperature, oxygen, and moisture. Thanks to properties like surface passivation, reduction of nonradiative recombination, or inhibition of ionic migration, remarkable achievements have been made on PCE and stability by realizing 2D/3D heterostructures, using new cations and innovative architectures. Nevertheless, the understanding of the phenomena driving the formation of the 2D/3D interface remains to be deepened as it is a crucial challenge for the optimization of devices. In order to study the formation mechanisms occuring at the interface between the 2D and 3D perovskites, we focus here on phenylethylammonium (PEA) based amino-groups, commonly used for synthesizing 2D-3D perovskites film with optimum optical properties for solar cells and light-emitting devices.

We first report on the synthesis of a 2D/3D perovskite heterostructure by depositing a solution containing the para-fluorophenylethylammonium iodide (4FPEAI) cation salt on a triple cation 3D perovskite layer, commonly used in efficient solar cells. This leads to the formation of a thin layer of 2D perovskite crystallized on top of the 3D bulk perovskite layer. In order to optimize the 2D layer, we tested different synthesis parameters, such as the concentration of 2D cation solution, the time soaking between the 2D cation solution and the 3D perovskite, and the lead iodide content of the 3D perovskite. We studied more particularly the formation mechanism of the 2D perovskite and the chemical and physical phenomena occurring at this interface, by performing a large panel of characterizations, ranging from the analysis of extreme surface (XPS) and morphology (SEM) to the optical and structural characterization (PL, XRD). We find that the 3D perovskite composition affects the stoichiometry of the 2D layer formed on top. We thus conclude that the 2D layer formation results from at least two concomitant mechanisms: the reaction of the PEA-based organic spacer with the excess PbI_2 from the 3D layer as commonly observed and a cation exchange reaction between the 3D phase and 4-FPEAI [1]. The presence of this second mechanism is confirmed by forming a 2D perovskite phase even after removing the PbI_2 excess from the 3D perovskite stoichiometry. We revealed that these mechanisms occur concurrently to form the 2D layer until all the 4-FPEAI cation is consumed, making it the limiting reactant of the process.

We then report the use of PEA in the synthesis of CsPbBr3 nanocrystals (NCs) to reach a very high monodispersity without the need for several centrifugation steps [2]. In this method, some polydisperse CsPbBr3 NCs are first synthesized with usual protocols. Then, their size and size distribution are reduced with the help of PEA acting as a pair of scissors cutting the preformed NCs. From optical and TEM characterizations, we propose a mechanism involving a cation exchange reaction between the 3D perovskite cation of the preformed NCs and the PEA , leading to a structural modification of 3D perovskite in a 2D perovskite structure. This step is then followed by a reorganization of the remaining CsPbBr3 NCs in presence of the reactants present in the solution.

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2:00 PM EL04.12.02

Solution Patterning Approach for Two-Dimensional Perovskite Nanocrystal Arrays Yoonho Lee, Jee Yung Park, Peiran Niu, Hanjun Yang, Dewei Sun, Libai Huang, Jianguo Mei and Letian Dou; Purdue University, United States

Two-dimensional perovskite crystals have attracted intensive interest for its diverse optoelectronic characteristics owing to their superior semiconducting properties. However, most studies to date have been limited to one single crystal that are difficult to implement for integrated device arrays due to their incompatibility with selective growth or typical lithography processes. Here, we report facile one-step solution process for synthesizing 2D perovskite crystal arrays through the meniscus-guided coating on pre-patterned substrates. We further utilize this novel method for synthesis of lateral hetero-structured perovskite nanocrystal arrays. Six different 2D perovskite crystal arrays showing red, blue, and green colored emission including heterostructures have been successfully realized. Structural and optical characterizations demonstrate that the crystals display excellent crystalline quality and optical properties. Moreover, the method has been used to prepare high-performance 2D perovskite crystal photosensors. We believe that this strategy can be utilized as a guideline for the fundamental investigation of optical properties and development of high-performance optoelectronics of perovskite materials including photosensors and displays.

2:15 PM EL04.12.03
Non-blinking, Wide-bandgap Single Photon Sources with Simultaneously High Brightness and Single Photon Purity Enabled by Surface Rigidity Engineering of Strongly Confined Perovskite Quantum Dots Yitong Dong and Chenjia Mi; The University of Oklahoma, United States

Single photon sources are essential elements of photonic based devices for quantum computing and quantum information sciences that can operate at room temperature. Current single-photon emitters (SPEs) are limited to specific materials, such as color centers and epitaxial quantum dots (QDs) that have well-spaced energy levels, and isolated luminescence centers to regulate emission dynamics under random classical light excitations. As a result, current SPEs material lack tunability to their emission energies and operating conditions. To date, most single photon emitters are limited to small band gap materials. Developing a wide-bandgap material emitting blue single photons are therefore highly desired for applications like free-space and underwater quantum communications. Additionally, a bright blue SPE can act as quantum excitation sources to enable passive SPEs using conventional fluorescence materials that are incapable of regulating emission dynamics and otherwise good SPE materials.

Colloidal QDs have emerged as promising SPE materials due to their high luminescence efficiency at room temperature and facile and scalable synthesis. However, traditional wide-bandgap II-VI QDs are subjective to low fluorescence efficiencies even with epitaxially coated shells. Lead halide perovskites emerge as a promising alternative QD material due to their unique defect tolerance, which allows perovskite nanocrystals to exhibit a high luminescence quantum yield without shells. Despite limited success on red and green perovskite SPEs, blue perovskite SPEs have not been demonstrated because of the challenges in modifying the surface of blue perovskite QDs such as strongly confined $CsPbBr_3$ perovskite QDs (SCPQDs) with sizes ranging from 4 nm to 7 nm.

Perovskite QD surface ions are extremely dynamic. When making SPE samples, the colloidal QDs must be diluted, and dried onto the substrate. During these processes, the surface ligand will detach from the QD, leading to the loss of surface halide ions which is detrimental to the photoluminescence quantum yield. Additionally, the labile surface of SCPQDs has profound effects on their photophysical properties such as fluorescence intermittency (also referred as “blinking”). This phenomenon reduces the emission stability and efficiency of the light source, posing a significant barrier to the development of QD SPEs.

In our pioneering work we have developed a method to embed SCPQDs in an organic halide salt matrix to inhibit the surface ion loss. Using this method, we have revealed a new blinking mechanism with in SCPQDs that happens when exciton is self-trapped by the soft surface lattices albeit being well-passivated. By using various conjugated organic ligands in the salt matrix and adjust the conjugations and crystallinities of organic molecules, we can tune the surface rigidity of SCPQDs. We found that the blinking can be strongly suppressed when the surface rigidity is increased. Additionally, the emission spectral linewidth of single SCPQD narrows down to < 50 meV when the surface ions are anchored with matrix that has high crystallinity. By introducing inorganic halide slat in matrix such as sodium bromide, we can further fix the surface lattices of SCPQDs and obtain essentially non-blinking SCPQDs. The new QD-in-matrix SPE material have enhanced photo-stability. Taking advantage of the unique ultrafast bi-exciton annihilation process in SCPQDs, high single photon purities (> 95%) can be achieved under high excitation rates that can usually compromise single photon purity in normal QDs. Our work will accelerate the adoption of photonic based quantum communication devices, and accommodate the application of SPEs that require tunable emission properties.

2:30 PM BREAK

SESSION EL04.13: Metal Halide Perovskites for Applications Beyond Solar XII
Session Chairs: Linn Leppert and Sebastian Reyes-Lillo
Friday Afternoon, April 14, 2023
Moscone West, Level 3, Room 3004

3:00 PM *EL04.13.01
Halide Perovskites Beyond Methylammonium Lead Iodide for More Than Optoelectronics Mikaël Kepenekian[1], B, Cucco[1], G. Volonakis[1], Claudine Katan[1] and Jacky Even[2]; [1]Univ Rennes, ENSCR, CNRS, ISCR-UMR 6226, France; [2]Univ Rennes, INSA Rennes, CNRS, Institut FOTON − UMR 6082, France

If 3-dimensional (3D) halide perovskites AMX_3 (A: organic cation, M: metal ion, X: halide) have shown spectacular results in optoelectronic devices, they offer limited choice of metals and organic cations. This is not the case of the other shapes that impose far less constraints over the chemical design of the organic spacer, such as layered (2D) halide perovskites A_2MX_4 [1]. In addition to strictly 2D and 3D materials, there is a wealth of compounds with features of both dimensionality and intriguing properties. Among those, one can find the ‘deficient’ or ‘hollow’ perovskites [2], but also perovskitoids consisting of not-only corner-shared octahedra [3] down to 1D materials. Another direction recently explored aims at moving away from toxic lead using double perovskites structures [4] or even by making a side-step towards cousin structures of perovskites where $[MX_6]$ octahedra are no longer corner-shared [5]. These compounds often present attractive properties beyond optoelectronic and are used for electronic component, spinorbitronic or photocatalytic devices [6].

However, once the 3D structural lock is lifted, the number of suitable candidates for A becomes so large that guidelines would be desirable for the design of future devices. Here, based on computational investigations conducted on experimental and model systems, we propose to contribute to the writing of those rules. In this contribution, we will navigate this wide range of materials and highlight how modelling and computational investigations, in close contact with experimental approaches, can help rationalize the electronic, optical, magnetic and ionic transport properties of compounds but also lay done rules for the design of new materials for targeted applications [7].

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3:30 PM EL04.13.02
Bright Circularly-Polarized Photoluminescence in 2D Chiral Lead-Halide Perovskites Shangpu Liu[1], Mikaël Kepenekian[2], Stanislav Bodnar[1], Sascha Feldmann[3], Markus W. Heindl[1], Natalie Fehn[4], Jonathan Zerhoch[1], Andrii Shcherbakov[1], Aras Kartouzian[4], Ian D. Sharp[5], Claudine Katan[2], Jacky Even[2] and Felix Deschler[1]; [1]Physikalisch-Chemisches Institut, Germany; [2]Univ Rennes, United States; [3]Rowland Institute, United States; [4]Catalysis Research Center and Chemistry Department, Germany; [5]Walter Schottky Institut, Germany

Chiral 2D hybrid halide perovskites, which combine the advantages of chirality and exceptional optoelectronic properties, are promising materials for chiroptical and opto-spintronics applications. However, hybrid perovskites with strong chirality from highly distorted crystal structures have shown low luminescence efficiencies so far. Here, we report chiral 2D $(R/S/Rac)\text{-}3BrMBA_2PbI_4$ perovskite single crystals and thin films with external photoluminescence quantum efficiency as high as 39% and circularly polarized photoluminescence up to 52%, at room temperature. We use single-crystal x-ray diffraction and density-functional theory to elucidate the chirality transfer from chiral crystal structures to spin orbit split band structures. Using time-resolved chiroptical spectroscopy, we find very fast radiative recombination rates, which outcompete loss channels and rationalize the excellent photoluminescence yields. We further find polarized excitons with depolarization times exceeding the radiative decay times, which underpin the highly polarized luminescence. We assign the superior optoelectronic properties of our layered hybrid perovskites to their unique crystal structures controlled by cation engineering. Our report paves the way for high-performance hybrid perovskite photonic devices for chiroptical and spin-orbit logic applications.

3:45 PM EL04.13.03
Chiral Halide Perovskite Based Spintronic Devices Matthew Hautzinger, Ian Leahy, Kirstin Alberi and Matthew C. Beard; National Renewable Energy Laboratory, United States

The chirality induced spin selectivity (CISS) effect is the ability of chiral molecules or chiral structural motifs to control electron spin orientation and propagation.[1] As a result, materials exhibiting the CISS effect can behave as an effective spin filter or spin polarizer in solid state devices producing spin polarized current. Recently, the CISS effect has been demonstrated in low dimensional hybrid organic-inorganic halide perovskite semiconductors with a chiral organo-ammonium cation being incorporated into the structure.[2] These “chiral halide perovskites” have been shown to exhibit circular dichroism, emit circularly polarized (CP) luminescence, and detect CP light.[3] The work we present here demonstrates the incorporation of chiral halide perovskites into electronic devices relying on spin polarized current. Specifically, we have integrated the chiral perovskites into new light emitting diode (LED) architectures, where the chiral perovskite serves as an effective spin filter, allowing only polarized current to be injected into the emissive layer. As a result, the LED emits circularly polarized light that is right or left-handed based on the chirality of the organic motifs. Complementary experimental results demonstrating the spin polarizing behavior of the chiral halide perovskites in pseudo spin-valve devices will also be presented. These results are significant steps forward towards understanding the CISS effect as well as incorporating chiral materials into spintronic devices.

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4:00 PM EL04.13.04
Surface Modification Strategies for Chiral Perovskite Nanostructures Markus W. Heindl[1], Tim Kodalle[2], Natalie Fehn[3], Lennart Reb[3], Shangpu Liu[1], Constantin Harder[3,4], Maged Abdelsamie[2], Lissa Eyre[5], Stephan V. Roth[6,4], Alexander S. Urban[7], Peter Muller-Buschbaum[3,3], Ian D. Sharp[3], Aras Kartouzian[3], Carolin M. Sutter-Fella[2] and Felix Deschler[1]; [1]Universität Heidelberg, Germany; [2]Lawrence Berkeley National Laboratory, United States; [3]Technische Universität München, Germany; [4]Deutsches Elektronen-Synchrotron (DESY), Germany; [5]University of Cambridge, Germany; [6]KTH Royal Institute of Technology, Sweden; [7]Ludwig-Maximilians-Universität München, Germany

The generation, manipulation and detection of light is a key requirement for a wide range of technologies reaching from consumer electronics to communication via fiber optic cable and state-of-the-art sensors. Recent discoveries on the design of chiral metal-organic perovskites now promise cheap, sustainable materials for energy efficient generation and detection of polarized light.[1-3] However, the available choices of chiral perovskite materials are so far limited to a range of one- and two-dimensional crystal structures that allow for the incorporation of chiral organic molecules. Colloidal perovskite nanocrystals or -sheets do present an appealing alternative and have been shown to display desirable chiroptical properties when modified with chiral ligands.[4-5] However, since these nanomaterials are more intricate to synthesize and process, research on perovskite nanostructure semiconductors with surface-induced chirality has been limited.

Here, we present novel strategies to produce perovskite thin films with chiral surface modification directly, without having to obtain colloidal nanocrystals first. For this we utilize the chiral small organic 3-aminobutyric acid for the modification of DMAPbI3 using a simple spin-coating-based approach. We find that the resulting compound displays strong circular dichroism effects in the blue spectral region, which can be adjusted in their intensity by varying synthetic parameters. Furthermore, we perform an extensive structural investigation into the origin of these phenomena utilizing XRD and GIWAX experiment. We also study the effects of synthetic parameters on material performance using in-situ optical spectroscopy methods, monitoring the film formation throughout the spin coating process.

Our findings provide a novel approach to introducing chiral properties into hybrid perovskite materials. Additionally, they give insights into the structural origins of effects relating to chiroptical properties and provide synthetic strategies for their maximization. Our surface-based modification can be transferred to other, lead-free metal-halide materials that do not typically allow for the integration of organic molecules into their crystal structure.

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SESSION EL04.14: Virtual Session: Metal Halide Perovskites for Applications Beyond Solar
Session Chairs: Stanislav Bodnar and Markus Heindl
Wednesday Morning, April 26, 2023
EL04-virtual

8:00 AM *EL04.14.01
Phenomena at Surfaces and Interfaces of Halide Perovskites Liang Z. Tan; Lawrence Berkeley National Laboratory, United States

Understanding surface and interface phenomena has been a long-standing area of research in materials science. In the halide perovskite materials, the combination of large spin-orbit interactions and unusual structural dynamics pose new questions in this area. In this talk, we present a first-principles theoretical study of electronic, structural, and magnetic behavior of their low-dimensional interfaces. We show that these systems host electronic layer edge states stabilized by internal fields, and support several edge phonon modes which suppress dynamic disorder at the surface. We examine the role of molecular ligands in eliminating surface trap states to enhance photoluminescence. Finally, we consider anisotropic excitonic behavior at grain boundaries, and its impact on the magneto-optical properties of these materials. These results point to surfaces and interfaces of the halide perovskites as being able to robustly support rich phenomena with applications in optoelectronics, spintronics, and beyond.

8:30 AM EL04.14.02
Anion Exchange via BMIM-PF$_6$ in the Solid Lattice of MAPbCl$_3$ Single Crystal Materials at Room Temperature—New Insights into the Mixed Halide Perovskites Behnaz Akbari; Boston University, United States

Due to high optical absorption and long carrier-diffusion lengths, lead halide perovskites (LHPs) or organo-lead halide perovskites [MAPbX$_3$ (MA = CH $_3$ NH$^+_3$, X = Cl$^-$, Br$^-$, or I$^-$)] have opened new avenues into the scientific spotlight, showing fascinating optoelectronic properties as well as developing efficient optical devices.
Since ionic liquids, as a novel class of compounds, have high ionic conductivity, a low melting point below 100 °C, high polarity, low vapor pressure, non-flammability, good thermal stability, wide electrochemical window and non-volatility, potential applications toward electrochemistry, molecular biology, materials science, engineering, Physics, and healthcare (particularly in drug delivery) have been introduced. The ionic crystal structure of the perovskite materials enables us to tune the band gap and optical absorption, which are intentionally performed by altering the ions while their original lattice structure is maintained.
To study morphology and halide transport inside a solid lattice of MAPbCl$_3$ single crystal, first, Methylammonium Lead Chloride (CH$_3$NH$_3$PbCl$_3$ or MAPbCl$_3$) single crystal was fabricated via oversaturated MAPbCl$_3$ precursor solutions as a new and doable methodology. After two months, small growing sizable and transparent crystals were observed at room temperature and then subjected to surface analysis for topographic analysis, elemental composition, and halide diffusion through a scanning electron microscope equipped with Energy-dispersive X-ray Spectroscopy (SEM-EDX) and a home-built microscope equipped with a Zelux camera and a field of view of AC254-150-AB.
Room-temperature processing simplifies the fabrication procedure, makes these hybrid organic-inorganic materials closer to commercial devices, and gives important advantages over current vapor-phase deposition designs for perovskite materials. With that in mind, attempts were made to introduce an optimized, simple, fast, and economical procedure for the dissolution of Methylammonium iodide (MAI) in 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF$_6$) as a halide ion source with a density of 1.38 gr/ml i) to monitor halide diffusion and ii) to form a gradient of mixed halides (MAPbCl$_{3-x}$(F/I)$_x$, $0 \leq x \leq 3$) at room temperature. After sonication at 50°C within 30 minutes, a bright yellow transparent solution was produced, and the MAI-BMIM-PF$_6$ was dissolved entirely. Before SEM-EDX analysis, a droplet of MAI-BMIM-PF$_6$ solution was placed on the MAPbCl$_3$ single crystalline samples. It was concluded that the ion exchange is controllable in supersaturated MAPbCl$_3$ perovskite materials. The outcome can be ascribed to discovering new approaches toward modulations in the composition of anions and cations inside the MAPbCl$_3$ single crystal materials under room temperature deposition and providing novel insight into the chloride-based perovskite materials in the fabrication of optoelectronic devices using BMIM-PF$_6$ ionic solution.

8:45 AM EL04.14.03
Light-induced Phase Segregation in Surface and Bulk of All-inorganic Mixed Halide Perovskites Nuerbiya Aihemaiti, Yifan Jiang, Yizhou Zhu and Siying Peng; Westlake University, China

Halide perovskites attract great attention because of easy synthesis, high visible light absorption, high quantum efficiency, etc. Mixed halide perovskites possess tunable bandgaps by modulating the ratio of halogen compositions. They have been widely used as active materials for photovoltaics, light-emitting diodes (LEDs), lasers, and photodetectors. Despite their extraordinary properties, instability under light (e.g. phase segregation) is one of the bottlenecks for their further commercialization. Under illumination, mixed halide perovskites phase segregate into iodide-rich (I-rich) phase and bromide-rich (Br-rich) phase by defect-assisted I and Br exchanges. The mechanism behind light-induced phase segregation in mixed halide perovskites is still to be studied.
We used the chemical vapor deposition (CVD) method to prepare single-crystal-like CsPbBr$_{2.1}$I$_{0.9}$ microplates. Combining time-dependent photoluminescence (PL), in-situ environmental PL with time-resolved photoluminescence (TRPL) and X-ray photoelectron spectroscopy (XPS), we investigated the influence of power density (e.g. carrier concentration), surface defects on phase segregation in this model material system.
The fast appearance of pure I phase followed by I depletion was observed under the illumination of a 500 nm laser beam at a power density of 2000 W/cm^2 by time-dependent PL, while a gradual I accumulation was observed under a focused beam laser at 3000 W/cm^2. Power density-dependent phase segregation evolutions indicate the influence of carrier concentrations. In-situ environmental PL results also show the appearance of pure I phase followed by I depletion under the influence of dry air (N$_2$ + O$_2$). Based on TRPL before and after illumination in air, carrier populations and carrier lifetime

increased due to oxygen-surface interactions. XPS characterizations after illumination show that illumination with oxygen decreased Pb^0 and I/Pb ratio. This indicates the possible decrease of deep-level defects I_i and Pb_I.
Our experimental results elucidate the effect of surface defects and carrier concentration on phase segregation evolution in crystalline mixed halide perovskites microplates. XPS results support that oxygen passivation of the surface is caused by superoxide filling and oxidation of Pb^0. Surface passivation increases carrier concentration (supported by TRPL) and further changes the evolution of phase segregation. Detailed microscopic phase segregation evolutions will be discussed based on experimental results.

9:00 AM EL04.14.04
Stability Of Mixed Lead Halide Perovskite Films Encapsulated In Cyclic Olefin Copolymer (COC) Mutibah S. Alanazi; University of Oxford, United Kingdom

Mixed lead halide perovskites (MHPs) like $CsPbBrI_2$ are attracting significant interest as promising candidates for optoelectronic applications due to their relative stability and infrared band gap. An outstanding challenge is that over time they segregate into Iodide-rich and Bromide-rich phases under illumination, which degrades their optical properties and could compromise the operational reliability of devices. Such halide segregation can be attributed to strain, photo-induced ionic defects and charge carrier stabilization along grain boundaries. Here, we use micro-photoluminescence spectroscopy and time-resolved photoluminescence to investigate the light impact on charge carrier dynamics and properties of $CsPbBrI_2$ films at room and cryogenic temperatures. We also provide an effective strategy to mitigate the halide migration of Br/I ions in the $CsPbBrI_2$ films by modifying their crystalline grains with cyclic olefin copolymer (COC). Our observations reveal that COC-treated films exhibit a lower phase segregation rate under prolonged illumination compared to untreated films at room temperature due to the suppression of non-radiative recombination processes by increasing the grain sizes, improving the crystallinity, and reducing trap states. Our results also show that COC-treated $CsPbBrI_2$films at cryogenic temperature show higher photo-stability and can effectively suppress the halide demixing- remixing cycle that occurs in pure $CsPbBrI_2$ films. Therefore, COC treatment is more likely to increase the energy barriers for halide ion migration and limit drivers like lattice strain, trap states or polaron effects.

9:05 AM *EL04.14.05
Charge Self-Trapping in Halide Perovskites Julia Wiktor; Chalmers University of Technology, Sweden

Metal halide perovskites have attracted remarkable interest as promising materials for optoelectronic applications and beyond. One of the characteristics underpinning their performance is the nature of the photogenerated excess charges. Compounds from the family of halide perovskites are generally easily polarizable, which leads to strong charge-lattice interactions, and formation of polarons. I will first discuss the computational challenges in modeling polarons in complex materials on the example of halide perovskites. In particular, I will show how various effects, such as self-interaction, spin-orbit coupling and temperature affect the computed properties of the polaronic states. I will then describe different types of polaronic states that have been predicted computationally in different types of halide perovskites and how they affect the functioning of devices based on these materials.

SYMPOSIUM

April 11 - April 27, 2023

Symposium Organizers
Viktoriia Babicheva, University of New Mexico
Ateet Dutt, National Autonomous University of Mexico
Svetlana Neretina, University of Notre Dame
Pier Carlo Ricci, Univ Cagliari

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* Invited Paper
\+ Distinguished Invited

SESSION EL05.01: Anisotropic Gold Nanoparticles
Session Chairs: Viktoriia Babicheva and Svetlana Neretina
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2000

10:30 AM *EL05.01.01
Gold Nanostars as Structural Valency Probes Teri W. Odom; Northwestern University, United States

Anisotropic gold nanoparticles exhibit shape-dependent optical properties beneficial for optical sensing, biomedical imaging, and photocatalysis. This talk will discuss the fundamentals and applications of gold nanostars that support positive, negative, and neutral curvature. We will describe the details of gold nanostar growth and mechanistic insight gained from unconventional analytical tools. We will also discuss their functionalization with biological ligands that can facilitate both nanoparticle assembly and single-particle imaging of live-cell interactions.

11:00 AM *EL05.01.02
Gold Nanostars – Ideal Plasmonic Substrates or Not? Amanda J. Haes; University of Iowa, United States

Gold nanostars exhibit size and shape tunable plasmonic properties. In this presentation, we explore how fine morphological variations influence (or not) their plasmonic properties. Implications of morphology are used simultaneously to tune the adsorption of small molecules in sensing applications using surface enhanced Raman scattering (SERS). Because molecules must interact with the metal at short distances, molecule-surface interactions are important for successful small molecule detection. Herein, the surface chemistry of Good's buffer-stabilized gold nanostars is evaluated using computational, microscopic, and spectroscopic methodologies. Evaluation of these materials in spectroscopic measurements is pursued for a variety of small molecules. Determination of when these materials yield reproducible results (or not) will be conveyed.

11:30 AM *EL05.01.03
Improving Sensing Efficiency through Controlled Synthesis Kaleigh Scher[1], Jinisha Chheda[1], Anita Nair[1], Supriya Atta[2] and Laura Fabris[3,1]; [1]Rutgers, The State University of New Jersey, United States; [2]Duke University, United States; [3]Politecnico di Torino, Italy

Anisotropic plasmonic nanoparticles can display exceptional field enhancement properties and tunable resonant modes that can be leveraged in several fields, from imaging to catalysis. Among these nanoparticles, gold nanostars have emerged as extremely promising, in particular as it concerns the creation of effective imaging tags, phototherapeutic agents, and hot electron-based photocatalysts. The intriguing properties of these nanostructures stem from their structure-property relationships, that can be fully exploited only through the rational control of their synthesis. In my talk, I will discuss our approach to the design and synthesis of nanostars focusing in particular on six-branch gold nanostars with high shape anisotropy. These particles combine the unique advantages of nanostructures fabricated from the top-down and those synthesized from the bottom-up, showcasing a unique plasmonic response that remains largely unaltered on going from the single particle to the ensemble. These nanostars display multiple, well-separated, narrow resonances, the most intense of which extends in space much farther than that observed before for any plasmonic mode localized around a colloidal nanostructure. Importantly, the unique close correlation between morphology and plasmonic response leads the resonant modes of these particles to be tunable between 600 and 2000 nm, a unique feature that could find relevance in cutting edge technological applications. Along with the fundamental properties of the bare nanostars, I will discuss the synthetic protocols we have developed to coat them with thin semiconductor shells, further extending their applicability in spectroscopy and catalysis, and the study of the fundamental molecule-metal interactions that lead to the realization of bright sensing tags for detection based on surface enhanced Raman scattering.

SESSION EL05.02: Plasmonic Sensing
Session Chairs: Viktoriia Babicheva and Svetlana Neretina
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2000

2:00 PM *EL05.02.02
Towards Real-Time Bacterial Detection in Wastewater with Tailored Plasmon-Pathogen Interactions Jennifer A. Dionne[1], Loza Tadesse[1,2], Liam Herndon[1] and Halleh Balch[1]; [1]Stanford University, United States; [2]Massachusetts Institute of Technology, United States

Elevated pathogen levels in wastewater are one of the first indicators of disease outbreaks, making wastewater a powerful tool for surveilling the infections present in a community. Wastewater-based epidemiology (WBE) has gained popularity for viral infections, particularly to monitor ongoing epidemics of COVID-19, monkeypox, and polio. WBE monitoring of bacterial pathogens is likely to become increasingly important, especially as antimicrobial bacteria become a threat to public health. However, bacterial WBE presents several outstanding challenges. Foremost, the nucleic acid-based methods currently used to identify pathogens in wastewater require amplification or sequencing, and are limited by the need for pathogen-specific probes; therefore, is challenging to scale WBE to the many dozens of bacterial species and strains that can be present in a community. Further, high false negative rates can result from substances in wastewater, such as nucleases that degrade nucleic acids, heavy metals that bind to nucleic acids, and sugars that inhibit the activity of enzymes involved in DNA amplification and sequencing.

Here, we describe a new method to rapidly and accurately detect and identify bacteria in wastewater without the need for targeted probes or nucleic acids by combining surface-enhanced Raman spectroscopy (SERS) of
pathogens with machine learning (ML). We: 1)maximize bacterial Raman signal in wastewater using plasmonic materials that selectively enhance the pathogen Raman spectra across a variety of pathogens; 2) create an ML algorithm that can discern between the most common bacterial species in wastewater; and 3) validate this identification system on real wastewater samples using an integrated microfluidic setup. Au nanorods with five distinct aspect ratios are synthesized using CTAB and NaOL as the surfactants. We also synthesize rods with polyethylenimine (PEI) and thiol polyethylene glycol (thiol-PEG) to vary the nanorod charge. Gram negative species such as *E.coli and S.marcescens, and* G positive species such as *S.epidermidis* and *S.aureus* are grown to log phase in Lysogeny broth (LB) culture medium and then spiked into wastewater with concentrations ranging from 10^5cells/mL-10^9 cells/ml. The nanorods are mixed into the wastewater, and liquid Raman spectra are collected in a miniaturized flow cell. By controlling the nanorod chemistry and concentration, we obtain uniform bacterial SERS enhancements of ~300X for all bacterial species, compared to the bacteria-only samples in both water and wastewater. We compare wastewater from various locations, each with their own unique compositions, pHs, and salinities, and show how machine learning based spectral data analysis enables high (>88%) classification accuracy of both species and antibiotic susceptibility for these bacteria. Our work allows high signal-to-noise bacterial SERS measurements from wastewater, providing a foundation for rapid and label-free bacterial WBE.

2:30 PM *EL05.02.03
Polymer-Enabled Plasmonic Sensing Christy L. Haynes; University of Minnesota, United States

There are a variety of small molecule toxins found in crops that present hazards in food production and consumption. This work exploits polymers as capture agents for various toxin targets such as mycotoxins. By attaching short, anchored polymer chains complexed with the target of interest to plasmonic substrates, surface-enhanced Raman spectroscopy (SERS) can be employed to detect the mycotoxins. SERS is an attractive analytical signal transduction mechanism due to its high enhancement factors and the ability to assign specific vibrational modes to certain molecules, even at very low concentrations. By providing fingerprint spectra for various targets, one can easily detect more than one target mycotoxin in relevant complex matrices. Pairing experimental SERS with computational modeling helps confirm hypotheses about binding and target/polymer interaction. Overall, this talk will demonstrate optimization of SERS sensing to achieve limits of detection comparable to current detection methods with a simpler and more flexible signal transduction mechanism, providing an opportunity for future applications in complex matrices where these toxins are traditionally found.

3:00 PM BREAK

3:30 PM *EL05.02.04
Metal-Adsorbate Interactions Modulate Molecular Reactivity in Plasmon-Driven Photocatalytic Reactions Hui Wang; University of South Carolina, United States

Molecular adsorbates on the surfaces of optically excited metallic nanostructures may undergo intriguing plasmon-mediated photocatalytic transformations that are mechanistically distinct from the catalytic reactions under thermal conditions. The energy distribution of the plasmonic hot carriers, the local electric field enhancements, and the plasmonic photothermal heating are all crucial factors that may profoundly influence the kinetic enhancement of the plasmon-driven photoreactions. While the photoexcitation and relaxation of localized plasmons involve ultrafast photophysical processes that occur on the timescales from fs to ns, the plasmon-driven photochemical reactions have been observed to be kinetically much slower, strongly suggesting that the rate-limiting kinetic bottle-neck of plasmon-driven photocatalysis is associated with the interfacial chemical transformations of molecular adsorbates rather than the plasmonic hot carrier or resonance energy transfer processes. Here we use plasmon-driven reductive coupling of nitrophenyl derivative adsorbates on Ag nanoparticle surfaces as a model reaction system to investigate how the chemical nature of the metal-adsorbate interactions influences the molecular reactivity and the reaction kinetics. We systematically compare the transforming behaviors of three nitrophenyl derivatives, including nitrothiophenol, nitrophenylisocyanide, nitrophenylacetylene, which chemisorb to the Ag surfaces using different functional groups. We use surface-enhanced Raman scattering as an in situ spectroscopic tool with unique time-resolving and molecular finger-printing capabilities to fine-resolve the mechanistic and kinetic features of the plasmon-driven coupling reactions. Fast reaction rates and high reaction yields are observed when the molecular adsorbates interact with Ag through σ-donation, whereas the reactions become significantly slower if the metal-adsorbate interactions are dominated by π-back donation. The experimental observations are further corroborated by density functional theory calculations.

4:00 PM *EL05.02.05
Correlating Carrier Density, Emergent Plasmonic Features and Light-Driven Catalytic Performance of $Cu_{2-x}Se$ Nanocrystals and Their Derivatives Jill Millstone; Univ of Pittsburgh, United States

Recently, a wide variety of non-noble metal materials have been identified as plasmonically active including earth-abundant species such as aluminum, highly doped semiconductors, and metal pnictides. For semiconductor compositions, plasmonic properties are tuned not only by traditional methods of particle size and shape, but also by carrier density. Here, we discuss the use of ^{77}Se solid state nuclear magnetic resonance spectroscopy to quantitatively determine charge carrier density in a variety of $Cu_{2-x}Se$-based nanoparticles and correlate this charge carrier density with both particle crystallinity and plasmonic figures of merit. With these correlations in hand, we then study the surface chemistry of the particles in detail using electron paramagnetic resonance spectroscopy, and are able to connect plasmonic behavior and surface chemistry to demonstrate plasmon driven chemical conversions.

4:30 PM *EL05.02.06
The Interface of Plasmonics and Catalysis Prashant K. Jain; University of Illinois Urbana-Champaign, United States

The interaction of light with molecules can be used to access new modes of chemical reactivity; however, this interaction is often difficult to exploit in a universal manner. I will describe how plasmonics is proving to be a general strategy for interfacing photons with molecules and activating chemical transformations. This strategy involves heterogeneous catalysts comprised of plasmonic nanoparticles. Plasmonic excitation of the catalyst generates electronically and vibrationally excited states, which modify chemical activity at the interface and even induce emergent activity. I will describe how catalysts based on plasmonic nanoparticles are allowing light to be used as a redox equivalent in chemical reactions, for driving non-equilibrium chemical processes, for modifying product selectivity, for photosynthesizing fuels, and for boosting electrochemical conversions. The ultimate vision is a future where plasmonic excitations can be used to power chemical transformations or direct them with bond-level precision.

SESSION EL05.03: Poster Session
Session Chairs: Viktoriia Babicheva and Svetlana Neretina
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL05.03.01
Quantification of Dopamine Using Surface-Enhanced Raman Scattering (SERS) of Constrained Vibrational Mode Yongheum Choi[1], Chang Su Jeon[2], Kwang Bok Kim[1], Hyun-Jong Kim[1], Sung Hyun Park[2] and Young Min Park[1]; [1]Korea Institute of Industrial Technology, Korea (the Republic of); [2]Speclipse, Korea (the Republic of)

Dopamine (DA) is known as a crucial neurotransmitter playing a significant role in the hormonal, nervous, and vascular systems. Abnormal DA levels is related to diverse neurological and psychiatric disorders, including Parkinson's disease (PD) and Alzheimer's disease (AD). Therefore, DA quantification in biological samples has drawn attention for the tracking, diagnosis, and therapeutics of DA-related diseases. To date, quantitative detection of DA has been developed using electrochemistry, chromatography, and fluorescence [1,2]. These approaches, however have still confronted great challenges due to low sensitivity and selectivity. Meanwhile, surface-enhanced Raman spectroscopy (SERS) has come into the limelight as an analytical tool over the past few decades due to its extraordinary advantages such as single molecular-level detection and finger-printing signals. Nonetheless, the low affinity of DA to metal surface attenuates DA selectivity and poses a challenge for SERS-based DA sensors [3]. Although aptamer, antibody, and molecular chelation bound noble metals have been employed in several studies to enhance DA selectivity, only few of them are validated with real biological samples [4]. Therefore, it is imperative to devise rapid and simple methods to detect DA with ultra-sensitivity and high-selectivity in complicated biofluids.
Herein, we introduce a SERS-based ultrasensitive DA quantitative sensor adopting Raman-peak shift resulting from the constrained vibration mode of 4-mercaptophenylboronic acid (4-MPBA). Ag nanostructure was fabricated on Si wafer with a simple one-step sputtering process using gas-flow sputtering to augment plasmon resonance. 4-MPBA is a biocompatible Raman reporter, capable of covalently bonding with DA and metal-thiol conjugation to Ag substrate. It is adopted as a linker to enhance the affinity between DA and Ag substrate and the Raman signal of DA. 4-MPBA was coated through vapor-phase deposition to curtail impurity and background noise in Raman spectra. We identified a shift in the position of representative SERS peak of 4-MPBA proportionally to DA concentration. Our experimental result, indicating the peak shift stemming from the combination between 4-MPBA and DA was well supported by numerical simulation based on density functional theory. To the best of our knowledge, although Raman-peak shift has been used in many sensor-based applications previously, it has never been reported for DA sensing with constrained Raman mode. Tracking the peak shift confers more stable

and reliable measurement than intensity-based quantification because it focuses more on the analytes themselves rather than the enhancement performances of individual SERS substrates that rely on chip-to-chip variation. We also applied human serum on the DA sensor to validate that it works out similar results in real biological samples. The proposed method based on SERS peak shift depicted the ability to quantitatively detect DA concentrations in biofluids exhibiting selectivity with respect to other biomarkers as well as high sensitivity up to picomolar level.

References

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5:00 PM EL05.03.02
Detection of Gunshot Residue Analytes on a Portable Raman Spectrometer using Magnetic Nanoparticles Ellen Hondrogiannis[1], Mary Sajini Devadas[1], Megan Harper[1], Taylor Shafirovich[1], Dariush Aligholizadeh[1] and Lynn Krushinski[2]; [1]Towson University, United States; [2]Purdue University, United States

The signal detection limit (SDL), limit of detection (LOD), and limit of quantitation of a portable Raman spectrometer were measured for organic gunshot residue (GSR) components, diphenylamine (DPA) and ethyl centralite (EC), in 1:100 ODCB:hexanes. Diphenylamine yielded the lowest LOD at 998 wavenumbers (cm^{-1}) and EC at 1003 cm^{-1}. The addition of iron cobalt (FeCo) nanoparticles (NPs) to the DPA and EC solutions produced statistically signficant changes in DPA and EC band intensities and band areas. The DPA 1220 cm^{-1} and EC 1599 cm^{-1} bands produced the greatest percent change in band intensities overall (244.92 ± 10.65 % and 736.38 ± 38.59 % for DPA and EC, respectively upon the addition of 48.4 µg/mL FeCoNPs). When FeCoNPs were added to a mixture containing both EC and DPA all DPA band intenities increased with the DPA 1220 cm^{-1} showing the greatest percent change in band intensity (219.19 ± 21.00 %). The EC 711 cm^{-1} band showed 291.56 ± 12.59 % percent change in band intensity. The EC 1003 cm^{-1} band was not differentiated from the DPA 998 cm^{-1} band with a new band maximum at 1001 cm^{-1}, and this band increased by 35.59 ± 3.04 % upon the addition of FeCoNPs. Likewise, the EC 1599 cm^{-1} and DPA 1608 cm^{-1} bands were also not differentiated on this instrument and produced a band maximum at 1608 cm^{-1} that increased by 163.58 ± 7.21 % upon the additon of FeCoNPs. Solvent extraction was succesful at recovering 78.93 ± 5.04% of the FeCoNPs indicating the potential for reusing the NPs. This recovery of the magnetic FeCoNPs, coupled with ehancement of the DPA and EC signals when in solution with FeCoNPs on a portable Raman spectrometer, illustrate that these NPs are promising surfaces for future development leading to the rapid and inexpensive screening of GSR in the field for forensics analysis.

5:00 PM EL05.03.03
Controlled Crystalline Assembly of Nanocubes Yeonhee Lee, Seungsang Cha, Yuna Kwak and Jwa-Min Nam; Seoul National University, Korea (the Republic of)

The bottom-up approach of self-assembling nanoparticles is a promising strategy for fabricating desired nanostructures. However, current methods that utilize ligands and physical/chemical stimuli to control the forces between particles have certain limitations, such as limited material selection or the use of a fluidic template. Thus, novel approaches in nanoparticle assembly are necessary for future applications.
In this study, we explore the synthesis and assembly of gold nanocubes with a focus on achieving controlled morphology and crystalline structure. Representative cases of assembled structures are presented using gold nanocubes. These advancements could open new ways for further expansion, including optics, sensing, imaging, and catalysis.

5:00 PM EL05.03.04
Designing Plasmonic Janus Microgels for Direct Raman Detection of Small Molecules in Pristine Samples Jiwon Yoon and Shin-Hyun Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Raman spectroscopy enables molecular identification since each molecular species has different molecular vibrational modes. However, the probability of Raman scattering is low, limiting its pragmatic use as a detection method. When metal nanostructures or metal nanoparticles (NPs) are illuminated, a strong electric field is generated nearby the metal surface through surface plasmon resonance at the specific wavelength of the incident light. This leads to the enhanced Raman signal of target molecules in the vicinity of the metal surface, referred to as Surface Enhanced Raman Scattering (SERS). For target molecules to approach the metal surface, metal needs to be protected from contamination by adhesives such as protein. Therefore, pretreatment is required to remove adhesives from samples before SERS detection.
The way to obviate the pretreatment is a metal nanoparticle-embedded hydrogel microparticle. The hydrogel network serves as a protection layer for the infusion of target molecules and the exclusion of adhesives. However, preparing gold nanoparticles (AuNPs) and encapsulating AuNPs with a hydrogel network using microfluidics is time-consuming. In addition, signal uniformity is not achievable due to the aggregation of AuNPs. In that sense, micromolding is an alternative to microfluidics, which can remarkably shorten the time taken to produce plasmonic microgel. Moreover, a gold precursor is reduced to AuNPs in the presence of PEGDA providing the nucleation sites. Combining these two, microgels where AuNPs are uniformly embedded are quickly produced. This not only obviates the preparation of AuNPs but also provides the signal uniformity of the microgel.
Here, we design charge-selective plasmonic Janus microcylinders produced by the micromolding method. Microcylinders make up the charge-selective plasmonic microgel for SERS detection and the photonic crystal. By imparting the charge to the SERS microgel, SERS sensitivity is enhanced through the concentration of oppositely charged molecules. Since the charge of the microgel is not distinguishable from the naked eye, photonic color plays a role as an indicator of the charge of the plasmonic microgel. To fabricate Janus microcylinders, a solution containing gold precursor, water, PEGDA monomer, charged monomer, and photoinitiator is infiltrated into the cylindrical hole arrays of the PDMS mold. The residual solution is removed, followed by the evaporation of water and the curing of the solution by UV for 10 min. As a result, the SERS microgel whose height is half the cylindrical hole is produced. Subsequently, silica-ETPTA suspension is infiltrated into the remaining holes of the PDMS molds on a slide glass. Suspension is cured and plasmonic Janus microcylinders are collected through blading. To develop vivid structural color, Janus microcylinders are immersed in HF solution to etch out the silica NPs. As the SERS sensitivity of microcylinders varies with the concentration of the photoinitiator and gold precursor, concentrations are optimized by measuring the SERS spectra of R6G molecules. A higher concentration of charged monomer concentrates more oppositely charged molecules, but it may interrupt the formation of AuNPs due to the competition between charged monomer and gold precursor toward PEGDA. Therefore, the concentration of charged monomer is also optimized and the internal structure is investigated to observe the AuNP density. Optimized microgels exhibit signal uniformity in any spot, indicating the uniform dispersion of AuNPs inside microgels. As proof of concept, we detected charged molecules using our

plasmonic Janus microcylinder. Since specific photonic color indicates the charge of the plasmonic microgels, molecules with a specific charge can be detected using the oppositely charged microcylinder. In the mixture of positively and negatively charged molecules, each molecule is identified with high sensitivity from the microcylinder based on photonic colors.

5:00 PM EL05.03.05
Fast, and Simple Fabrication of Core-Satellite Plasmonic Nanostructures from Different Shapes and Materials for Robust, Stable, and Reproducible Surface-Enhanced Raman Scattering Hoa D. Trinh and Sangwoon Yoon; Chung-Ang University, Korea (the Republic of)

Developing low-cost, fast, and easy fabrication methods for highly sensitive and stable surface-enhanced Raman scattering (SERS) substrates is an actively pursued goal in sensors and diagnostics. In this study, we present a simple but efficient method for constructing different core-satellite (CS) configuration plasmonic nanostructures. CS nanostructures with multiple hotspots are assembled using small linker molecules that also serve as SERS labels. Multiple hot spots in the structures and narrow nanogaps in each hot spot produce a significantly enhanced Raman scattering signal. The sequential and alternating immersion of glass slides in different noble nanoparticles (Au or Ag) and linkers forms CS nanostructures with perfect yield and wide range of optical resonances. The method is highly reproducible and flexible that can be applied to many types of nanoparticles with different shapes, sizes, and capping ligands. The assembling process is fast and simple which is assisted by air plasma treatment. The CS nanostructures show robust, reliable, and stable SERS signal intensity. Furthermore, it is possible to detach CS nanostructures from supported glass slides and then encapsulated them in silica (CS@SiO_2) which makes the CS@SiO_2 an ideal SERS probe for sensitive detection of diseases and viruses.

5:00 PM EL05.03.06
Tunning the Shell Thickness for Plasmonic-TiO 2 Core-Shell Nanoparticles and its Effect on the ROS Generation Luis G. Morales Valenzuela[1,2], Paulina Segovia Olvera[1] and Jose M. Romo-Herrera[2]; [1]Centro de Investigación Científica y de Educación Superior de Ensenada, Mexico; [2]Universidad Nacional Autónoma de México, Mexico

The direct conversion of solar energy to chemical energy using photocatalysts has received significant attention in the last decade due to the great potential for fuel generation using environmentally friendly energy.

Conventionally, semiconductors are the basis of heterogeneous photocatalysis, trapping light with the energy necessary to generate electron-hole pairs, capable of generating reactive oxygen species (ROS) of great utility for the transformation of different molecules into fuels.

Although Titanium oxide (TiO_2) is one of the most efficient semiconductors as photocatalyst, its band gap is of 3.2 eV in anatase phase, which limits its application to light in the Ultraviolet region of the electromagnetic spectrum. During the last decade, Plasmonic NPs have been promoted as efficient additives to TiO2 to increase and take advantage of the harvesting of visible light and increase the photocatalytic efficiency of the hybrid material. Nanoparticles (NPs) with a core-shell architecture (AuNPs@TiO2) are examples of this type of hybrid materials, where the properties of both materials can be combined by having them in close contact, generating a synergy between them.

Plasmonic NPs have caught great attention due to their optical properties, low toxicity and good chemical stability. They can interact with visible and/or infrared light generating a resonance condition known as "localized surface plasmon resonance" (LSPR). This LSPR is very useful for applications in photochemistry, photodesorption, photothermal or detection of analyte molecules at low concentrations.

In this work it will be shown the synthesis of core-shell NPs (AuNPs@TiO_2), from the seed-mediated growth of the gold NPs (AuNPs) cores for tunning their size and plasmonic properties, to the subsequent controlled coating with TiO_2 using SOL-GEL method.

During this process, different shifts of the LSPR peak are observed from the UV-Visible spectroscopy signal of the AuNPs, which are directly related to the type of material and its thickness around the AuNPs. Therefore, such shifts can be used to monitor the synthesis process of AuNPs@TiO_2 coreshell NPs at each stage, using simple and standard tools such as a UV-Visible spectrophotometer.
Then, a theory-experiment study is presented using transmission electron microscopy (TEM) complemented with numerical simulations (COMSOL multiphysics) to validate the causes of the LSPR peak shifts for its usage as a monitoring tool at each stage of this type of synthesis.

Even more, the synthesis methodology was optimized to modify the thickness of the TiO_2 grown as a shell on the AuNPs. This allowed us to study the effect of the thickness of the shell on the generation of reactive oxygen species (ROS), which will contribute improving the efficiency of conversion of light energy to chemical energy towards the generation of alternative fuels using environmentally friendly processes.

5:00 PM EL05.03.07
Highly Sensitive Near-Infrared SERS Nanoprobes for *In Vivo* Imaging Using Gold-Assembled Silica Nanoparticles with Controllable Nanogaps
Yun Sik Choi[1], Sungje Bock[2], Dae Hong Jeong[1], Hyejin Chang[3] and Bong-Hyun Jun[2]; [1]Seoul National University, Korea (the Republic of); [2]Konkuk University, Korea (the Republic of); [3]Kangwon National University, Korea (the Republic of)

In vivo imaging using NIR light has attracted considerable attention owing to good penetration ability of NIR raditation through tissues. However, previous NIR imaging probes still possess issues such as lack of multiplex capacity, due to spectral overlap. In vivo imaging using surface-enhanced Raman scattering (SERS) has emerged as effective solution, owing to its high sensitivity, multiplexing ability, and non-photobleaching feature. To take such advantages, development of highly enhanced SERS nanoprobes in near-infrared (NIR) region is needed. A well-controlled morphology and biocompatibility are essential features of NIR SERS nanoprobes. Among several types of nanoparticle(NP)s, Gold(Au) NPs has been widely used under biological conditions owing to its good biocompatibility, but nanoprobes based on Au NP still suffer from weak SERS signal enhancement ability. Herein, we suggest Au-assembled nanostructures with controllable nanogaps with highly enhanced SERS signals within multiple hotspots as an breakthrough.

Au-assembled silica (SiO_2) nanoparticles (NPs) (SiO_2@Au@Au NPs) as NIR SERS nanoprobes are synthesized using the seed-mediated growth method. SiO_2@Au@Au NPs with six different sizes of Au NPs (SiO_2@Au@Au_{50}–SiO_2@Au@Au_{500}) were prepared by controlling the concentration of Au precursor in the growth step. The nanogaps between Au NPs on the SiO_2 surface could be controlled from 4.16 to 0.98 nm by adjusting the concentration of Au precursor (hence increasing Au NP sizes), which resulted in the formation of effective SERS hotspots. SiO_2@Au@Au_{500} NPs showed effective absorption of NIR light, with a 0.98-nm gap between Au NPs. SiO_2@Au@Au_{500} NPs showed high SERS enhancement factor of approximately 3.8×10^6 under 785-nm photoexcitation with good uniformity. SiO_2@Au@Au_{500} nanoprobes showed detectable *in vivo* SERS signals at a concentration of 16 µg/mL in animal tissue. SiO_2@Au@Au_{500} nanoprobes showed good penetration ability at animal tissue, detectable until it reaches 7 mm deep inside the porcine tissue. SiO_2@Au@Au_{500} NPs with 14 different Raman label compounds exhibited distinct SERS signals upon subcutaneous injection into nude mice. SiO_2@Au@Au NPs showed high potential for *in vivo* applications as multiplex nanoprobes with high SERS sensitivity in the NIR region.

5:00 PM EL05.03.08
Shifting the Size-Dependent Redox Potential of Gold Nanoparticles Using CTA^+ Micelles Randy Espinoza, Daniel B. Valenzuela Cahua and Son C. Nguyen; University of California, Merced, United States

Here, we demonstrate an unusual negative shift in the size-dependent reduction potentials of gold nanoparticles (AuNPs) attributed to the presence CTA^+ micelles. Our model reaction follows the chemical equilibrium reaction of CTAB-protected gold nanospheres and the Fe^{3+}/Fe^{2+} redox couple which allows us to use the Nernst equation and compute their standard redox potentials. The measured redox potentials decrease with decreasing nanoparticle size, following a size-dependent trend that negatively shifts by ~300 mV under the presence of CTA^+ at micellar concentration. This shift in the redox potential of AuNPs suggest that controlling the metal-ligand complex interactions with the micelles can serve as a strategy to tune the redox potential of metallic nanoparticles and metal-surfactant complexes. This reaction strategy can also be useful to compute the formation constant of the metal-surfactant complex in relevance to growth and etching of metal nanoparticles.

5:00 PM EL05.08.10
Emission Mechanism of Luminescent Silver Nanodots in the Presence of Calcium Sungmoon Choi and Junhua Yu; Seoul National Univ, Korea (the Republic of)

Stable luminescent silver clusters, named as silver nanodots (AgNDs), have been successfully encapsulated in several scaffolds. Silver nanodots consisting of a few silver atoms are becoming excellent fluorophores thanks to their small size, high brightness and excellent photostability. The synthesis of a series of spectrally-pure silver nanodots with emissions ranging from the blue to the near-IR prompts the application of such fluorophores for optical imaging. The high brightness and two photon absorption cross section of silver nanodots make them useful for cellular imaging. Particularly, the cost-effective poly(acrylic acid)-stabilized silver nanodots (PAA-AgNDs) show advantages of easy preparation and good stability.

In addition to its chemical properties, the low emission efficiency and loose structure of the PAA-AgNDs enable such nanodots a useful platform as optical probes. We found that PAA-AgNDs are extremely sensitive to the presence of calcium ions. The complexes between PAA-AgNDs and the ions significantly enhance the emission quantum yields due to cross-linking of the polymer chain by positively-charged metal ions. The high selectivity towards calcium ions can be explained by guest-host chemistry, in which the best match between the polymer chain and the ions further increases the rigidity of the polymer chain, and consequently minimize the non-radiative decay from the excited states of the PAA-AgNDs.

We have further developed these complexes to gels by surface printing for probing in various environments.

SESSION EL05.04: Synthesis of Plasmonic Nanostructures
Session Chairs: Svetlana Neretina and Pier Carlo Ricci
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2000

9:00 AM *EL05.04.03
Colloidal Synthesis of Copper Nanocrystals for Plasmonic and Related Applications Younan Xia[1] and Zhiheng Lyu[2]; [1]Georgia Institute of Technology, United States; [2]University of Illinois at Urbana-Champaign, United States

Copper (Cu) nanocrystals have received a lot of interest in recent years because of the high natural abundance and low cost of copper, as well as their outstanding performance in applications related to plasmonics, electronics, and catalysis. In this talk, I will discuss a number of solution-phase methods for the colloidal synthesis of Cu nanocrystals with well-defined and controllable shapes or morphologies. The methods involve both self-nucleation and seed-mediated growth. In the presence of proper capping agents, the nanocrysatls could be directed to grow into nanoscale cubes and right pyramicds, as well as one-dimensional rods and wires with a penta-twinned structure. The surface of these nanocrystasl is typcially enclosed by {100} facets. These nanocrystals could be prepared in high purity, together with controllable edge lengths down to 20 nm, offering an interesting system for the exploration of plasmonic application and electrocatalytic conversion of CO_2 to ethylene.

9:30 AM BREAK

10:00 AM *EL05.04.04
Synthesis of Metal-Metal Oxide Core-Shell Nanostructure with Plasmonic Properties Jingyi Chen; University of Arkansas, United States

Inorganic hybrid core-shell nanoparticles integrate the material properties from individual components which may open doors for new applications. However, the synthesis of core-shell nanoparticles made of dissimilar materials such as metal and metal oxide remains challenging due to strain and interfacial mismatch. In this work, we develop a metal-on-metal thin film growth approach to control the conformal deposition of nonprecious metal shells on the Cu-based metal cores to form core-shell structures of metal-metal oxide hybrids. The deposition kinetics could be controlled by a temperature-regulated, thermal decomposition of zero-valent transition metal complexes. It is found that the conformal deposition can be promoted by keeping the initial deposition temperature close to the thermal decomposition temperature of the zero-valent precursors. While maintaining a slow reaction kinetics, the strain reduction and interdiffusion facilitate conformal deposition over island growth in the synthesis. This study provides insightful guidance to metal-on-metal growth in solution at the nanoscale and thus the seed-mediated approach to hybrid core-shell structures. The optical properties of these metal-metal oxide hybrids are investigated experimentally and interpreted by theoretical simulation. Despite damping effects, the plasmonic properties of these Cu-based core-metal oxide shell structures may have the potential to enable plasmon-enhanced applications. Coupling with selective chemical etching of the Cu core, this synthesis approach developed in this study allows to access hollow nanoshells of metal oxides with well-defined morphology adopted from the core.

10:30 AM *EL05.04.05
Plasmon-Assisted Synthesis of Hybrid and Reconfigurable Nanomaterials Michelle L. Personick; Wesleyan University, United States

The synthesis of plasmonic nanomaterials with tailored interfaces requires fine control over competing reductive and oxidative chemical processes. Differentially modulating the rates of these reactions using only chemical and thermal parameters can be prohibitively challenging. In such cases, excitation of the plasmon resonance of the growing nanoparticles using visible light can yield hybrid structures and morphological transformations that are not accessible via standard colloidal approaches. For example, in the synthesis of hybrid bimetallic nanoparticles composed of a plasmonically-active silver (Ag) core and a catalytically-active platinum (Pt) shell, excitation of the plasmon resonance of the core nanostructure selectively drives the reduction of a Pt precursor under chemical conditions that limit the competing galvanic exchange between Pt ions and Ag. The combination of plasmon-driven reduction rate control with chemical reduction rate control also enables the synthesis of Ag core-Pt satellite nanostructures that are not accessible via other approaches. In another example, plasmonic excitation of Ag triangular prisms drives a cycle of oxidation and re-reduction of Ag to yield a conversion of the planar twinned prisms to multiply twinned icosahedra. The use of light to reconfigure the defect structure of Ag nanoparticles opens opportunities for visible-light-tunable catalysis and recyclable catalyst materials.

11:00 AM *EL05.04.06
Plasmonic Nanostructures on Paper Test Strips for Acute Disease Testing Nianqiang Wu; University of Massachusetts Amherst, United States

This talk will present our effort to develop plasmonic nanostructures toward testing of acute diseases such as traumatic brain injury, HIV and COVID-19. We tailor the chemical composition, microstructure and geometry of plasmonic metallic nanostructures to tune the optical mode of surface plasmonic resonance for light management. We construct surface-enhanced Raman spectroscopy (SERS) and fluorescence sensor and amplify optical signals with plasmon. Next, we incorporate plasmonic optical sensors into paper-based lateral flow assays to develop all-in-one test strips, which enables testing by laypersons at home, clinics and emergency departments.

SESSION EL05.05: Assembly of Plasmonic Nanostructures
Session Chairs: Svetlana Neretina and Pier Carlo Ricci
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2000

2:00 PM *EL05.05.02
Modeling the Effect of Ligands on Growth and Assembly of Nanocrystals Michael Engel; Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Ligands play a central role for the energetics and kinetics of plasmonic nanocrystals. During nanocrystal synthesis, ligands bind to the surface of a growing seed. Growth can result in shapes distinct from equilibrium Wulff polyhedra if ligands are designed with specificity for crystallographic facets. Ligands are also important during nanocrystal assembly. They act as spacers and provide functionality by controlling nanoparticle interactions. Finally, a surplus of ligand molecules in solution can result in depletion effects. Here, we present advances in the computational modeling of ligand effects on both nanocrystal growth and nanocrystal assembly. We model nanocrystal growth via a grand-canonical kinetic Monte Carlo simulation where ligand covering is described by kinetic factors. We observe a roughening transition at high temperature and search for optimal conditions for desired nanocrystal shapes. For understanding the effects of ligands on assembly, we utilize coarse-grained simulations of nanoprisms with directional, facet-specific interactions. For this purpose, we develop a generalizable two-step simulation methodology that, in a first step, generates a table for the interaction of two ligand-covered nanocrystals and, in a second step, utilizes this table in molecular dynamics. We apply our simulations to a number of self-assembly experiments of anisotropic nanocrystals with polymer ligands. Our macromolecular ligand-engineering strategies control, characterize, and model four molecular parameters of grafted polymer chains: chain length, chain dispersity, grafting density, and chain distribution. This work is a step towards theoretical models for particle brush materials and paves the way for the precision synthesis of nanocrystal hybrid materials.

2:30 PM *EL05.05.03
Periodic Arrays of Epitaxially Aligned Atomically Flat Single-Crystal Gold Nanoplates Robert Hughes, Robert Neal, Spencer Golze, Zachary Lawson, Walker Tuff and Svetlana Neretina; University of Notre Dame, United States

Well-tailored nanomaterials with a single-crystal character provide ideal building blocks for on-chip plasmonic devices. Although colloidal methods have demonstrated mastery over the synthesis of such structures, it has proven quite difficult to deploy these same nanomaterials on substrate surfaces in a highly deterministic manner where precise control over position and orientation is ensured. Only three examples currently exist in the literature where standalone single-crystal noble metal nanoplates have been formed on substrate surfaces in periodic arrays. These demonstrations, while impressive, are deficient in that they have either been demonstrated over small areas (< 1 mm^2) or where the nanoplate yield is low (78%). In this talk, we demonstrate the utility of using a crystalline substrate as the primary driver for forming substrate-based gold seeds with the internal defect structures and crystallographic alignment required for nanoplate growth. Using this capability along with other controls that are unique to substrate-based syntheses, we implement chemical reduction methods for generating large-area arrays of gold hexagonal and triangular nanoplates. The devised methods, hence, advance the integration of single-crystal gold nanoplates into device platforms and provide an overall fabrication strategy that is adaptable to other nanomaterials.

3:00 PM BREAK

3:30 PM *EL05.07.01
Plasmonic Hotspots Illuminate Cellular Biochemical Response to Environmental Conditions Regina Ragan; University of California, Irvine, United States

Bacterial responses to stress are critical to their survival in dynamic and challenging environments. Stresses can be general, e.g., nutrient deprivation, or specific, e.g., targeted antibiotic activity. Regardless, they result in rapid and profound shifts in metabolite concentrations within cells to maintain homeostasis. Thus, new technology for facile and rapid decoding of the complex cascade of chemical signals has been developed for medical diagnostics and environmental monitoring. I will present results of chemically assembled of plasmonic hotspots with defined nanogap chemistry able to tune interactions with metabolites, leading to single molecule limits of detection and quantification. Sensors are integrated in a microfluidic channel and performance is comparable on a confocal microscope and a portable spectrometer due to molecular scale control of nanofabrication over large area. Machine learning analysis of vibrational spectra of metabolite changes provides insight into the biochemical network response. Spectral feature analysis of *Pseudomonas aeruginosa* and *Escherichia coli* post antibiotic exposures indicates that purine biosynthesis is disrupted within 5 min of exposure, thus providing a rapid antibiotic susceptibility test for use in clinics. Further results to be presented show that *E. coli* cells can be used for transducing metal ions into chemical signals via the biochemical network response. Machine learning analysis of the vibrational spectra of metabolites released in response to chromium and arsenic exposure detects concentrations 10^8 times lower than those leading to cell death. Consequently, this platform is promising for monitoring changes in water quality below regulatory limits to provide early warning of water contamination and accurate longitudinal tracking of contaminant concentrations. The network response is detectable at ratios on the order of one metal ion to bacterium in solution, according to the level of toxicity. For example, the ratio of metal ions to bacterium in solution is 0.6 for As^{3+} and 8.2 for Cr^{6+}, showing sensitivity at the single cell level. These values correlate well with the fact that the EPA regulatory limit of Cr^{6+} is ten times higher than As^{3+}. Due to their distinct mechanisms of toxicity in bacteria, this sensing platform also distinguishes the metabolic response of As^{3+} and Cr^{6+} with 99% accuracy when analyzed with support vector machine models. Machine learning analysis shows the largest variance is in the spectral range between 700-750 cm^{-1}, which is a band consistent with SERS features associated with DNA methylation associated with the stress response of *E. coli*. Transfer learning of trained algorithms are further demonstrated to be generalizable to unseen tap water and wastewater samples using data obtained in less than 10 min. Drinking water safety, i.e., above or below WHO recommended limits is determined with greater than 96% accuracy. For more complex samples, secondary treated wastewater, with multiple background contaminants, the fine-tuned models can determine if waste water samples are above or below recommended safety limits with 92% accuracy. Thus, this platform provides an alternate technology to sophisticated and centralized analytical instruments identify biochemical networks involved in cellular response to environmental conditions.

4:00 PM EL05.05.05
Open- and Close-Packed Oligomers via Template-Directed Assembly of Shape-Engineered, Lithographically-Fabricated Nanoparticles Yiyu Cai[1], Asma Fallah[1], Shengsong Yang[1], Yun Chang Choi[1], Aaron Stein[2], James M. Kikkawa[1], Nader Engheta[1], Christopher B. Murray[1,1] and Cherie R. Kagan[1,1,1]; [1]University of Pennsylvania, United States; [2]Brookhaven National Laboratory, United States

We report a top-down lithographic fabrication process for producing nanoparticles (NPs) with well-defined sizes, shapes, and compositions that are not accessible synthetically. Using a template-assisted assembly technique, lithographically-fabricated Au NPs are driven by capillary forces to assemble into open or close-packed structures. The sizes and shapes of the templates control the interparticle gap size, coordination number, disorder, and location of defects such as voids in the NP assemblies. We characterize the optical properties of our assembled structures using dark-field scattering spectroscopy. Fano resonances are observed in the spectra and show dependencies on the symmetry, interparticle distance, and orientation with respect to the polarization of incident light. We further develop a multistep assembly method to co-assemble different types of NPs into multimaterial architectures.

4:15 PM EL05.05.06
Creating Chiral Plasmonic Nanostructures with Circularly Polarized Light Tian Qiao, Tsumugi Miyashita and MingLee Tang; The University of Utah, United States

Chiral plasmonic nanostructures have attracted much interest in recent years as new platforms for polarization modulation. Other than photonic devices, chiral plasmonic nanostructures facilitate the ultrasensitive detection of chiral biological materials, e.g. DNA. To synthesize chiral plasmonic nanostructures, the most well-established method is chirality transfer from biological materials to the inorganic nanostructures. Alternatively, circularly polarized light can be used to control the formation of the plasmonic enantiomeric nanostructures, where the chirality of the product is solely defined by the polarization of the light. This synthesis method may be more cost-effective while allowing the wavelength and intensity of light to be used as tunable parameters. Here we investigate the use of circularly polarized light to create chiral gold nano bipyramids. Hot charge carriers can be generated with light and consumed to fabricate chiral plasmonic structures. Scanning electron microscopy (SEM) coupled with cathodoluminescence measurements comparing the nano bipyramids before and after circularly polarized light illumination is used for characterization. We will show that both dielectric or plasmonic chiral additions can be deposited depending on the identity of reagents. Circular dichroism (CD) spectra of the chiral plasmonic nanostructures further demonstrate the polarization dependent light-matter interaction of the materials synthesized.

4:30 PM *EL05.05.07
Stress Induced Mesoscale Assembly of Nanoparticles for Active Nanostructures Hongyou Fan; Sandia National Laboratories, United States

Due to the size- and shape-dependent properties, nanoparticles have been successfully used as functional building blocks to fabricate 1-3D ordered assemblies for the development of artificial metamaterials. At ambient pressure, entropy driven self-assembly of monosized or binary nanoparticles generally results in polycrystalline 2- or 3D close-packed arrangements, and extensive efforts have been made to develop structural perfection of nanoparticle arrays or ‘single crystal-like’ domain structures with precise long range order for their definite advantages for electron transport. To date, fabrications of ordered nanoparticle assemblies have been relied on specific interparticle chemical or physical interactions such as van der Waals interactions, dipole-dipole interaction, chemical reactions, etc. Recently we have discovered a pressure-induced assembly method to engineer nanoparticle assembly at mesoscale and to fabricate new nanoparticle architectures without relying on specific nanoparticle interactions. We show that under a hydrostatic pressure field, the unit cell dimension of a 3D ordered nanoparticle arrays can be manipulated to reversibly shrink, allowing fine-tuning of interparticle separation distance. Under a uniaxial pressure field, nanoparticles are forced to contact and coalesce, forming hierarchical nanostructures. Depending on the orientation of the initial nanoparticle arrays, 1-3D ordered nanostructures including nanorod, nanowire, and nanoporous network can be fabricated through the pressure-induced self-assembly method. Guided by computational simulations, we were able to rationalize the pressure-induced self-assembly of nanoparticle arrays for predictable nanostructures. Moreover, we discovered for the first time a transition from an ordered polycrystalline nanoparticle mesophase to quasi-single crystalline nanoparticle lattices induced by PDA process. Exerting pressure-dependent control over the structure of nanoparticle arrays provides a unique and robust system to understand collective chemical and physical characteristics and to develop novel electronic and photonic behavior for energy transduction related applications.

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SESSION EL05.06: Active Plasmonics I

Session Chairs: Svetlana Neretina and Pier Carlo Ricci

Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2000

8:30 AM *EL05.06.01
Synthesis and Applications of Plasmonic Hydrogels Francis Zamborini, Rajiv Singh, Sharadkumar Karangiya and Harikrishnan Nambiar; Univ of Louisville, United States

The drop-wise addition of sodium alginate to a solution of calcium ions results in the formation of spherical Ca-alginate hydrogel beads. Gold nanoparticles (NPs) or nanoclusters (NCs) of varied size become incorporated into the hydrogel beads by adding them to the sodium alginate solution prior to synthesis. The extent of NP/NC loading depends on the concentration used in the sodium alginate solution while the size of the beads depends on the drop size and water content. The synthesis of hydrogel beads with gold NPs of varied size, shape, and aggregation state leads to plasmonic hydrogels with controlled optical properties due to their different wavelengths of the localized surface plasmon resonance (LSPR) peak of the NPs in the beads. The plasmonic properties can be further tuned by changing the composition of metal NPs within the hydrogel beads. The chemistry and properties are very different compared to the behavior of the NPs in water solutions without incorporation into the hydrogel. Functionalization and cross-linking the hydrogel by linkages other than Ca also affects the properties and provides advantages in terms of chemistry, stability, and applications. The hybrid hydrogel-metal NP plasmonic materials have applications in optical sensing, electrochemical analysis, photochemistry, and catalysis.

9:00 AM *EL05.06.02
Synthesis and Photocatalytic Properties of Hybrid Metal-Semiconductor Nanoparticles Yongchen Wang and Jing Zhao; University of Connecticut, United States

Metal and semiconductor nanoparticles exhibit excellent light absorbing ability and size-tunable properties. When the two components are combined in one hybrid structure, effective charge separation could occur upon photoexcitation and the long-lived charge-separated state along the electrons or holes to transfer to molecules nearby; therefore, they can be employed to catalyze photochemical reactions. In our work, we developed a method to synthesize Ag-tipped CdS nanorods with varying lengths using a seed-mediated growth method. The length of the nanorods can be controlled by the ratio of the Ag and Cd/S precursors. The Ag-CdS nanorods were applied as photocatalyst for methyl orange degradation reaction and their catalytic activities were affected by their length. Specifically, rods of intermediate lengths showed higher degradation rates than the short and long ones. Steady-state and time-dependent fluorescence spectroscopy was used to measure photoluminescence (PL) spectra and decays of the Ag-CdS nanorods and rod-like CdS nanoparticles. The Ag-CdS nanorods exhibited broad, red-shifted PL spectra and much slower PL decays compared to that of the CdS nanoparticles. By fitting the PL lifetime distribution of the decay curves, we attributed the high photocatalytic activities of the intermate-length Ag-CdS nanorods to the higher probability of populating the charge-separated states than that of the short or long rods.

9:30 AM *EL05.06.03
Detection of Nanoplastics in Ocean Water using Plasmonic Effects Tengfei Luo[1], Seunghyun Moon[1], Leisha Martin[2], Seongmin Kim[1], Qiushi Zhang[1] and Wei Xu[2]; [1]University of Notre Dame, United States; [2]Texas A&M University, Corpus Christi, United States

Plastics production surpasses all other synthetic materials globally, with 5-13 million tons of them entering the oceans every year, posing serious environmental challenges. Plastics in the environment can be fragmented by UV irradiation and mechanical means into micro- or even nano-particles. Although nanoplastics have been detected in ocean water using techniques like mass spectrometry, they have never been visually seen and thus their morphological features are unknown, which are critical to their toxicity. Here we report the direct observation of nanoplastics in ocean water around the world leveraging a unique shrinking surface bubble deposition (SSBD) technique. SSBD concentrates suspended nanoplastic particles onto a surface, allowing direct visualization using electron microscopy. With the plasmonic nanoparticles co-deposited in the SSBD process, surface-enhanced Raman spectroscopy effect is enabled for chemical identification of trace amount of nanoplastics deposited on the surface. From the water samples collected from locations on the coastlines of China, South Korea, and the United States, and deep (>300 m) in the Gulf of Mexico, we observed nanoplastics with a variety of compositions, including polycaprolactam (Nylon), polystyrene (PS), and polyethylene terephthalate (PET) – all commonly used in daily consumables (e.g., textiles, coffee cup lids and water bottles). The plastic particles we found possessed diverse morphologies, such as nanofibers, nanoflakes, and ball-stick nanostructures. These diverse nanoplastics may have profound impacts on marine organisms, and our results can provide important information for appropriately designing their toxicity studies.

10:00 AM BREAK

10:30 AM *EL05.06.04
Hot Electron Generation in Plasmonic Nanocrystals as a Mechanism for Photo-Growth and Photochemistry Alexander Govorov; Ohio University, United States

Energetic (hot) electrons contribute to the kinetic processes observed in colloidal nanocrystals, metal-semiconductor hybrids, plasmonic Schottky photodetectors, and metastructures [1,2]. This talk will discuss photochemical and photo-growth processes triggered by hot electrons in plasmonic nanostructures made of unconventional materials and in nanocrystals with complex shapes [3,4].

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11:00 AM EL05.06.05
Noble Metal-Nonstoichiometric Copper Chalcogenide Dual-Plasmonic Hybrid Heteronanostructures with Tunable Optical Properties and Optimized Photocatalytic Activities Hao Jing[1], Mariia Ivanchenko[1], Vida Nooshnab[2], Andrew Evangelista[1], Alison Carroll[1], Nicolas Large[2], Alline F. Myers[3] and Andrea Brothers[4]; [1]George Mason University, United States; [2]The University of Texas at San Antonio, United States; [3]National Institute of Standards and Technology, United States; [4]American University, United States

Multicomponent plasmonic nanoparticles, especially structurally well-defined noble metal-nonstoichiometric copper chalcogenide (p-type) dual plasmonic hybrid hetero-nanostructures, have emerged as an intriguing platform of superstructures due to their synergistically reinforced optical properties. The integration of two intrinsically dissimilar plasmonic constituents in one nano-entity empowers us to explore many new-yet-unexpected features, holding tremendous potential for plasmon-mediated energy transfer, plasmon-enhanced photocatalysis, and plasmon-related photothermal and photodynamic theranostics. Over the past decades, the research on dual plasmonic nanostructures has been burgeoning and much progress has been made with respect to the synthesis of a wide variety of dual plasmonic nanostructures with distinctive sizes, shapes or mophologies. Several dual-plasmonic hybrid heteronanostructures with geometrically tunable optical properties and tailored photocatalytic performance synthesized and characterized in our lab will be discussed in this symposium.

11:15 AM EL05.06.06
Synthesis & Functionalization of Hybrid Plasmon-Semiconductor Nanoparticles for Cancer Phototherapy Yuzhou Pu and Thomas Pons; ESPCI Paris PSL, France

Clinical modality based on light activation and photosensitizers, phototherapy, has been recognized as a novel alternative for cancer therapy owning to its high selectivity, safety and compatibility with other tumor ablation modalities. However, key challenges such as low light penetration, low generation rate of reactive oxygen species (ROS) for photodynamic therapy (PDT) or of heat for photothermal therapy (PTT), along with poor distribution specificity of photosensitizers have restricted its widespread clinical use, which requires rational design and improvement on photosensitizers. Herein we propose a strategy that combines plasmonic gold nanorods (AuNR), which can efficiently generate hot electrons under laser irradiation thanks to its localized surface plasmon resonance, with semiconductor materials such as TiO_2. The generated hot electrons can be injected into the conduction band of TiO_2 and eventually produce ROS (Hydroxyl radicals), radicals that will lead to cell apoptosis. By controlling the aspect ratio of AuNR, the longitudinal absorption of AuNR can be tuned from 700 to 1000 nm, a region where light gets an optimal penetration into the tissue. We characterized the production of hydroxyl radicals by AuNR/TiO_2 nanoparticles under continuous wave or pulsed irradiation at 800 nm by measuring the degradation rate of methylene blue. Then we designed surface polymeric ligands based on polyethylene glycol to ensure the colloidal stability of these hybrid AuNR/TiO_2 nanoparticles in a physiological environment. Finally, these functionalized AuNR/TiO_2 nanoparticles were incubated with HeLa cells. We demonstrated that irradiation of these nanoparticles by a continuous 808 nm laser was effective to produce ROS and kill cancer cells, while incubation with nanoparticles in the absence of irradiation or irradiation in the absence of the nanoparticles did not modify the cell viability.

11:30 AM *EL05.06.07
Multiscale Chirality of Self-Assembled Nanostructures Nicholas A. Kotov; University of Michigan, United States

Nanoscale chirality is a rapidly emerging field in science and engineering. The early observation of giant circular dichroism for assemblies of gold nanoparticles due to their high polarizability and dimensional match with visible wavelengths. They encompass a large family of mirror-asymmetric constructs from metals, semiconductors, ceramics, and nanocarbons with multiple chiral geometries with characteristic scales from Ångströms to microns. Versatility in, scales, dimensions and polarizability of the inorganic materials enables their multiscale engineering to attain a broad range of optical and chemical properties. These capabilities as chiral materials enabled their fast technological translation for biosensing and optoelectronics, which, in turn, opened new venues for scientific inquiry into the unifying role chirality at the interface of materials science, biology, chemistry, and physics.
In this talk the relationships between multiscale chirality, structural/functional complexity and strong chiroplasmonic activity will be established. The concept of chirality vectors with scale-specific chirality measures will be introduced. Engineering of the self-assembled structures wither complexity starting from the tetrahedrons of gold nanoparticles, twisted nanorods pairs, chains of gold nanorods and chiral superlattices from tetrahedrons will be discussed. These self-assembled structures open a pathway to a large family of complex hierarchical structures with gradually tunable chiroptical properties for biosensing and chiral photonics.
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[2] L. Xu, et al, Enantiomer-Dependent Immunological Response to Chiral Nanoparticles**,** *Nature,* **2022**, 601, 366–373.
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SESSION EL05.07: Active Plasmonics II
Session Chairs: Ateet Dutt and Pier Carlo Ricci
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2000

1:30 PM *EL05.07.02
Active Epsilon-Near-Zero Photonics Aleksei Anopchenko, Sudip Gurung, Christopher Gonzalez, David Dang, Quynh T. Dang, Leon Zhang, Kent Nguyen, Yu-Hsun Chen, Scott Kiehn, Juan M. Calixto and Ho Wai (Howard) Lee; University of California, Irvine, United States

Discovery of novel active materials is fundamental for photonic applications. The epsilon-near-zero (ENZ) materials have been shown to be as one of the most promising optical materials in the recent years as the electromagnetic field inside media with near-zero permittivity has been shown to exhibit unique optical properties, including strong electromagnetic wave confinement, enhanced quantum emission near ENZ media, non-reciprocal magneto-optical effects, unique topological properties, and abnormally large optical nonlinearity. While ENZ optics have been investigated extensively in the last few years, the current commonly used ENZ materials suffer from limited optical enhancement because of the lack of precise control of ENZ frequency, loss, and thickness for efficient ENZ mode excitation. In addition, the active tunability and enhanced nonlinearity and emission properties in ENZ materials have yet been fully experimentally explored.

This talk will review our recent studies on the active linear, nonlinear, and emission properties of conducting oxide and metallic nitride epsilon-near-zero materials in planar and optical fiber platforms [1-7]. I will present a method to engineer the field intensity enhancement of the Al-doped zinc oxide (AZO) ENZ thin films synthesized by atomic layer deposition (ALD) technique. I will then discuss the observation of abnormal nonlinear temporal dynamic of hot electrons and enhanced optical nonlinearity in AZO and ITO ENZ thin films under different pump fluences and excitation angles using a degenerate pump-probe spectroscopy technique. Finally, I will also discuss the first experimental demonstration of optically confined ENZ resonance excitation in an optical fiber waveguide uniformly coated with AZO nanolayer. These studies enrich the fundamental understanding of emission and nonlinear properties on ENZ thin films and the integration of ENZ materials and optical fiber will open the path to revolutionary ultracompact in-fiber optical devices for optical communication, imaging, sensing/laser applications.

This work was supported in part by the National Science Foundation (grant number: 2113010), and Air Force Office of Scientific Research (FA9550-21-1-02204) (AFOSR-AOARD, FA2386-21-1-4057)

2:00 PM EL05.09.01
Self-Assembly of Cadmium Dipeptide Nanoparticles into Bowtie Complex Microparticles with Chirality Continuum Prashant Kumar[1], Thi Vo[1], Minjeong Cha[1], Anastasia Visheratina[1], Ji-Young Kim[1], Wenqian Xu[2], Wonjin Choi[1], Sharon Glotzer[1] and Nicholas A. Kotov[1]; [1]University of Michigan, United States; [2]Argonne National Laboratory, United States

Mathematical descriptors of mirror asymmetry are continuous, but chirality in chemical disciplines is often viewed as a binary characteristic of molecules and there was no known chemical structure with widely variable chirality measures. Here we show that sub-microscale nanostructured particles can be self-assembled from anisotropic building blocks with widely variable geometry, chirality measures and optical asymmetry while retaining consistent bowtie shapes. The self-limited self-organization of anisotropic building blocks [1] makes possible high synthetic reproducibility and computational predictability of their geometries for different concentrations of reagents, ionic components, enantiomeric compositions, media polarity and other parameters. The positive and negative chiroptical peaks observed from UV to IR parts of the spectrum originate from absorptive and scattering phenomena with contribution from both dipolar and quadrupolar modes characteristic of nanostructured particles with submicron scale chirality.[2] The dependence of geometrical chirality measures and chiroptical characteristics enable the predictive synthesis of bowties with desirable polarization rotation. Controllable pitch, length, width, and thickness leads to tunable chiroptical activity across from UV to IR, which can be used to print chiroptical metasurfaces for photonic markers for machine vision devices. [3]

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2:15 PM EL05.09.03
Mechanically Interlocked Plasmonic Nanocatenanes Yoonhee Kim and Jwa-Min Nam; Seoul National University, Korea (the Republic of)

The design of nanostructures is often inspired by the geometries of molecular systems. Inspired by mechanically interlocked catenane architectures, here we report the synthesis of permanently interlocked inorganic nanocatenanes. In this presentation, I will cover the novel insights on the chiroptical and opto-mechanical properties of the plasmonic nanocatenanes and demonstrate the underlying principles stemming from the mechanically interlocked structure. Assemblies of colloidal inorganic nanocrystals show outstanding optical, magnetic, and catalytic properties not found in individual nanostructures. However, because of the weak nature of the interparticle interactions, the structural stability of such assemblies is vulnerable to environmental conditions. To overcome this intrinsic limitation, unbreakable bonds between the constituent nanostructures are required. Thus, the nanocatenanes are invented and prepared in a strategy analogous to the template synthesis of [2]catenane developed by Jean-Pierre Sauvage. As we use plasmonic materials to synthesize gold nanocatenanes (AuNCats), the structural characteristics of catenane architectures are combined with the distinctive optical properties of plasmonic materials. We present an analysis of the behavior of the localized surface plasmon resonance of AuNCats comprised of two gold nanorings in terms of D_{2d} spatial symmetry. Moreover, the rocking motion of one nanoring relative to the other causes structural desymmetrization into D_2 symmetry, and induces mechano-helical chirality of an AuNCat as a structural analogy of the [2]catenane. This results in the occurrence of chiroptical responses and remarkably high g-factors. As a proof of concept, we constructed a nanoactuator using an AuNCat in tandem with a thermoresponsive polymer. The incident light induces interband transitions of gold and the resultant thermal actuation of the plasmonic nanomachine transforms rectilinear force into rotational mechanical motion, which enables control of the circular dichroism of the plasmonic nanostructure. We anticipate that mechanically interlocked plasmonic platforms will introduce a new class of nanostructures with unprecedented capabilities. This work was selected as the cover for the August issue of *Nature Synthesis* and introduced in *Research Briefing* in the issue.

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2:30 PM EL05.09.04
Pre-ceramic Polymer-Assisted Nucleation and Growth of Anisotropic, Chalcogenide Nanostructures Patricia A. Loughney[1], Kara Martin[2], Paul Cuillier[1], Edward Trigg[2,3], Nicholas Posey[2,3], Matthew Dickerson[2], Timothy Pruyn[2] and Vicky Doan-Nguyen[1]; [1]Ohio State University, United States; [2]Air Force Research Laboratory, United States; [3]UES, Inc., United States

Polymer-derived ceramics (PDC) are of interest due to their industrially favorable processing steps which allow shaping to various form factors not readily achievable with conventional ceramics. PDCs are also a viable material to mix with functional nanoparticles to produce advanced nanocomposites. PDCs are already highly tunable systems without property-rich nanoparticle dispersion, and the inclusion of functional nanoparticle fillers allows for increasingly tailorable properties. This has made PDCs a viable matrix for several applications including photocatalysis, energy storage, and functional coatings. Nanoparticle fillers can lend interesting properties to a ceramic matrix that are tunable based on nanoparticle size and morphology if in a small enough regime (<10 nm). Often, these morphologies are targeted with a bottom-up thermolysis route due to its control over the nucleation and growth events for nanostructures already established in the field. However, conventional capping ligands used in nanoparticle thermolysis have poor miscibility with pre-ceramic polymers due to dissimilar geometry, chain lengths, and chemical components. This leads to aggregated nanofillers and therefore diminished functional properties. To control dispersion, secondary nanoparticle processing is performed by adhering PCP-miscible caps to the nanoparticle surface after synthesis. This often sacrifices size control established for small and reactive, non-noble nanoparticles. In this work, we have successfully eliminated the need for secondary nanofiller processing prior to dispersion through the development of a novel, one-pot, copper sulfide synthesis in which a pre-ceramic polymer with dual functionality both assists the stable formation of nanoparticles and serves as the final graft molecule. We monitored the success of this pre-ceramic polymer-assisted nucleation and growth (PPANG) and the role of the pre-ceramic polymer in the reaction through several characterization methods probing both the nanoparticle core and polymer graft. These methods include synchrotron X-ray scattering and pair distribution functions, transmission electron microscopy, *in-situ* small-angle X-ray scattering, nuclear magnetic resonance, and Fourier transform infrared spectroscopy. In our findings, we have discovered that the pre-ceramic polymer acts as a reducing agent, reactant, capping ligand, and shows promise to control and tune growth to various sizes and anisotropic morphologies for chalcogenide nanoparticles.

2:45 PM EL05.09.05

Dual SERS Enhancement Using Silver Nanoshells and Graphene Quantum Dots Hanyoung Lee and Hyejin Chang; Kangwon National University, Korea (the Republic of)

Recently, advanced Raman enhancement platforms using plasmonic nanoparticles (NPs) and non-plasmonic materials such as graphene or graphene quantum dots (GQDs) simultaneously have been reported, named 'dual enhancement' platforms. Compared to plasmonic substrates generally used, the dual enhancement platform has several advantages from advanced charge transfer-induced chemical mechanism enhancement (CM) between the molecules and graphene and attracting the analyte molecules even with weak affinity to plasmonic NP surfaces. In this study, novel design of dual SERS substrate is proposed based on bumpy Ag nanoshells (Ag NSs) and two type of GQDs with different edge structures, zigzag and armchair form. The fabricated SERS substrates were characterized by SEM, EDS, AFM and Raman spectroscopic analysis. Our dual SERS substrate exhibits enhanced signal compared to Ag NSs substrates. By controlling edge of GQDs, electronic structure of GQDs was tuned, leading to different CM effect for Rhodamine 6G. Detailed results will be described in the presentation.

SESSION EL05.08: Applications I
Session Chairs: Ateet Dutt and Pier Carlo Ricci
Friday Morning, April 14, 2023
Moscone West, Level 2, Room 2000

9:00 AM EL05.08.01
***In Vivo* Real-Time Multiplex Detection of Plant Signalling Molecules Using Surface-Enhanced Raman Scattering Nanosensor** Won Ki Son, Seon-Yeoung Kwak and Dae Hong Jeong; Seoul National University, Korea (the Republic of)

International food crisis caused by population growth, environment pollution and climate change has been emerged as one of humanity's the most important problems demanding new agricultural approaches such as smart farm. To understand the biological and chemical dynamics of plants is essential part in next-generation agriculture, and various sensor technologies are studied and applied. The chemicals as known as '*signalling molecules*' which are released against adverse stimuli to activate defense system of plants are drawing attention as a key to understand plant's biological status under stressors. As one of the analytical approaches to detect signalling molecules, surface-enhanced Raman scattering (SERS)-based optical nanosensor has shown strong potential for its non-invasiveness, water-transparency and capability of real-time detection of chemical dynamics from fingerprint spectra which depend on molecules' own vibration modes.

In our research, we fabricated PDDA-capped Ag bumpy nanoshell (AgNS@PDDA) which has high enhancement factor of *ca*. 10^7 and introduced it into plants by infiltrating through stoma. Infiltrated AgNS@PDDA were found to be localized in intercellular space. Thanks to the plasmonic properties of AgNS@PDDA in near-IR window, it was possible to evade chlorophyll's strong autofluorescence and obtain SERS signals with signal-to-noise ratio of up to 64 with an acquisition time of ~100 ms. PDDA polymer provided aqueous stability for maintaining colloidal stability and effectively attracted signalling molecules most of which are negative conjugate base form by coulombic interaction. As an example, adenosine triphosphate (ATP), known to play a critical role in plant autoimmune systems, is difficult to detect in SERS because of its poor affinity toward metal surface. However, with the PDDA chain forming hydrogen bonding, it was possible to detect with LOD of 10 nM in aqueous solution. Since the interaction between the polymer chain and analytes was reversible, AgNS@PDDA was found to be effective to monitor the change of the concentration of signalling molecules in real time. Also, for quantitative analysis in complicate mixture, we made mathematical models to calculate the concentration of each component from the intensities of SERS signals.

Then, we studied the plant's reaction against biotic and abiotic stress with SERS signal monitoring. When plants leaf was physically wounded, nasturlexin B, one of the phytoalexin, and eATP were detected and those molecules were successfully to monitor the change of concentration in real time for 1 hour after the wound occurred. In addition, glutathione could be detected in watercress exposed to non-freezing cold stress (4 °C, 24 h). The signals from both stresses showed statistically significant difference compared to the signals from the control group. Meanwhile, biotic stress was studied for the plants infected with fungal disease. *F. Graminearum* was cultured and injected into the plant, and the emerging of signaling molecules in the plant was monitored with nanosensors according to the elapsed days after injection. Even only 2 hours after the fungi injection, when no lesion was detectable, SERS signals of eATP and salicylic acid related to systemic acquired resistance (SAR) were successfully detected. Fungal signals were also detectable after day 2 when the lesion began to be visible. It indicated that the fungal infection was successfully diagnosed at a very early stage with SERS nanosensor, while real-time PCR analysis, an existing diagnostic method, could not confirmed fungal infection until day 1.

Based on our research, we expect that the SERS nanosensors provide novel approach for plant stress diagnosis and early diagnosis of diseases.

9:15 AM EL05.08.02
Dynamic Surface-Enhanced Raman Spectroscopy (d-SERS) Using Plasmonic Metal-Semiconductor Hybrid Nanoparticles for Biosensing with Improved Sensitivity, Selectivity and Reliability Tabitha Jones and Tung Chun Lee; University College London, United Kingdom

Hybrid nanomaterials of plasmonic metals and semiconductors have been the focus of growing research in surface-enhanced Raman spectroscopy (SERS).[1] Significant increase in SERS signals can be achieved by harnessing additional chemical enhancements which occur due to photo-induced charge transfer between a plasmonic metal and a semiconductor. A notable example is photo-induced enhanced Raman Scattering (PIERS), where additional boost of SERS signals can be achieved via UV-light irradiation that creates oxygen vacancies and consequently activates the chemical enhancement.[2] Recently, our group demonstrated the first UV-irradiation-free PIERS effect by employing nanoscale coatings of SnO_2 that are intrinsically rich in oxygen vacancies.[3]

Here, we present a new and unusual SERS phenomenon.[4] Colloidal Ag@SnO_2 core@shell nanoparticles (NPs) were synthesised and fabricated into a compact layer of solid substrate. When SERS measurements were performed, the signal showed a significant and irreversible increase over time (up to 25-fold enhancement after an hour). We name this effect dynamic-SERS (d-SERS). While not observed for uncoated Ag NPs, d-SERS results in much larger signals than conventional SERS (by more than 1 order of magnitude) and reveals target-specific dynamic information. We performed d-SERS measurements for a range of clinically relevant analytes, including uric acid and ketamine, achieving sub-mM limit of detection. Notably, the rate of increase of the characteristic SERS peaks can be used for quantitative detection of these analytes, showing improved reliability of the measurement by reducing the signal variability due to non-uniform substrate morphologies.

In attempt to elucidate the underlying mechanism of d-SERS, we performed X-ray photoelectron spectroscopy (XPS) and studies on laser powers and external heating. We propose that the enhancement is due to plasmonic heating of the Ag NPs, which generates additional oxygen vacancies in the SnO_2 enabling charge transfer and boosting the chemical enhancement component of SERS. This work opens up new possibilities for plasmonic metal-semiconductor hybrid SERS and paves the way for improved detection of a range of analytes, with applications in healthcare, security and environmental monitoring.

[1] Langer, J. *et al. ACS Nano,* **2019**, 14, 1, 28-117
[2] Ben-Jaber, S. *et al. Nat Commun.,* **2016**, 7, 12189
[3] Davison, G. *et al.* **2022** [Manuscript submitted for publication]
[4] Jones, T. *et al.* **2022** [Manuscript in preparation]

9:30 AM EL05.08.03
The Translational Approach of Colloidal Surface-Enhanced Raman Nanoparticles— Multiplexed Biomedical Imaging and In Vivo Clearance
Jung Ho Yu, Jianghong Rao and Sanjiv Sam Gambhir; Stanford University School of Medicine, United States

In this presentation, I will present our chemistry efforts to engineer surface-enhanced Raman scattering (SERS) nanoparticles for multiplexed biomedical imaging and its translation.
(i) Along with the biomedical applications of SERS for molecular assays and sensing, we have utilized the high spectral resolution of SERS signals for multiplexed preclinical imaging of cancer. To gain sufficient brightness for the in vivo imaging condition, we controlled SERS nanoparticles oligomerization to produce multicore SERS nanoparticles, which displayed Raman scattering as bright as near-infrared (NIR) fluorescence. The large enhancement factor from hot-spot geometry of the multicore nanoparticles along with the NIR-resonant Raman reporters produced the SERS signals as bright as NIR fluorescence. With the multicore SERS nanoparticle palettes, we demonstrated noninvasive and five-plex ratiometric imaging of tumors in live preclinical models, which simulated the noninvasive assessment of multiple biological targets within tumors (Yu JH *et al*. ACS Nano 2021).
(ii) While the colloidal SERS nanoparticles have limited their use in humans because of their inability to excrete from the body, we address this problem by creating supraparticles composed of small-sized nanoclusters. We performed the FDTD simulation of the supraparticle design, in which the maximum enhancement factor of 10^6 was achieved. Then, we chemically synthesized bright supraparticles that enabled in vivo Raman imaging of rodent models. Furthermore, the supraparticles were highly excretable, offering great potential for clinical application of the surface-enhanced Raman scattering imaging by replacing non-excretable SERS nanotags (Yu JH *et al*. bioRxiv 2022).

References
1. Yu JH *et al*. Noninvasive and Highly Multiplexed Five-Color Tumor Imaging of Multicore Near-Infrared Resonant Surface-Enhanced Raman Nanoparticles *In Vivo.* ACS Nano **2021,** *15,* 19956-19969.
2. Yu JH *et al.* Highly Excretable Gold Supraclusters for Translatable In Vivo Raman Imaging of Tumors. bioRxiv 2022. (https://www.biorxiv.org/content/10.1101/2022.10.18.512314v1).

9:45 AM EL05.08.04
Designing Sequence-Defined Peptoids for Bio-Inspired Synthesis of Plasmonic Nanomaterials Chun-Long Chen; Pacific Northwest National Laboratory, United States

In nature, biomolecules (e.g. proteins) play significant roles in the assembly of hierarchical structures and delivering sequence-specific functions ranging from photosynthesis, to molecular separation, selective ion transport, and tissue mineralization. Inspired by nature, many sequence-defined polymers have been designed and exploited for the bio-inspired materials synthesis. [1] While bio-inspired synthesis offers great potential for controlling nucleation and growth of inorganic particles, precisely tuning polymer-particle interactions has been a long-standing challenge. [2] On the other hand, despite that the morphology-dependent physical and chemical properties of plasmonic nanomaterials are significant for applications in sensing, photonics and catalysis, achieving the high-level of control over morphology seen in biomineral formation controlled by proteins and peptides is still a significant challenge and the rules governing bio-controlled formation of plasmonic nanomaterials remain to be exploited. [3] Among various peptide mimetics, peptoids have received particular attention for achieving predictive materials synthesis because they offer unique opportunities for tuning inter-molecular and molecule-particle interactions solely through variations in side-chain chemistry, while still emulating the capacity of peptides and proteins for molecular recognition. [4]
In this talk, I will report our recent progress in designing sequence-defined peptoids for controlled synthesis of well-defined plasmonic nanomaterials. By engineering peptoid sequences and investigating resulting particle formation mechanisms, we developed a rule of thumb for designing peptoids that predictively enabled the morphological evolution from spherical to nanocoral-shaped metallic nanoparticles. We demonstrate that the individual nanocoral-shaped gold particles exhibit a plasmonic enhancement as high as 10^5 fold. Our study shows that tuning peptoid-peptoid and peptoid-particle interactions and peptoid amphiphilicity are crucial for driving particle attachment during the early stages of formation of the branched nanostructures. [3] In another study, [5] we used variations in peptoid sequence to manipulate peptoid-Au interactions, leading to the synthesis of concave five-fold twinned, five-pointed Au nanostars *via* a process of repeated particle attachment and facet stabilization. Control over peptoid-particle interactions provides diverse possibilities for directed formation of plasmonic nanomaterials. These mechanistic studies will offer molecular level understanding of peptoid-induced plasmonic nanomaterials formation and guide the design of new peptoid sequences that enable the precise tuning of peptoid-peptoid and peptoid-particle interactions for particle attachment and facet-specific stabilization.

References: 1). C. L. Chen, N. L. Rosi, Peptide-based methods for the preparation of nanostructured inorganic materials. *Angew. Chem., Int. Ed.* **49**, 1924-1942 (2010). 2) B. Cai, Z. Li, C.-L. Chen, Programming Amphiphilic Peptoid Oligomers for Hierarchical Assembly and Inorganic Crystallization. *Acc. Chem. Res.* **54**, 81-91 (2021). 3) F. Yan *et al.*, Controlled synthesis of highly-branched plasmonic gold nanoparticles through peptoid engineering. *Nat. Commun.* **9**, 2327 (2018). 4) W. Yang, Q. Yin, C.-L. Chen, Designing Sequence-Defined Peptoids for Biomimetic Control over Inorganic Crystallization. *Chem. Mater.* **33**, 3047-3065 (2021). 5) Z. Li, B. Cai, W. Yang, C.-L. Chen, Hierarchical Nanomaterials Assembled from Peptoids and Other Sequence-Defined Synthetic Polymers. *Chem. Rev.* **121**, 14031-14087 (2021). 6) B. Jin *et al.*, Peptide-Directed Formation of Five-Fold Twinned Au Nanostars through Particle Attachment and Facet Stabilization. *Angew. Chem., Int. Ed.* **61**, e202201980 (2022).

10:00 AM BREAK

10:30 AM EL05.08.05
Ag Nanogap Shell-Based SERS Immunoassay for Diagnosis of Pancreatic Cancer Chanhee Choi, In-Jun Hwang, Sin Lee, Yoonhee So, Ye-Sol Myeong, Jun-Hyeong Lee and Jong-Ho Kim; Hanyang University, Korea (the Republic of)

Cancer is one of the most leading causes of death in the world. In particular, pancreatic cancer shows the lowest 5-year survival rate mainly due to difficulty in its inaccurate diagnosis at the early stage. In the early stage of pancreatic cancer, most of the patients have no subjective symptoms, and some blood biomarkers used for its diagnosis are very low in concentration. Hence, it is of great significance to design a sensitive diagnostics that can effectively detect the blood biomarkers, including CA19-9, at the early stage of pancreatic cancer in a rapid and accurate manner. Herein, we demonstrate a surface enhanced Raman scattering (SERS) nanoprobe-based immunoassay capable of sensitively detecting blood biomarkers for the diagnosis of pancreatic cancer. To this end, Ag nanogap shells (AgNGS) were prepared as SERS nanoprobes emitting very strong signals through the Raman labels-mediated kinetic control of nanogap sizes. The as-prepared AgNGSs exhibited their own SERS signals with an enormous intensity enhancement of 10^7 and the superior signal stability. After a detection antibody specific for CA19-9 was conjugated onto AgNGSs (denoted AgNGS nanoprobes), they were incubated with capture antibody-conjugated magnetic nanoparticles to detect the target CA19-9 based on the AgNGS SERS signals. This AgNGS nanoprobes-based sandwich immunoassay was able to detect CA 19-9 as the concentrations as low as 0.35 ng/mL from serum samples. The use of this AgNGS nanoprobes-based immunoassay can be extended for the sensitive and selective detection of various blood biomarkers, allowing the early-stage diagnosis of other diseases.

10:45 AM EL05.08.06
Nanoplasmonic On-Chip Immunoassay for Cancer-Derived Exosome Profiling and Exosome-Mediated Cell Communication Analysis Chuanyu Wang, Chung-Hui Huang and Pengyu Chen; Auburn university, United States

Exosomes are nano-sized extracellular vesicles (EVs) that carry unique surface compositions derived from their cells of origin. Tumor cell-derived exosomes play a vital role in the development of cancer by creating a biological milieu in which primary tumor cells can interact with their microenvironment to enhance cancer cell survival, proliferation, and the evasion of immune surveillance. Recent studies suggest that tumor cells can evade immune inspection by secreting excessive exosomes with surface expression of programmed death ligand 1 (PD-L1). Moreover, tumor cell-derived exosomes can stimulate immune cells to secrete cytokines with pro-tumorigenic function. Therefore, we have developed on-chip immunoassays to analyze the role of tumor cell-derived exosomes in the immune system. First, Au@Ag core-shell nano-bipyramids and gold nanorods based on-chip nanoplasmonic sandwich immunoassay provide rapid, sensitive quantification of exosomes and also accurate subtyping exosomes upon PD-L1 expression levels. Second, a specially designed on-chip device consists of cell isolation chambers and a gold nanosphere-based nanoplasmonic digital immunoassay, rendering *in situ* remote cell communication and immune analysis of cellular secretions and traces. These developed platforms provide new methods for tumor cell-derived exosome detection and analysis that have high potential as a future clinical diagnostic tool for monitoring cancer progression and as an analytical tool for accurate and comprehensive analysis of the immune system.

11:00 AM EL05.08.08
Degradation of Rhodamine B Through Plasmon-Assisted R.O.S Generation of Gold Nanorods Ramprasath Rajagopal, Tianhong Ouyang, Gwen Liu, Shyamsunder Erramilli and Bjoern Reinhard; Boston University, United States

Plasmonically enhanced femtosecond irradiation was found to exhibit a remarkable selective inactivation of pathogens while exhibiting minimal side effects on representative biologic and mammalian cell targets. Within the rich set of femtosecond light-matter interactions, nanocavitation was found to be the primary method of inactivation. Under comparable conditions, we report R.O.S mediated degradation of Rhodamine B in the presence of gold nanorods with longitudinal surface plasmon resonance (LSPR) of 750-760nm irradiated by 800nm 100-fs Ti-Sapphire regeneratively amplified laser pulses up to $3mJ/cm^2$. Rhodamine B is a known carcinogenic waste-water pollutant that cannot be degraded easily by current waste-water treatment technologies. We also utilize it as a reporter of generated R.O.S, through a robust and accessible fluorescence monitoring scheme to track kinetics of Rhodamine B degradation. We elucidate the dependence of R.O.S generation on nanorod volume, presence of ligands, and pump fluences. Alongside ongoing theoretical and experimental studies on plasma and R.O.S generation through ultrafast irradiation of gold nanorods, it is interesting to explore R.O.S generation for therapeutic and chemical applications, and better theoretical understanding of the ultra-fast high power light-matter interactions.

11:15 AM EL05.08.09
Tuning Multi-Polar Plasmonic Modes of NIR Absorbing Long AuNRs Toward Ultra-Sensitive Optical Sensor Kyoungweon Park[1,2], Eva Yazmin S. Santos[3], Alexander Govorov[3] and Richard A. Vaia[1]; [1]AFRL, United States; [2]UES, Inc., United States; [3]Ohio University, United States

Ensembles of large aspect ratio gold rods (AuNRs) are of technological interest due to their extreme optical extinction coefficients at visible and near infrared wavelengths, ultra-fast plasmonic and excitonic character, and self-assembly and field responsivity in concentrated systems that tunes optical and rheological behavior via permanent or temporal order. Furthermore, with increasing aspect ratio and volume, higher order harmonics appear due to phase retardation within the excited particle. Such multipole plasmonic resonances exhibit even larger quality factors due to greater electromagnetic field localization, and are useful in applications pertaining to light signal routers, light manipulators, or multistep enhancers in processes such as second harmonic generation. However, suspensions of large aspect ratio AuNRs often exhibit large polydispersity, which obscures these physicochemical behaviors across the ensemble and at the macroscale. Herein, we discuss synthesis procedures that simultaneously satisfy production scalability with no loss to quality and geometric tunability. Quadrupole and octupole resonances are observed in solutions and films from an ensemble of concentrated AuNRs (>1 mg/mL) with aspect ratios ranging from 5 to 10 and structural dispersity less than 0.1. The relationship between multipole resonance, aspect ratio, particle volume, dielectric environment, and polarization agrees with theoretical predictions.

SESSION EL05.10: Virtual Session I
Session Chairs: Ateet Dutt and Pier Carlo Ricci
Thursday Morning, April 27, 2023
EL05-virtual

8:00 AM *EL05.10.01
432 Symmetric Chiral Gold Nanoparticles for Enantioselective Sensing Ki Tae Nam; Seoul National University, Korea (the Republic of)

Characterizing molecular chirality and understanding their roles in physiochemical situations has been important in broad research scope such as, biology, chemistry, and pharmaceutics. Despite its importance for biochemical principles and relevant applications, it has been considered impossible to in-situ monitor the chirality change of a few molecules with simple optics because of the scale mismatch with the incident light. Previously we demonstrated strong polarization controllability in 432 symmetric chiral gold nanoparticles (432 helicoids) [1,2], synthesized by exploiting chirality transfer between peptide and high-Miller-index gold surfaces. Based on the 432 helicoids, here we discovered a new mode of circular dichroism (collective CD) that can emerge as a result of collectively resonant oscillations (collective resonance) of hexagonally assembled 432 symmetric chiral gold nanoparticles (2D helicoid crystal) and admit extremely low-density enantioselective detections [3]. The slanted incidence of circularly polarized light (CPL) on the 2D helicoid crystal results in collective oscillation and spinning behavior of optically induced electric dipoles of helicoids, and these spinning dipoles leads to strong and uniform chiral electromagnetic field (optical helicity) across the array. The chiral molecules interact with this field modulate the electromagnetic energy of the 2D helicoid crystal depending on the molecular handedness, which substantiated by the asymmetric shift of transmission spectra. Furthermore, we found the opposite optical responses in 2D helicoid crystal for illumination of oppositely handed CPL which leads drastic contrast in CD spectra. Utilizing the new mode of circular dichroism, we achieved the fluidity-based, in-situ monitoring of molecular chirality at an ultrahigh sensitivity. Then, we further elucidated the importance of collective circular dichroism by translating it into the proof-of-concept devices such as a colorimetric cuvette chiral sensor, an on-chip chiral sensor, the total reflection based SPR system, which enable in-situ, enantioselective, and picomolar monitoring of the DNA/RNA hybridization and the protein folding of the SNARE complex. We believe that our collective circular dichroism-based strategy offers a new paradigm and rational design rules of chiral plasmonic structures for robust enantioselective sensing.

8:30 AM *EL05.10.02
Modeling Colloidal Photonic Nanostructures - from Quantum Simulations to Optimizing Self-Assembled Plasmonic Nanoparticle Superlattices
Jost Adam; University of Southern Denmark, Denmark

Designing new plasmonic nanomaterials with unique physical and chemical characteristics and outstanding optical properties remains a critical task for advanced energy conversion and sensing concepts. Optimizing the material properties to improve their functionality and performance in plasmonic applications is a subsequent challenge to be tackled. This presentation will overview recent advances in the computational design of potential future plasmonic materials, such as transition metals and transparent conducting oxides, and their application in colloidal plasmonic structures. The extraction of complex dispersion characteristics from density functional theory (DFT) calculations allows the integration into subsequent electromagnetic modeling steps, ranging from isolated particles of various shapes and materials to self-assembled plasmonic nanoparticle superlattices, exhibiting collective plasmonic crystal responses.

The talk will furthermore propose a path to minimize the gap between combined quantum- and electromagnetic simulations and experimental characterization of self- or chemically assembled nanostructures, employing a combination of statistical image analysis (based on SEM images of self-assembled clusters), finite-element modeling, and material- and structure optimization. Based on image statistics, we introduce and superimpose various morphological irregularities in our model alongside optimization of particle morphology, potential shell thickness, and particle materials. Our results, corroborated by electromagnetic simulations and complemented by optical characterization and SERS measurements, provide insight into the near-field enhancement of nanospheres, nanorods, and nanotriangles, arranged in sub-wavelength superlattices of macroscopic dimensions.

9:00 AM *EL05.11.04
Growth, Assembly and Transformation of Plasmonic Nanostructures in Confined Spaces Yadong Yin; University of California, Riverside, United States

Growth, assembly, and transformation in confined spaces represent a set of indirect methods for producing colloidal plasmonic nanostructures with highly tunable morphologies and configurable optical properties. We will discuss the basic working mechanisms involved in such synthesis and assembly strategies, their applicability, and the directions of future efforts. We will reveal the unique feature of the space-confinement method in creating thermodynamically unstable nanostructures. Upon removing the confinement, these nanostructures transform into more stable morphologies through reconstruction, providing opportunities for designing new nanostructures with promising applications in sensing, anti-counterfeiting, information encryption, and displays. Further, we will discuss the many opportunities of this synthesis strategy in creating hybrid nanostructures that integrate the plasmonic property with other physical properties

SESSION EL05.11: Virtual Session II
Session Chairs: Ateet Dutt and Svetlana Neretina
Thursday Afternoon, April 27, 2023
EL05-virtual

1:00 PM *EL05.11.01
Photocatalysis Enhanced by Plasmonic Nanoparticles Dongling Ma; Institut national de la recherche scientifique (INRS), Canada

Due to their unique, size- and shape-tunable surface plasmon resonance, plasmonic nanostructures have recently been explored for increasing the efficiency of photocatalysis. Essentially they enhance and/or broaden solar photon harvesting via improved light scattering, strong near field effect and/or hot electron injection. In this talk, I will present our recent work on the synthesis of plasmonic nanoparticles and hybrid nanomaterials (the assemblies of plasmonic nanoparticles and semiconductor photocatalysts) as well as their applications in solar fuel and photocatalytic degradation of pollutants in our environments [1-5]. Rational design of hybrid nanomaterials, which is the key to maximize the beneficial plasmonic effects, is highlighted. One example is about developing an in situ ligand method to load cost-effective, plasmonic semiconductor CuS nanoplatelets on rationally selected BiOCL semiconductor nanosheets and nanoplates, with a close interface, monodispersion and relatively large interface. As a result, we achieved the efficient hot hole collection from the CuS nanoplatelets as supported from largely broadened photocatalysis. Theoretical modelling revealed that the transverse mode dominates the hot hole generation and has a greater contribution to photocatalysis than the longitudinal mode. This work demonstrates the feasibility of harvesting hot holes from plasmonic semiconductors and opens a new route for rational design of broadband and cost-effective plasmonic photocatalysts.
Related references:
[1] *Applied Catalysis B: Environmental*, 2022, 317, 121792
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[3] *Chemistry of Materials*, 2021, 33, 695
[4] *Advanced Functional Materials,* 2015, 25, 2950
[5] *Nature communications*, 2022, under revision.

1:30 PM EL05.11.02
Optical Coupling of Plasmonic and Surface Lattice Resonances in Gold Nanocube Arrays Marlo Vega[1], Jean-Francois Bryche[1], John Hulse[2], Michel Canva[1], Paul Charette[1] and Li-lin Tay[2,1]; [1]Université de Sherbrooke, Canada; [2]National Res Council Canada, Canada

The ability of localized surface plasmon to confine light to a sub-diffraction-limited mode volume can drive coherence effects in quantum emitter systems that lead to quantum photonic applications. Periodic arrays of plasmonic nanostructures can further sustain photonic lattice resonances (also referred to as surface lattice resonance) that can be tuned to couple with plasmonic resonance. Here, we will demonstrate the varying degrees of optical coupling that arise when periodic arrays of gold nanocubes (AuNC) are grown atop a gold mirror. This architecture allows us to independently control the two distinct optical modes, a plasmonic gap mode between the AuNC and the gold surface and a lattice resonance mode resulting from constructive interference from the scattering of the periodic array. From electromagnetic simulation and reflectance spectroscopy, we will show that these two resonance modes can be tuned and show a varying degree of coupling that is dependent on the nanostructure geometry, lattice pitch and lattice symmetry. A series of periodic arrays of 73 nm of AuNC on top of a 100 nm Au mirror with a 4.6 nm polymethyl methacrylate (PMMA) spacer and with periodicity ranging from 500 nm to 950 nm were fabricated through a Si nanofabrication services. The gaps between the AuNCs are partially filled by SiO2 spacer. Electromagnetic simulation of these structured arrays has shown that the breadth and peak of the lattice resonance mode sharpens and red-shits with increasing periodicity. In the lowest periodicity array, only plasmonic gap modes are observable. When the periodicity reaches 500 nm, two optical modes become visible with the longer wavelength reflectance peak corresponding to the plasmonic gap mode and the shorter wavelength peak associated with the lattice resonance. A visible coupling of the plasmonic gap mode to the surface lattice mode was observed in an AuNC array with 600 nm periodicity which is indicative of mode hybridization. We will also discuss the impact that particle geometry and material have in this presentation.

1:35 PM EL05.11.03
Bimetallic Superatomic Bi-icosahedral Au_xCo_y Clusters for Data Storage Benjamin Raufman, Desmond Smith, Zaid Qureshi, Dariush Aligholizadeh and Mary Sajini Devadas; Towson University, United States

Atomically-precise gold nanostructures have garnered considerable research interest over recent years because of their applications in imaging, catalysis, sensing, medicine, and more. One of the most investigated gold nanostructures is the thiol-capped Au25 nanocluster due to its exceptional stability, facile synthesis, and the ease with which its physiochemical properties can be manipulated. The stability of this nanocluster derives from its “magic-number”, meaning its closed outer-electron shell. Au_{25} also exhibits superatomic properties due to its ultra-small size and construction from an even smaller superatom: the Au_{13} nanocluster. The Au_{25} cluster has been synthesized in two structural varieties: the icosahedron and the bi-icosahedron forms. Recent studies have shown this cluster can be easily doped with other metallic atoms, each offering unique properties and insights, although most of these studies focus on the icosahedron structures. Many of these studies demonstrate some advanced property, such as increased fluorescent quantum yield, increased catalytic effect, or magnetism, which have been taken advantage of for applications in both the biomedical field and advanced chemical research.

Herein, we report a method to synthesize and purify a novel bi-icosahedron cobalt-doped $Au_{25-x}Co_x(PPh)_{10}(SR)_5Cl_2$ cluster for the first time. Although the synthesis is straightforward, the purification is cumbersome. Once purified, UV-vis absorption, fluorescence, NMR, and electrochemical analysis were utilized to characterize the novel cluster. Data gathered using these methods showed results consistent with the expected results based off previous reports on its theoretical icosahedral counterpart, as well as the un-doped bi-icosahedral cluster. The UV-vis spectra of the novel clusters is highly similar to that of the un-doped cluster, with the most notable difference being a splitting of the peak in the NIR region. The fluorescent quantum yield shows a slight decrease from that of the un-doped cluster. Most importantly we see the effect of spin-orbit coupling in the doped clusters. These results suggest a number of future potential applications for these clusters in computers.

SYMPOSIUM

April 11 - April 25, 2023

Symposium Organizers
Fei Ding, University of Southern Denmark
Min Seok Jang, Korea Advanced Institute of Science and Technology
Xi Wang, University of Delaware
Jinghui Yang, University of California, Los Angeles

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* Invited Paper
\+ Distinguished Invited

SESSION EL06.01: Dynamic Metamaterials and Metasurfaces I
Session Chairs: Min Seok Jang and Xi Wang
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3022

10:30 AM *EL06.01.01
“Meta”-Optical Fibers—Integration of Metaphotonics with Fiber Optics Andrew Palmer, Leon Zhang, Stuart Love, Zoey Liu and Ho Wai (Howard) Lee; University of California, Irvine, United States

Optical fiber is a well-established and efficient light-guiding medium. Although optical fiber is efficient for transmitting light, its functionality is limited by the dielectric material of the core, which has poor optoelectronic, magneto-optical, and nonlinear-optical responses and has a dielectric diffraction limit.

Therefore, the optical properties of the optical fiber such as phase, amplitude, polarization, and mode profile, cannot be altered after the fiber drawing fabrication, thus limiting the development of novel in-fiber devices. Integration of new materials and nanostructures into fiber will enhance processing/transmission capabilities and novel functionalities.

In this talk, I will present our recent development of “Meta”-optical fiber, an advanced optical fiber integrated with emerging nanophotonic concepts such as optical metasurfaces, plasmonic nanowires, and zero-index photonics. I will present the development of ultrathin optical metalens which is cascaded on the facet of a photonic crystal fiber that enables light focusing. I will also discuss the first experimental demonstration of zero-index resonance excitation in an optical fiber coated with AZO nanolayer and excitation of plasmonic resonances on holey optical fiber for advanced optical sensing and tip-enhanced Raman spectroscopy. These advanced “meta”-optical fibers open a pathway to revolutionary in-fiber lasers/spectroscopies, optical imaging/sensing, and optical communication devices.

11:00 AM *EL06.01.02
Singularity Engineering and Structured Light by Meta-Optics Ahmed Dorrah and Federico Capasso; Harvard University, United States

Metaoptics offer fresh opportunities for structuring light as well as dark. I will discuss metasurfaces that enable light’s spin and OAM to evolve, simultaneously, from one state to another along the propagation direction[1,2], along with nonlocal supercell designs that demonstrate multiple independent optical functions at arbitrary large deflection angles with high efficiency.[3] In one implementation the incident laser is simultaneously diffracted into Gaussian, helical and Bessel beams over a large angular range and in another one a compact wavelength-tunable external cavity laser with arbitrary beam control capabilities including hologram lasing is demonstrated. We also propose a new class of computer-generated holograms whose far-fields have designer-specified polarization response, dubbed Jones matrix holograms.[3] We provide a simple procedure for their implementation using form-birefringent metasurfaces. In particular, we demonstrate holograms whose far-fields implement parallel polarization analysis and custom waveplate-like behavior. The realization of 2D phase and polarization singularities and the unique applications that they will open will be discussed[4] ·along with recent results on the realization of an equally spaced liner array of 0D phase singularities using inversed designed cylindrically symmetric phase only metasurfaces. Finally, a complete, topologically protected polarization singularity has been reported for the first time; it is located in the 4D space spanned by the three spatial dimensions and the wavelength and is created in the focal region of a lens using a metasurface.[5] The field Jacobian plays a key role in the design of such higher dimensional singularities, which can be extended to multidimensional wave phenomena, and pave the way to novel applications in topological photonics.
1. Ahmed H. Dorrah, Noah A. Rubin, Aun Zaidi, Michele Tamagnone & Federico Capasso
Nature Photonics **15**, 287 (2021)
2. Ahmed H Dorrah, Noah A Rubin, Michele Tamagnone, Aun Zaidi, & Federico Capasso *Nature Communications* **12,** 6249 (2021)
3. Noah A. Rubin, Aun Zaidi, Ahmed H. Dorrah, Zhujun Shi, & Federico Capasso *Science Advances*, **7**, eabg7488 (2021)
4. Soon Wei Daniel Lim, Joon-Suh Park, Maryna L. Meretska, Ahmed H. Dorrah, & Federico Capasso *Nature Communications*, **12**, 4190 (2021)
5. Christina M. Spaegele, Michele Tamagnone, Soon Wei Daniel Lim, Marcus Ossiander, Maryna Meretska, Federico Capasso arXiv:2208.09054 (2022)

11:30 AM *EL06.01.03
Electrochemically Actuated Metasurfaces Jason G. Valentine; Vanderbilt University, United States

In this talk I will explore the hidden potential of electrochemically actuated metasurfaces. Electrochemical actuation is unique in that it provides for control over both the volume expansion of a scatterer as well as the free electron density for permittivity control. I will explore this freedom in dynamic tuning of titanium dioxide and silicon-based metasurfaces, materials already popularized in the field of photonics for their high index and low loss throughout the visible spectrum. Using these materials, we leverage electrochemical intercalation of lithium to initiate phase changes in a continuously tunable, reversible, and bi-stable manner, using bias voltages that are an order of magnitude less than similar devices.

SESSION EL06.02: Dynamic Metamaterials and Metasurfaces II
Session Chairs: Fei Ding and Jason Valentine
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3022

1:30 PM *EL06.02.01
Controlling the Thermal, Optical and Mechanical Properties of Metasurfaces for Applications Towards Laser Sails Victor Brar; University of Wisconsin--Madison, United States

I will discuss how the materials used in metasurface-based laser sails set limits on their thermal stability and the maximum powers that can be used for propulsion. It will be shown that under high optical intensities, non-linear processes and temperature-dependent absorption can create thermal runaway effects in commonly used dielectrics such as silicon. In particular, the combination of two-photon absorption and temperature-dependent bandgap narrowing sets the equilibrium temperature for Si-based metasurfaces in high fluence conditions, and we find the conditions where no equilibrium is achievable. We will also show that the thermal runaway can nucleate near material defects and zodiacal dust, and we demonstrate the time evolution of those processes. Design strategies for mitigating such processes and simultaneously achieving high efficiency will be proposed which include minimizing non-linear materials, and including sacrificial zones on the sail that prevent the spreading of damage. Finally, we will discuss how thermal cooling can be used to impart mechanical stability on the sail, allowing for minimal movement within the drive laser beam.

2:00 PM *EL06.02.02
Nonlinear Optics in Space and Time with Novel Materials Vladimir Shalaev[1], Soham Saha[1], Samuel Peana[1], Mustafa Ozlu[1], Eran Lustig[2], Ohad Segal[3], Alexandra Boltasseva[1] and Mordechai Segev[3]; [1]Purdue University, United States; [2]Stanford University, United States; [3]Technion–Israel Institute of Technology, Israel

The emerging near-zero-index (NZI) materials have recently opened up new chapters of nonlinear optics by enabling strong light-matter interactions in both nanophotonic and hybrid photonic/plasmonic systems as well as greatly enhanced optical phenomena such as negative refraction, time refraction, and photon acceleration. Building up on our work on the extraordinary modulation of the refractive index in transparent conducting oxides (TCOs), we have demonstrated negative refraction in time-varying, strongly coupled optical media. We show large changes in the epsilon-near-zero (ENZ) points in undoped zinc oxide, with 20-ps response time, and utilize the permittivity modulation to enhance the third-harmonic generation, and develop optically controlled polarization switches. We also used the large nonlinearities in NZI TCO films for ultrafast pulse characterizations. Furthermore, we showed that the femtosecond modulation of TCO permittivity can be achieved by a tightly controlled pulse, opening new directions in nonlinear optics where a temporal modulation of permittivity can result in phenomena such as time refraction, reflection, and open bandgaps in the momentum of a photon pulse. This forms the basis of our investigations in photonic time crystals which can pave the way in gain-free lasing, non-reciprocal optics, and many other exciting fields.

2:30 PM EL06.02.03
Chemically and Electrically Driven Geometric Reconfiguration of Soft Polymer Metasurfaces for Dynamic Wavefront Manipulation Siddharth Doshi[1], Anqi Ji[1], Ali I. Mahdi[1], Scott T. Keene[2], Yi-Shiou Duh[1], Philippe Lalanne[3], Eric A. Appel[1], Mark L. Brongersma[1] and Nicholas Melosh[1]; [1]Stanford University, United States; [2]University of Cambridge, United Kingdom; [3]Université Bordeaux, France

The optical transfer functions of engineered metasurfaces are defined by the geometric arrangement and material properties of their constituent meta-atoms. Optical metasurfaces have traditionally been fabricated with rigid inorganic materials and accordingly, have geometries that are fixed upon fabrication. Tuning of dynamic metasurfaces based on inorganic materials typically relies on modulation of their refractive index. While significant progress has been made in tuning with semiconductors (by free carrier generation), TMDC monolayers (by exciton generation) and phase change materials, these devices still face challenges including limited index tuning ranges and low power efficiencies.

In contrast, the geometric dimension of polymer materials can be widely reconfigured by a diverse range of stimuli, providing a powerful lever to control optical responses. For example, some thin polymer films can swell by 2-3 times their original thickness in the presence of different solvents or by electrically induced ion uptake. We leverage this property to create dynamically reconfigurable optical metasurfaces that that offer control over the intensity and phase of reflected light. Our platform consists of a spacer layer of the widely used and commercially available conducting polymer, PEDOT:PSS, situated between a metallic mirror and plasmonic nano-antennae. The degree of swelling of the PEDOT:PSS spacer is reversibly tuned through fluidic application of solvents with varying degrees of solvation energies. We thereby change the distance between the mirror and plasmonic nano-antennae and hence control the phase of light scattered from individual nano-antennae. We use this platform of “Expansion Plasmonics” to demonstrate high diffraction efficiency beam steering and continuous tuning of colour over a full gamut. In contrast to systems relying on changes in the dielectric constant of specific materials over limited spectral ranges, our approach, involving geometric reconfiguration of transparent polymers, could in principle enable full light field control across a broad range of spectral regions, spanning from UV to THz. Finally, we demonstrate the wider applicability of our platform by tuning our metasurface with other stimuli, including electrochemical control of local ion concentrations.

Our work opens the door to the broad integration of a range of polymers, engineered to respond to specific chemical stimuli, into reconfigurable optical elements with applications in bio-sensing, display, and imaging.

2:45 PM BREAK

3:15 PM *EL06.02.04
Analog Optical Image Processing and Computing with Metastructures Andrea Alu and Michele Cotrufo; City University of New York, United States

In this talk, I will discuss our recent progress in the area of analog signal processing using metasurfaces and metastructures, and the associated opportunity in the context of low-energy, ultra-fast computations using light at the nanoscale. I will also discuss the potential opportunities stemming from using feedback in these structures to realize analog optical computation, and the possible impact for photonic technologies.

3:45 PM *EL06.02.05
Dynamic Wavefront Shaping with High Quality Factor Metasurfaces Jennifer A. Dionne[1], Mark Lawrence[2], Elissa Klopfer[1], Sahil Dagli[1] and Hamish Carr[1]; [1]Stanford University, United States; [2]Washington University in St. Louis, United States

Wavefront shaping and control is essential for advancing optical technologies spanning communication, computation, and sensing. Metasurfaces promise to miniaturize future optical components, like beam steerers and lenses, for lightweight, compact, and on-chip platforms. However, most current metasurface designs are static, unable to flexibly tune their responses to environmental or operational cues once fabricated.

Here, I present the design, fabrication, and characterization of dynamic metasurfaces that efficiently modulate their behavior, based on integration of high quality factor (high-Q) resonances. High-Q resonances have two primary features that augment metasurface tuning mechanisms. First, high-Q resonances are characterized by very sharp spectral features that are extremely sensitive to refractive index variation, allowing even very small perturbations to strongly vary the resulting optical response. Second, high-Q resonances are accompanied by strongly-enhanced near fields, which can improve modulation mechanisms that rely on electromagnetic near-fields, such as nonlinearities.

This presentation describes several novel devices enabled by high-Q metasurfaces. First, we demonstrate tunable high-Q metasurface lenses. Controlling the spectral position of the high-Q resonances via thermal or nonlinear effects enables high-fidelity modulation of the focal characteristics. Second, we demonstrate reconfigurable high-Q beamsplitters and beamsteerers through electro-optic control. The inclusion of lithium niobate and direct control of each nanoantenna resonance in the device opens up full operational control through voltage biasing. Finally, we demonstrate how high-Q metasurfaces enable dynamic detection of molecules and their interactions, with the potential for single-molecule vibrational spectroscopy.

SESSION EL06.03: Poster Session
Session Chairs: Fei Ding, Min Seok Jang, Xi Wang and Jinghui Yang
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL06.03.01
Development of Integrated Optofluidic Biosensor to Image Protein-Protein Interactions Yunju Chang and Jiandi Wan; University of California, Davis, United States

Protein-protein interaction plays a pivotal role in most cellular activities, including cell division, proliferation, and signaling. Therefore, studying protein

interactions is essential for understanding the fundamental mechanism of cellular activities, disease diagnosis, and drug development. Conventional approaches to study protein interactions include the enzyme-linked immunosorbent assay (ELISA) and the Forster resonance energy transfer (FRET), but the drawback is that these technologies require optical labeling. Currently, label-free photonic biosensors are getting attention because of their high sensitivity, small footprint, and multiplex assay. However, applications for photonic biosensors are mostly limited to the detection of biomolecules either by trapping the analyte of interest or by immobilizing interacting ligands. Therefore, our goal of this study is to develop label- and immobilization-free optofluidic biosensors that can image freely interacting proteins. The technological gaps are that (*i*) the current approaches to integrate microfluidic channels are not confined to the sensing area which requires larger sample volume than needed and (*ii*) to our best knowledge, there have been no studies reported with surface modification or functionalization which enables proteins to interact freely.
Here, we demonstrate ring-assisted Mach-Zehnder Interferometer (RA-MZI)-based biosensor with microfluidics confined on the sensing area. RA-MZI photonics component measures the change of local refractive index upon protein-protein interaction. Due to the innate characteristic of the resonator, such as high quality factor or large extinction ratio, ring resonator-based sensors show low limit of detection and high sensitivity. To overcome the fabrication variations and further maximize the sensitivity of sensor, we have incorporated microheater on both reference and sensing arms. By manipulating the temperature, we have increased the extinction ratio, and in return, increased the sensitivity. Our next steps will be to coat the microfluidics surface with supported lipid bilayer so that we can image protein interaction while both interacting proteins are relatively freely moving on the lipid membrane. This label- and immobilization-free optofluidic biosensor will allow us to discover novel approaches to early-stage detection by studying the mechanisms and fundamentals of disease-associated protein interactions.

5:00 PM EL06.03.02
Thermally Triggered Multilevel Diffractive Optical Elements Tailored by Shape Memory Polymers for Temperature History Sensors Dokyung Kyeong, Minsu Kim and Moon Kyu Kwak; Kyungpook National University, Korea (the Republic of)

Shape memory polymers (SMPs) have been widely used as sensory material due to capability to induce morphological transition in response to external stimuli. Diffractive optical elements (DOEs) have shown their attractive potential as sensing platforms owing to the high sensitivity provided by the real-time response of far-field diffraction patterns. Many studies have demonstrated a series of reconfigurable DOEs with SMP based on conventional template molding process, which is fast, inexpensive and has no limitation in materials. However, in most cases, simple surface relief structures such as micro-groove grating were chosen as a proof of principle model due to their straightforward relationship between ridge height and diffraction intensity. Thus, they still need to be validated in a much more complex diffraction pattern which facilitates achieving higher information content to provide greater flexibility in device design and operation. Here, by combining the temperature-sensitive characteristic of SMP and the display characteristic of multilevel DOEs, an optical temperature sensing film showing the temperature information as a change of far-field diffraction images is proposed. To achieve this, micropatterns of the DOEs are imprinted on epoxy based SMP film, which can be programmed to hold a temporary optical image and revert to its original image when exposed to a specific temperature. Convolutional neural networks (CNNs) are utilized to detect and measure the optical image transformation depending on temperature. Furthermore, the threshold temperature where the image transformation occurs can be customized by varying the chain flexibility of the SMP. Based on a range of transition points, imprinting the desired combination of SMP-DOEs on a film, a sensor that can record and inform the temperature history is demonstrated. This work can be used for the compact and reliable optical temperature indicator, which can be applied in temperature-sensitive industries such as food and pharmaceutical.

5:00 PM EL06.03.03
Self-Assembled Optofluidic 3D Chemical Sensors Zihao Lin, Chunhui Dai and Jeong-Hyun Cho; University of Minnesota, Twin Cities, United States

Most plasmonic-based sensors are designed on two-dimensional (2D) planar surfaces with an enhanced electromagnetic field close to it. The enhancement effect decays in exponential form as samples move away from the surface. This results in a tiny nanoscale sensing area where long distances between the sensing position and the micro/nano specimen is undesired. Here, we introduce a method that enforces the specimen to be located close to the sensing area (plasmonic structures) using three-dimensional (3D) nano architectures self-assembled with nanoscale precision. A sensor (nanosplit rings) patterned on the inner surface of nano tubular 3D structures allows a strong interaction between the specimen and the optical sensor. The self-assembly process offers great flexibility in scaling tube diameters from 500 nm down to 100 nm. The proposed method also bridges the large gap between nanofluidics and nanoplasmonics. Here, a dynamically optofluidic sensing behavior can be achieved during biomolecular transportation in the tube, at the same time, these biomolecules can be detected via nanosplit rings inducing an electromagnetic field enhancement effect. Different 3D plasmonic structures, including nanocylinders, parallel plates, and prisms, were self-assembled and simulated. The results indicate that nanocylinders have the highest optical enhancement. Tests were first carried out to verify the nanotubes' ability to flow liquid inside them then hemoglobin was used as the target biomolecule and was flowed in the fabricated 3D plasmonic tubular structures. Raman result demonstrates that a 22 times higher enhancement intensity was realized for hemoglobin fingerprints in the 3D structure compared to a 2D planar surface. This result shows the power of utilizing 3D architectures in nanoscale, leading to enhanced physical (optical) properties.

5:00 PM EL06.03.04
Asymmetric Pairing of Cholesteric Liquid Crystal Droplets for Programmable Photonic Cross-communication Sihun Park[1], Sang Seok Lee[2] and Shin-Hyun Kim[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)

Chiral nematic liquid crystals, or cholesteric liquid crystals (CLCs), are one of the liquid crystal phases that display unique optical properties. The CLCs are typically formulated by the self-assembly of LC molecules in the presence of a chiral dopant. The introduction of chirality into an achiral LC host induces a regular rotation of the director of LC molecules along the helical axis. As the periodic modulation in refractive index between ordinary and extraordinary values occurs due to the helical structures, the CLCs can develop a photonic stopband property, selectively reflecting circularly-polarized light with the same handedness as the helical structure at the stopband region. In particular, structural colors are produced by wavelength-selective diffraction when the stopband lies in the visible spectrum. The position of the stopband in terms of wavelength can be dynamically tuned with external stimuli, such as temperature, light, and electric field. These stimuli-responsive optical properties make the CLCs fascinating as anti-forgery materials, sensors, and optical particles. For specialized applications, the CLCs have been enclosed by curved surfaces, transforming into droplets, shells, microparticles, and microcapsules.
Interestingly, the spherical geometry gives rise to additional optical patterns for the CLC compartment, which are otherwise difficult to obtain in a bulk film format. For identical and contiguous CLC droplets, a color pattern arises by the retroreflection comprising double or triple reflections at the curved surfaces and the direct single reflection on the top surfaces, which is referred to as photonic cross-communication. CLC shells with a thin-top shape or buckled shape can show another pattern of color rings through internal reflection. When multiple CLC compartments are combined to form CLC multishell, additional color patterns develop through internal cross-communication. These diverse kinds of color patterns are particularly promising for optical encryption in anti-forgery applications. However, the encryption of optical codes is extremely dependent on the direct single reflection from the top surfaces of CLC droplets. To exploit various color patterns as optical authenticators, it is essential to formulate the color patterns in a programmable way. In this study, we investigate the photonic cross-communication taking place between two distinct CLC droplets with different sizes and stopband

wavelengths, thereby establishing an optical platform for programming resulting color patterns. The CLC droplets with a size variation and a stopband wavelength variation are prepared using capillary microfluidic devices, which are then positioned in contact to form a set of asymmetric pairs. As discussed, color patterns are generated by double reflections of light at an angle of 45° at each surface. However, when two CLC droplets with distinct stopband wavelengths yet the same size are paired, the optical path for the double reflections is imperfect due to a mismatch in stopbands. That is, it is necessary to construct asymmetric pairs with an optimum size ratio for two different stopband wavelengths to maximize the photonic cross-communication. We have experimentally investigated the relationship between stopband-wavelength ratios and droplet-size ratios for the most effective photonic cross-communication using various sets of droplet pairs and verified the relationship using a mathematical model. Furthermore, we have demonstrated that the wavelength of the photonic cross-communication is affected by refraction at the surfaces of CLC droplets. With the principle of design, we have shown the evolution of bright photonic cross-communication patterns between asymmetric pairs of distinct CLC droplets. We believe that various pairs of CLC droplets with distinct stopband wavelengths and consequent photonic cross-communication patterns will open a new chapter in advanced optical encryption for anti-counterfeiting.

SESSION EL06.04: Adaptive Nanophotonic Materials I
Session Chairs: Zizwe Chase and Kevin MacDonald
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3022

8:30 AM EL06.04.01
Machine Learning Driven Steering of Incoherent Emission from III-V Metasurfaces Saaketh S. Desai[1,2], Prasad Iyer[1,2], Sadhvikas J. Addamane[1,2], Remi Dingreville[1,2] and Igal Brener[1,2]; [1]Center for Integrated Nanotechnologies, United States; [2]Sandia National Labs, United States

Spatiotemporal control of incoherent emission from LEDs and thermal sources remains a critical challenge for state-of-the art beam steering methods designed for coherent sources. Recently, we have shown that photoluminescence (PL) from InAs quantum dots embedded in GaAs metasurfaces can be dynamically steered over 70° using structured optical pumping. This was achieved by creating a dynamic spatially varying resonant phase gradients across the metasurface using an ultrafast (80fs, 1 Khz rep rate, 3mJ/cm^2) 800nm pump which images the pattern from a spatial light modulator (SLM) onto the metasurface. This photoluminescence (beam) steering was done solely based on periodic blaze grating order patterns, which created a periodic refractive index profile using Drude free-carrier refraction, resulting in a spatial phase gradient on the metasurface and ultimately directing the momentum of the light emission. In this work, we solve the inverse problems of steering PL towards a specific direction using generative models and active learning from aperiodic spatial pump patterns. We use a variational autoencoder to generate novel pump patterns beyond human-intuition, and use Bayesian optimization to discover these pump patterns on the SLM that steer the photoluminescence towards specific angles. We find that these pump patterns are 10x more efficient in beam steering compared to the initial periodic blaze grating pump pattern designed using human intuition. Our work provides a novel machine learning driven closed-loop platform to understand and discover the physics of incoherent emission steering from metasurfaces with potential applications for augmented and virtual reality displays.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy. Sandia National Laboratories is a multi- mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. The views expressed in this article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.
** These authors contributed equally*

8:45 AM EL06.04.02
Electrochemically-Gated $La_{1-x}Sr_xCoO_{3-\delta}$ (LSCO) as a Phase-Change Material for Active Metasurfaces Rohan D. Chakraborty, William M. Postiglione, Supriya Ghosh, K. A. Mkhoyan, Chris Leighton and Vivian Ferry; University of Minnesota-Twin Cities, United States

Metamaterials have aided the development of infrared nanophotonics through applications in photonic circuits, telecommunications, thermal imaging, and more. While the optical response of traditional metamaterials is static, recent advances have imparted *tunability* to these metamaterials by pairing them with materials that undergo controllable refractive index changes.

Here, we present ion-gel-gated perovskite $La_{1-x}Sr_xCoO_{3-\delta}$ (LSCO) thin films as a new class of room-temperature, electrically tunable, phase-change materials along with their applications. We will show Kramers-Kronig consistent refractive index models before and after gating of LSCO films at $0.00 < x < 0.70$, ranging from the visible to mid-infrared spectral range, as measured with a combination of spectroscopic ellipsometry and infrared optical spectroscopy. The measured optical properties are correlated with insights from XRD, TEM, and electronic transport.

We find that as-grown perovskite LSCO films are high index insulators at $x < 0.18$ but highly lossy Drude metals at $x > 0.18$, following the percolation-induced insulator-metal transition known to occur in the perovskite phase. When LSCO is implemented in ion-gel-gated transistors, positive gate voltage and resulting oxygen vacancy formation drives electrochemical reduction, in some cases inducing a topotactic transition from the perovskite phase to an oxygen-vacancy-ordered brownmillerite phase, $La_{1-x}Sr_xCoO_{2.5}$. Electrochemical gating of $x > 0.18$ LSCO films reveals a metal-insulator transition from the highly lossy perovskite phase to a high index, low loss insulating phase. LSCO films at $x < 0.18$, despite their nominally insulating character, still undergo remarkable refractive index changes to another lower index, lower loss insulating state. Finally, electromagnetic simulations of a tunable plasmonic absorber show that insulator-insulator contrast in $x = 0$ LSCO can shift the surface plasmon resonance wavelength of a gold nanodisk by $\Delta\lambda > 600$ nm, and metal-insulator transitions in $x = 0.50$ LSCO can achieve single-wavelength reflectance modulation of $\Delta R > 60\%$, even at LSCO film thicknesses as low as 20 nm. Together, these findings frame electrochemically-gated LSCO films as a library of room-temperature phase-change materials for infrared applications including telecommunications and thermal radiation control.

9:00 AM EL06.04.03
Reconfigurable Switches and Color Pixels Based on Metal-Hydrides Systems Micah Karahadian and Jeremy N. Munday; University of California, Davis, United States

Adaptive and reconfigurable photonic devices are critical to a variety of applications from photonic circuits and color pixels to computing and quantum information processing. One promising class of materials are metal-hydrides, which can undergo extreme changes in optical properties via insertion of hydrogen atoms into the metallic lattice, which can be controlled through applied bias or gas pressure. Here we present our recent work on developing reconfigurable optical devices based on switchable metal-hydrides. In addition to optical, mechanical, and chemical characterization [1], we have developed vivid color pixels with wavelength shifts (>100 nm) during hydrogenation of various materials. Through appropriate design, we have produced structures that have five orders of magnitude change in reflectivity, as well as systems for physical encryption and counterfeit detection. We find alloying of these metal films not only improves cyclability, but also leads to higher hydrogen fractions than previously obtained as a result of film stresses and microstructuring [2]. Finally, we will show how novel optical substrates can enhance these effects [3] and how nanostructuring can lead to additional opportunities for adaptive systems with tunable optical behavior.

[1] KJ Palm, et al., *ACS Photonics*, **5**, 4677–4686 (2018)
[2] KJ Palm, et al., *ACS applied materials & interfaces* **11**, 45057-45067 (2019)
[3] KJ Palm, et al., *Optics Express* **30**, 21977-21989 (2022)

9:15 AM EL06.04.04
Active Optical Metasurfaces Based on Low Loss Phase Change Materials Fouad Bentata[1,2,3], Lotfi Berguiga[4,2], Xavier Letartre[4,2], Stephane Monfray[1], Patrice Genevet[3] and Sébastien Cueff[2,4]; [1]STMicroelectronics, France; [2]Institut des nanotechnologies de Lyon, France; [3]Centre de Recherche en Héterostructures et Epitaxie et ses Applications, France; [4]Ecole Centrale Lyon, France

Metasurfaces are promising optical components that enable light engineering by controling the phase, amplitude or/and polarization achieving large panel of applications such as optical filtering, focusing, holographic projection, spatial light modulation, lidar and neuromorphic computing. Inherent passive functionality limits full integration into smart devices and multi-functionality on demand. Active metasurfaces are a potential solution for a wide range of applications. Several use cases have been detected based on the level of design complexity. First, the correction of manufacturing aberrations in post-fabrication for mass production and highly sensitive applications. Second, increasing the functionality of fixed features into binary or continuously adjustable features is of great interest. Finally, an on-demand addressable meta-atom would allow arbitrary light control.
Among the different tuning mechanisms, the exploitation of phase change materials (PCMs), such as GeSbTe, GeTe, seems particularly relevant as they possess remarkable optical properties that can be strongly modulated by reversibly changing the crystallinity of the material. This also-called standard PCMs, widely used in non-volatile memories, exhibit high optical losses in the visible and near infrared range, which limits the efficiency of optical devices. A new class of PCMs called low-loss PCMs, such as Sb2Se3, Sb2S3, GeSbSeTe, is more suitable for optical metasurfaces given the low optical losses and phase change properties[1].

In this work, we focus on the design, fabrication and characterization of metasurfaces based on low-loss PCMs, especially Sb2S3. First, an active metasurface based on the Pancharatnam Berry principle is optimized to passively encode the deflection angle information in a given polarization state, and then, depending on the crystallinity state, we switch from one polarization state to the other, realizing a binary beam deflection. Next, an active filter will be presented, allowing both independent passive control of an extremely high Q factor using design-controlled perturbation and active spectral control using the active properties of PCMs. After showing examples of potential designs of the active spectral and spatial light control, we finally present the nanofabrication and characterization challenges that have been addressed.

Reference:
[1] Elena Mikheeva, Christina Kyrou, **Fouad Bentata**, Samira Khadir, Sébastien Cueff, Patrice Genevet “Space and Time Modulations of Light with Metasurfaces: Recent Progress and Future Prospects*”,* ACS Photonics, 2022

Acknoledgements:

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9:30 AM BREAK

10:00 AM *EL06.04.05
Programmable Photonics with Metal Insulator Transition Jiachen Li, Tiancheng Zhang, Kaichen Dong, Jie Yao and Junqiao Wu; University of California, Berkeley, United States

Materials with metal insulator transition can provide real-time reconfigurability of photonic devices, which would create new optical functionalities via recompilation of photonic operators. Exploiting the hysteretic phase transition of vanadium dioxide, we achieved an all-solid, rewritable metacanvas on which nearly arbitrary photonic devices can be rapidly and repeatedly written and erased. More recently, we fabricated a reconfigurable twisted bilayer photonic moire superlattice that hosts a localized mode in the mid-infrared spectral range, immune to fluctuations in layer separation and twist angle but subject to the metal insulator transition. The ease and flexibility in fabrication make it a promising platform for probing new physics in moire superlattices.

10:30 AM *EL06.04.06
3D Meta-Optics for Sorting Light by Wavelength, Polarization and Angle of Incidence Andrei Faraon, Gregory Roberts, Conner Ballew and Ian Foo; California Institute of Technology, United States

Modern imaging systems can be enhanced in efficiency, compactness, and range of applications through introduction of multilayer nanopatterned structures for manipulation of light based on its fundamental properties. Metaoptical components can be tailored to respond to these varying electromagnetic properties, but have been mostly explored in single-layer, ultrathin geometries, which limits their capacity for multifunctional behavior. Here we show the design of several pixel-sized scattering structures which sort light efficiently based on its wavelength, polarization state, and spatial mode. The multispectral and polarimetry devices are further fabricated via two-photon lithography and experimentally validated in the mid-infrared.

SESSION EL06.05: Adaptive Nanophotonic Materials II
Session Chairs: Victor Brar and Min Seok Jang

Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3022

1:30 PM *EL06.05.01
Picophotonics - Subatomic Optical Localization Beyond Thermal Fluctuations Tongjun Liu[1], Cheng-Hung Chi[1], Bruce Ou[1], Kevin F. MacDonald[1] and Nikolay I. Zheludev[1,2]; [1]University of Southampton, United Kingdom; [2]Nanyang Technological University, Singapore

Despite recent tremendous progress in optical imaging and metrology, the resolution gap between atomic scale transmission electron microscopy and optical techniques has not been closed. Is optical imaging and metrology of nanostructures exhibiting Brownian motion possible with resolution beyond thermal fluctuations? Here we report on an experiment in which the average position of a nanowire with a thermal oscillation amplitude of ~150 pm is resolved in single-shot measurements with accuracy of 39 pm using light at a wavelength of $\lambda = 488$ nm, providing the first example of such sub-Brownian metrology with ~$\lambda/12{,}000$ resolution. To localize the nanowire, we employ a deep learning analysis of the scattering of topologically structured light, which is highly sensitive to the nanowire's position. As a non-invasive optical metrology with sub-Brownian absolute errors, down to a fraction of the typical size of an atom (Si: 220 pm diameter), it opens the exciting field of picophotonics.

2:00 PM *EL06.05.02
Active Metasurface Systems for Angle-Sensitive and Low Intensity Imaging Harry A. Atwater; California Institute of Technology, United States

The ability to dynamically control the optical response in the quasi-static and time-modulated regimes opens a multidimensional design space that can be fully harnessed by developing appropriate nanophotonic structures for arbitrary manipulation of light. Active metasurfaces have potential as building block components of meta-imaging systems, in which each cascadable element enables dynamic, independent, and comprehensive control over all constitutive properties of light in both reflection and transmission. Active metasurfaces can also form the components angle-selective lens-less imaging systems. I will discuss the properties and characteristics of angle-selective active metasurface imaging systems and compare their characteristics to conventional lens-coupled image sensors. I will also describe the use of active metasurfaces as elements of single-photon/pixel imaging systems for low intensity image acquisition using thermal and weak scattered light sources.

2:30 PM BREAK

SESSION EL06.06: Reconfigurable Photonic Integrated Circuits I
Session Chairs: Fei Ding and Xi Wang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3022

3:00 PM *EL06.06.01
Hybrid Photonic Systems for Neuromorphic Processing Wolfram Pernice; Heidelberg University, Germany

Optical computing methods are seeing a resurgence of popularity due to recent advances in integrated photonics and neuromorphic engineering. Photonic systems are very suitable for analog computing approaches with moderate accuracy, yet very high processing speed. These features hold promise for implementing photonic accelerator systems for computationally expensive tasks such as matrix vector multiplications (MVM). Here I will introduce a nanophotonic approach for realizing chip-scale MVM-units by making use of hybrid integration. Using phase-change photonic devices allows for creating parallel processing circuits in which analog multiplications can be carried out at high speed. Hybrid integration of active and passive integrate photonic chips via 3D printed optical interconnects enables the realization of compact neuromorphic architectures for ultrafast information processing. Applications lie in the implementation of photonic convolution processers, as well as the realization of associative photonic memories and ultrafast correlation systems. In combination with the development of novel light sources, such photonic approaches offer new opportunities for creating brain-inspired hardware for artificial intelligence applications.

3:30 PM *EL06.06.02
NEO-PGA—Nonvolatile Electro-Optically Programmable Gate Array Arka Majumdar; University of Washington, Seattle, United States

Reconfiguration of silicon photonic integrated circuits relying on the weak, volatile thermo-optic or electro-optic effect of silicon usually suffers from large footprint and energy consumption. Non-volatile phase change materials, such as Ge2Sb2Te5 (GST) provide an attractive solution to solve this problem. I will talk about our effort on integrating GST with silicon photonics to demonstrate an energy-efficient, compact, non-volatile, reprogrammable platform. By adjusting the energy and number of free-space laser pulses applied to the GST, we characterized the strong broadband attenuation and optical phase modulation effects of the platform, and perform quasi-continuous tuning enabled by the thermo-optically induced phase changes. As a result, a non-volatile optical switch with high extinction ratio as large as 33 dB is demonstrated [1]. We also solved the problem of large absorptive loss in GST by designing a new type of directional coupler, and demonstrated an optical switch with less than 1dB insertion loss, even though the material itself has very high loss [2]. Using silicon p-i-n heater, we demonstrated electrical actuation of the phase transition to create a prototype of electrically controlled reconfigurable switch with ultra-low power consumption [3,4]. Finally, I will discuss new phase change materials[5], and device engineering to create next generation low-loss reconfigurable optical switch and phase-shifters.

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4:00 PM *EL06.06.03
Reconfigurable Photonics on Thin Film Lithium Niobate Mengjie Yu; University of Southern California, United States

Lithium niobate (LN) is an excellent nonlinear photonic material due to its large electro-optic (EO) coefficient, second order and Kerr () nonlinearity, along with a wide optical transparency window. Thanks to the recent advances in nanofabrication technology, monolithic LN waveguides with high optical confinement and ultralow linear loss has been achieved, which was critical to the success of the silicon-based platform in the past decade. Highly efficient and controllable light-matter interactions can be achieved using optical, electrical, or mechanical waves at extremely compact footprints. In this talk, I will review our recent developments of thin-film LN nonlinear devices for high power and reconfigurable EO frequency combs, femtosecond pulse synthesis and spectral-shaping of single photons. Combination of multiple nonlinearities of LN unlocks ultrabroadband electromagnetic spectrum from microwave to mid-infrared. Lastly, I will discuss the potential of LN photonic platform for scaling up and accelerating classical and quantum technologies in sensing, photonic computing, and communication networks.

4:30 PM *EL06.06.04
Fast-Tunable and Low-Loss Stress-Optical Microsystems Sunil A. Bhave; Purdue University, United States

Silicon Nitride (SiN) is an outstanding material for on-chip photonic systems because of its extremely low optical loss, outstanding optical power handling and controllable non-linearity. SiN photonic integrated circuits (PICs) are becoming more commonplace in high performance systems including LIDAR, Optical Frequency Combs, Spatial Light Modulators and Photonic Quantum Processors. In such microsystems, low-loss photonics enhances lidar resolution and range, octave-spanning combs for optical clocks, longer-distance free-space communication and higher intensity light incident on detectors in photonics quantum processors.

However, modulation and tuning of SiN has been limited to thermal heaters because it’s a dielectric amorphous material with no electro-optic coefficients. In this presentation I will present architectures based on piezoMEMS technology to demonstrate stress-optical modulation and tuning of silicon nitride optical ring resonators. Specifically, I will demonstrate high speed tuning of self-injection locked lasers for LIDAR and frequency combs and GHz frequency mechanical resonant actuators for implementing magnetic-free optical isolators. If time permits, I will discuss optomechanical inertial sensors and microwave-to-optical quantum converters in our Piezo-on-Nitride technology platform.

This research is in close collaboration with Professor Tobias Kippenberg’s group at EPFL.

SESSION EL06.07: Adaptive Nanophotonic Materials III
Session Chairs: Victor Brar and Fei Ding
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3022

8:00 AM *EL06.04.07
Reprogrammable Nanophotonic and Metaphotonic Devices Enabled by Phase-Change Materials Sajjad Abdollahramezani, Hossein Taghinejad, Tianren Fan and Ali Adibi; Georgia Inst of Technology, United States

A new platform for miniaturized programmable nanophotonics through integration of dielectric, semiconductor, and plasmonic materials with nonvolatile phase-change materials will be discussed. This platform enables reconfigurable photonic building blocks with subwavelength features. Two groups of reconfigurable devices based on integrated photonic structures and metasurfaces along with their unique features for state-of-the-art applications will be discussed. Design, fabrication, and application of this platform for state-of-the-art devices and systems will be covered.

8:30 AM EL06.07.01
All-Dielectric, Switchable Metalenses Using Sb2S3 Phase Change Material Siddharth Padmanabha[1], Isaac Oguntoye[2], Jesse Frantz[3], Robert Bekele[4], Anthony Clabeau3[4], Vinh Nguyen[3], Jasbinder Sanghera[3] and Matthew D. Escarra[1]; [1]Tulane University, United States; [2]Intel Corporation, United States; [3]U.S. Naval Research Laboratory, United States; [4]University research Foundation, United States

All-dielectric metasurfaces have recently been shown to be excellent candidates for advanced wavefront manipulation devices in phase delays, beam steerers, metalenses, metaholograms and more. These devices allow for significant size, weight, and cost reduction in comparison to their traditional refractive optic counterparts, while allowing for creative use of non-linear responses of these structured surfaces. One limitation, however, for these devices is the lack of post fabrication tunability. To break this limitation, the fastest and most efficient approach would be utilizing refractive index-tunable materials. Phase change materials (PCMs) are one such category of materials. Huygens metasurface based optics utilizing these PCMs hold the possibility of high transmission and full 2π phase control of incident wavefronts which are tunable post-fabrication. In this work, we present a design and fabrication pathway for reconfigurable cylindrical metalenses in the visible utilizing one such PCM, antimony trisulfide (Sb2S3).
PCMs aid in active optical modulation when switched between their different non-volatile phases. The selected PCM for this study, Sb2S3, exhibits a visible wavelength refractive index contrast of 0.75 with low losses when switched between its amorphous and crystalline phases (hereby called optical states). The metalens design presented here is comprised of an arrangement of pixelated arrays of homogenous nano-antennas. Each pixel is designed as an array of cylindrical nano-antennas in a repeating square lattice. Different geometric parameters are cycled through to generate a pool of Huygens’ meta-atoms to act as building blocks for individual pixels. We choose to discretize the continuous (ideal) 0 to 2π phase profile for a cylindrical lens into an arbitrary N = 4 phase levels. To create the discretized wavefronts necessary in both optical states, a total of N2 = 16 elements are chosen. This selection of elements informs the pixel sizes that are necessary for the wavefront-shaping. To address the inter-element coupling issues inherent in highly resonant Huygens metasurfaces, an inter-pixel gap of 1.5μm is employed, which effectively reduces the crosstalk between adjacent pixels.
Individual nano-antenna arrays are optimized to ensure maximum generalized diffraction efficiency in both optical states of the PCM utilizing a figure of merit (FOM) first presented in [1]. This design FOM allows for a computationally effective and efficient synthesis of the reconfigurable metalens without the need for a full wave electromagnetic simulation of the entire metalens system in both optical states. The resulting compound metasurface acts as a reconfigurable cylindrical metalens with focal lengths of 3.5cm and 5cm depending on the optical state of the PCM The design predicts focusing

efficiencies of 72.9% and 79.7% for the amorphous and crystalline phases, respectively.
Sb2S3 thin films are created by ion sputtering with in situ substrate heating. The patterns are written using the Raith VOYAGER 100 electron-beam lithography tool on a Sb2S3 -PMMA- chromium stack and etched off in a single-etch process by reactive ion etching. This stack is then encapsulated with a layer of SiO2 to form a capping layer. The capping layer is necessary to prevent lateral migration of sulfur during the phase-change process, and to act as a mechanical protection layer for the metalenses. Optimization of nanofabrication, investigation of optically reversible phase changes, and experimental characterization of these metalens are all in progress.
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8:45 AM EL06.07.02
Single-Photon Emission from Monolayer 2D Materials Coupled with Chiral Plasmonic Nanoparticles Soon-Jae Lee[1], Jae-Pil So[1], Kwang-Yong Jeong[2], Ryeong Myeong Kim[3], Ki Tae Nam[3] and Hong-Gyu Park[1]; [1]Korea university, Korea (the Republic of); [2]Jeju National University, Korea (the Republic of); [3]Seoul National University, Korea (the Republic of)

The single-photon emitter carrying spin angular momentum is a key component in quantum information and quantum cryptography, promising highly secure information processing without leakage. Nonreciprocal single-photon configurations and deterministic spin-photon interfaces are possible with chiral quantum optics. Recently, quantum confinement in atomically thin transition metal dichalcogenides (TMDCs) has been investigated for single-photon emission based on naturally or artificially occurring defects. By applying mechanical strains to the TMDCs, it is feasible to precisely control the position and polarization of a single-photon emitter [1]. Strains in TMDCs have been induced using various nanostructures including dielectric pillars and nanogaps. In this work, we demonstrate a new type of single-photon emitter with chirality. Atomically thin tungsten diselenide (WSe_2) is placed on silica-encapsulated plasmonic chiral nanoparticles [2]. As a result of efficient coupling between the single-photon emitter and the chiral plasmonic nanoparticle, Purcell enhancement and increased intensity from the single-photon emitter were observed, showing circular or elliptical polarization directions. In the experiment, we observed that strain-induced single-photon emission with a chiral nanoparticle was >10 times stronger than unstrained WSe_2 photoluminescence. The single-photon characteristics were clarified using the Hanbury-Brown and Twiss (HBT) measurement setup. Furthermore, due to the coupling with the metal nanoparticle, the single-photon emitter had the reduced lifetime (0.8 ns) compared to the uncoupled emitter (20 ns). By measuring the polarization of the emitter coupled with the chiral nanoparticles, a degree of circular polarization of 0.8 was obtained. Last, numerical simulation demonstrated that chiral nanoparticles can generate spin angular momentum. Therefore, our approach will be useful for demonstrating a quantum light source for next-generation photonic integrated circuits.

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9:00 AM EL06.07.03
Vortex and Anti-Vortex Lasing Modes in Disclination States Ha-Reem Kim[1], Min-Soo Hwang[1], Daniel Leykam[2], Yuri Kivshar[3] and Hong-Gyu Park[1]; [1]Korea University, Korea (the Republic of); [2]Centre for Quantum Technologies, National University of Singapore, Singapore; [3]The Australian National University, Australia

In photonics, the ability to control the angular momentum of light has long been of significant interest. For the purpose of creating different degrees of freedom in spatially distinct channels for data transmission, the orbital angular momentum (OAM) is particularly useful. Although the directional output and generation efficiency of OAM beams in previous works are impressive, considerable scattering loss and large energy consumption are unavoidable when constructing ultra-small optical devices due to the absence of mechanisms related to high-quality light confinement. Furthermore, additional work is required to tune the pump beam when the emission chirality of vortex microlasers depends on circularly polarized optical pumping. Realizing ultra-compact laser systems that can self-configure vortex modes with OAM properties and reliably localize resonant modes is therefore still challenging.
A more recent development is the introduction of photonic topological insulators (PTIs), which are attractive tools for the localization of topological states and robust light manipulation. PTI research has expanded to include topological defects such as dislocations and disclinations, which typically break the symmetric geometries of topological crystalline insulators (TCIs) [1,2]. Notably, the presence of a fractional charge in the disclination leads in topological bound states in TCIs. [3]. Disclination defects, however, have not yet been used in the realization of ultra-small light sources with quantized OAM states. Here, we report on two novel topological lasing modes with OAM states found in disclination defect nanocavities: vortex and anti-vortex modes.
The photonic disclination structure was constructed by cutting the crystal into four identical sectors, applying the Frank angle of $\Omega = +90°$, and adding one sector to a square-lattice photonic crystal structure. Different disclination defects were examined by shifting the air holes in the C5 symmetric core and the nearest layer to the core. Numerical simulations using finite-element method (FEM) were performed to optimize the structural parameters. Then, the localized in-gap states were opened at the disclination defect, and vortex and anti-vortex modes appeared in the gap, showing different polarization distributions. For the experimental demonstration of the vortex and anti-vortex nanolasers, we fabricated pentagon-shaped photonic crystal structures based on the FEM simulation results in a InGaAsP slab incorporating three quantum wells. We demonstrated the vortex and anti-vortex lasing modes in the disclination defects of topological photonic crystal structures. The OAM states of these modes were identified by measuring the polarization-dependent spatial intensity profiles and interferences patterns. The realization of the photonic disclination states may open up new opportunities for creating distinctive OAM vector laser beams for the next-generation optical communication.

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9:15 AM EL06.07.04
Optoelectronic Characterization of tunable Luminescent organic molecules Arya Karappilly Rajan, Ryan Brisbin, Sayantani Ghosh and Ryan Baxter; University of California, Merced, United States

Luminescent organic molecules (LOMs) are interesting compounds, as they combine the photo-induced charge carrier generation and recombination of inorganic semiconductors with the lightweight and easy fabrication techniques common to organic materials. LOMs therefore offer the potential to be used in the development of inexpensive, flexible, and tunable organic electronic and optoelectronic devices as alternatives to inorganic semiconductors. Examples of such devices include organic light emitting diodes (LEDs), solar cells, chemical and biochemical sensors, field-effect transistors, and nonlinear optical media for lasing applications.

We present results of a novel class of LOMs, Benzoyl Pyraziniums, whose optical properties can be controlled by tuning the electronic and chemical structure, as well as their concentration and interaction with surrounding materials. Optical characterization of the three differently substituted (methoxy, fluorine and unsubstituted) salts of the LOMs exhibited interesting results. The photoluminescent (PL) emission intensity increased, and the emission spectra shifted to higher energies, with decreasing concentration. The recombination lifetimes of all three salts decreased as the solution concentration was increased from 0.1 to 100 mM. As pyridiniums are capable of intramolecular charge transfer, assuming that the primary concentration dependent non-radiative decay is through this pathway, these results can be explained by a corresponding increase in the number of non-radiative decay pathways with increase in the concentration. Most recently, we have discovered an optical activation pathway in these LOMs, where the absorption and emission spectra changed significantly on UV exposure. These changes are dependent on the energy of the UV excitation, time of irradiation, as well as their concentration. To study the behavior of these LOMs as composites in the mesoscale regime, we further looked at their cumulative emissions in solid state, via spin-casted thin films. While thin films also demonstrate the spectral blue-shift with decreasing concentration, the shift is only on the order of a few nanometers (nm) over the entire range of 0.1 – 100 mM with a significantly narrowed emission.
Further investigations of the electrochemistry of these molecules offer unique perspectives on the charge transfer properties within them, which is used to optimize their optical emission and establish these LOMs as highly suitable candidates for organics LEDs.

Funding:
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9:30 AM EL06.07.05
Electro-Optics with Quantum Paraelectric Materials Christopher P. Anderson, Giovanni Scuri, Alexander D. White, Daniil Lukin, Erik Szakiel, Josh Yang, Melissa Guidry, Kasper Van Gasse, Wentao Jiang, Amir Safavi-Naeini and Jelena Vuckovic; Stanford University, United States

Tuning optical properties of materials with electric fields is key to many quantum and classical applications. In particular, photonic modulation in cryogenic environments is an outstanding challenge, as traditional tuning mechanisms degrade at low temperature. In this talk, I present SrTiO3 as an attractive cryogenic electro-optic photonic material. Displaying a quantum paraelectric phase at low temperature, this material on the verge of ferroelectric instability results in a massive but stable electric susceptibility and tunability. I will first discuss our measurements of the electro-optic effect in this material near a quantum critical point. I then describe the creation of thin films of patterned SrTiO3 for high quality photonics. Finally, I will review how this material can transform microwave-to-optical quantum transduction, photonic quantum computing, and light-based control of superconducting systems.

9:45 AM EL06.07.06
Scalable, Milliwatt-Level, Switchable Electrochromic Resonator for Full-Color Generation Joo Hwan Ko, Serim Kim, Hyeon-Ho Jeong and Young Min Song; Gwangju Institute of Science and Engineering, Korea (the Republic of)

Display is an inseparable device for visually conveying information in today's daily life. Although the conventional color-filter-based light emitting devices have made great progress by the world's leading companies, there is still the important problem of power consumption. Alternatively, reflective displays and/or electronic paper utilize ambient light as a light source, thus, it does not consume energy for light emission, resulting in drastically reduced power consumption. Behind these advantages, electronic paper shows the black and white operation method, which has been treated as a limitation for colorful image production. In recent years, state-of-the-art coloration technologies have been introduced including thin-film cavity, plasmonics, and metasurface [1]. These systems have been combined with functional materials such as liquid crystals, phase change materials, or electrochromic polymers to successfully turn on and off these reflective surfaces [2]. Nevertheless, due to the individual RGB sub-pixel configuration, each color can only occupy up to 1/3 of the total gamut, which not only reduces chromaticity but also requires a lot of incident light [3].
Here, we present full-color electrically tunable reflective display (ETRD) with the milliwatt-level power-consumption. The RGB implementation allowed us to present effective displays with a single reflective pixel with multiple colors (monopixels) instead of relying on adjacent pixels with fixed colors. By introducing planar resonant structure, the scalable and full-colored reflective display is presented over wafer lever. Based on the structural design to have sensitive chromatic responsivity, the refractive-index-engineered/porous meta-medium has been introduced on metal film for the resonance promoting, which shows a great chromatic sensitivity to electrochromic materials. For the active modulation, we used polyaniline (PANI), which show great complex refractive index modulation level, resulting in distinct color modulation over RGB range. In this process, we successfully coated the PANI layer on meta-medium with great uniformity, enabling scalable fabrication. Furthermore, the monopixel configuration is adopted as a display unit pixel for prohibiting degradation of chromaticity. In particular, the protonation reaction of PANI enables the fast/low-voltage operation (from - 0.2 to 0.8V) with comparable switching time (~34 ms). Also, the minimized voltage levels lowered the power consumption as milliwatt-level (≈ 1 mW cm−2). In addition, we designed the pixelated reflective display module, which possesses the addressing ability. Finally, the full-color range switchable device shows a great lifetime over 200 cycles without degradation. In conclusion, we presented an electrically tunable reflective display based on electrochromic material for low power consumption and dynamic colorations. The electrically tunable reflective display with planar configuration provides a wide range of color generation in the reflection mode. We also designed the pixelated display module, which is capable of addressing ability. The investigated ETRD can indeed serve as the highly chromatic display with low-energy consumption striving toward wide color purity as electronic papers or affordable display.

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10:00 AM BREAK

SESSION EL06.08: Reconfigurable Photonic Integrated Circuits II
Session Chairs: Jinghui Yang and Mengjie Yu
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3022

11:00 AM EL06.08.02
Electrically Controlled, High On/Off Ratio Active Tamm Plasmons for Photonic Integrated Circuits Dong Hyun Seo, Joo Hwan Ko and Young Min Song; Gwangju Institute of Science and Technology, Korea (the Republic of)

The forefront of reconfigurable photonics is advancing towards more promising due to fast information transfer and high density multi-spectral operation in data-processing/ telecommunications. With the advent of state-of-the-art material engineering and lithography technologies, recently, a number of progresses have been reported for on-chip switchable devices. Representatively, based on the phase change materials (PCMs) embedded with micro-/nano-heater (i.e., electrothermal Joule heating), electrically reconfigurable photonics have been presented, with Ge2Sb2Te5 (GST). Although the fast response and large refractive index change of PCMs promoted the distinct variation of optical output, the requirement of constant energy consumption in heating process. Furthermore, under the metal-insulator transition, the introduction of free carriers leads to the optical losses. Especially, in the tele-communications frequencies (e.g., C- band around 1550 nm or O-band around 1310 nm), the loss limits not only optical modulation ratio but also the transmission rate. To overcome the limitations, over the last several years, remarkable progress of material engineering for lowering the optical loss of PCMs (e.g., Ge2Sb2Se4Te1 (GSST), Sb2S3, and Sb2Se3) have been presented. Nevertheless, even subtle extinction coefficient of GSST, it still hinders highly efficient light transport. In case of Sb2S3 and Sb2Se3, although they eliminated the optical loss, the tunability is too small.

As an alternative approach, recent works on dynamic photonics have shown that organic conducting polymer can redox reaction under electric field, enabling large complex refractive tuning, including polyaniline (PANI), polypyrrole, and poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). Among them, PEDOT:PSS, which intrinsically possesses metallic characteristics in the infrared, shows a drastic transition into a nearly perfect dielectric state under -1 V. Nevertheless, the previous works have been focused on its concept functions (beam steering and neuromorphic computing) rather than high contrast optical switching.

The designed photonic integrated circuit shows a high-optical modulation through the active Tamm resonator. The optical state change induced by the metal-to-insulator transition of the polymer(PEDOT:PSS). In the mirror state, the polymer shows insulating properties. Thus, the photonic cell fully reflects input light and satisfies the optical 'ON' state. On the other hand, in the Tamm state, the polymer acts as a metal layer inducing strong absorption of the input light. The nearly unity absorption corresponds to the optical 'OFF' state. We confirmed a high on/off ratio (~74 %, - 8.3 dB) under the favorable range for the CMOS technology (0 ~ 3.3 V).

Interestingly, the high-contrast optical modulator showed a hysteresis property by applying sequential voltages. We investigated the reflectance-voltage (RV) hysteresis of the photonic cell. The two distinct states of the reflectance at the read state (0 V) can be realized due to its large memory window. To prove the stability of the photonic cell, we measured the dynamic variation of reflectance in response to cyclical write and erase state, confirming the high-contrast response without striking degradation.

Here, we presented a high-contrast optical switch by designing it to have strong light-material interaction even introduction of a subtle extinction coefficient. On the other hand, at the reduced state (-1 V), it fully reflects the incident light without any optical loss. Based on this property, we characterized the response tendency corresponding to the pulse stimulation. Furthermore, interestingly, the high- contrast optical modulator showed a hysteresis loop by cyclical write and erase state. Using the function, we showed memory characteristic by alternatingly applying the voltages.

11:15 AM EL06.08.03
Micro Holographic Effects with Sub-7nm Photonic CMOS Transistors for Nonlinear Optoelectronic Processors and Optical Computers James Pan; American Enterprise and License Company, United States

Three dimensional holograms are formed using the optical holography technique. There have been reports on improved performance with Digital Holography and Incoherent Digital Holography. These advanced technologies focus on macroscopic scale holograms. External lasers and digital tools are required. In this report, we will focus on microscopic holographic effects using sub-7nm photonic CMOS transistors. Due to the resonance and coherent holographic process, there are more information in the photonic CMOS output signals, which makes wide-band optical computing a reality.

A hologram contains more information, because it is formed by interference / modulation of split coherent lights. A regular picture is produced by reflection of an incident light from an object. A hologram is produced by interference of an incidence light and its split coherent light affected by an object. As the result, the 3-D features are enhanced and delineated by holography. In some ways holography is similar to a Michaelson Interferometer.

If two lights are coherent, their phases are organized. If the two lights are incoherent, their phases are not related. Although incoherent digital holography has been demonstrated, more complicated setup would be required. In this paper only coherent holography will be presented.
A photonic CMOS transistor includes a laser in the drain area, and another laser in the source area, and photon sensors in the well region. When the MOSFET is on, the lasers and photon sensors are also on. When the MOSFET is off, all devices are off. The MOSFET, lasers, and photon sensors are fabricated as one integral transistor.

A resonance chamber is formed at the center of the CMOS transistor, when the source laser and the drain laser are coherent, and only the drain laser / sensor receives an input light signal. This creates a holographic effect in the resonance channel region. The output light signal will include the holographic messages, which can be transmitted to other transistors for optical processing. The performance is superior due to the more sophisticated interference and modulated split coherent lights.

The CMOS transistor is designed for only the drain laser and drain photon sensors to receive external light signals, as there is a depletion region located only at the drain side. External lights are blocked from the source laser.

We will present data examining the coherence vs. sub-7nm transistor parameters, such as Rch and Rds (channel and source drain resistance). For femtosecond pulsed lasers, we will look into the effects of frequency as a function of the quality of the coherent holographic signals. Device features, and process integration will be discussed for the micro holographic effects. How optical computing can be implemented, taking advantage of the nonlinear optoelectronic CMOS with micro holography will be presented.

The design of an optical processor relies on transmission of optical signals either through an micro optical waveguide or confined free space. Laser communications between photonic transistors in an optical computer become more efficient if the lights are encoded with micro holographic techniques. We will introduce a few examples of logic gate designs (AND, OR, NAND, NOR, XOR, Comparator, OP AMP) and SRAM for optical computing using micro holography.

Finally, we would like to discuss how to enhance the micro holographic effects using nonlinear optical materials in optical waveguides and photonic CMOS, from UV to NIR and Terahertz spectral ranges. The photonic CMOS needs to be configured with nonlinear optical materials, in order to adapt to such nonlinear micro holographic process. A few different approaches will be presented.

11:30 AM EL06.08.04

Photonically Modulated Synaptic Plasticity for Neuromorphic Vision in Zinc-Tin Oxide and Gold Nanoparticles Heterostructure Transistor Li-Chung Shih, Fang-Jui Chu, Ching-Hsiang Yang, Ya-Chi Huang and Jen-Sue Chen; National Cheng Kung University, Taiwan

Inspired by the human brain, neuromorphic computing systems have great advantages of strong fault tolerance and improved power efficiency for complex real-time information processing. In parallel, the biologically inspired computer vision is a growing computing paradigm, aiming at mimicking human visual perception to capture valuable information from images and videos. To integrate the two operations in one, photosynaptic devices with modulation of conductance via applying the optical and electrical spikes will be a prudent approach to emulate photosensitive synaptic plasticity change for the realization of neuromorphic photonics.

Transparent semiconducting oxides have received considerable attention in state-of-the-art neuromorphic image sensor arrays owing to their high light sensitivity, carrier mobility, and low-temperature processability. In this study, we demonstrate a photosynaptic transistor based on zinc-tin oxide (ZTO) with embedded Au NPs heterostructure. The ZTO/Au NP photosynaptic transistor exhibits high-performance capabilities and versatile transistor characteristics that are driven by electrical and optical stimuli. The electron detrapping effect at the ZTO/Au NP interface and localized surface plasmon resonance (LSPR) effect of Au NPs are realized using a negative gate voltage (V_G = -5 V) and at an illumination of 520 nm light, respectively, leading to the increasing drain current (I_D). Intriguingly, the synergistic optoelectrical coupling effect is observed with the simultaneous application of electrical and optical spikes, which is attributed to a greater probability of charge separation between the photogenerated electrons and ionized oxygen vacancies in the ZTO with an external electric field. It is worth noting that this synergistic effect corresponds to the behavior of the biological synapses, that is, the released neurotransmitters can significantly activate glutamate receptors and facilitate synaptic plasticity for learning and memory under light illumination. As a result, the ZTO/Au NP photosynaptic transistor shows the potential to be implemented in sensor networks and pave the way to mimic visual perception for with the minimal power consumption.

11:45 AM EL06.08.05

Probing the Material Impact of Nanofabrication on Integrated Thin-Film Lithium Niobate Photonic Device Performance David R. Barton, Matthew Yeh, Julia Mundy, Marko Loncar and Evelyn Hu; Harvard University, United States

Thin-film lithium niobate on insulator (TFLN) has emerged as a promising platform for integrated classical and quantum photonics due to its intrinsically large electro-optic effect and wafer-scale availability. The direct connection between driving electric fields and refractive index in this platform has enabled new schemes for creating pulsed lasers on chip, high-bandwidth and energy-efficient modulators, and devices for integrated nonlinear photonics. However, it is generally recognized throughout the community that the reliability of thin-film lithium niobate modulators is subject to unstable electro-optic response at low frequencies, and undesired photorefractive index changes due to defect absorption at high optical powers. Post-processing methods such as annealing have been developed to reduce these deleterious effects, but their microscopic origins remain unclear. It is also not known if these effects relate to fundamental materials issues, might be exacerbated for materials in thin-film form with possible strain inhomogeneities, and indeed might arise from thin-film preparation, which involves ion implantation, and chemical-mechanical polishing.

Here, we employ a combination of X-ray photoelectron spectroscopy (XPS) and atom probe tomography (APT) to analyze a commercial x-cut congruently-grown lithium niobate on insulator wafer, and thereby illuminate the surface and bulk composition as a function of nanofabrication process conditions. First, we show through XPS that the etch conditions and standard acid cleans used in our thin-film processing dramatically impact the surface, either by removing lithium from the surface or by locally reducing Nb^{5+} to Nb^{4+}. Specific chemical cleans remove the damaged layer, while annealing at moderate temperatures in an oxygen environment restores the surface Li:Nb ratio to its unprocessed status. We gained additional insight by using APT to map out the material composition in 3D. Surprisingly, we found that the lithium composition within the unprocessed material varies substantially over length scales on the order of 10 nanometers, suggesting that local defect structures such as the small polaron (reduced Nb antisite defect: $\mathrm{Nb}^{\cdot\cdot\cdot\cdot}_{\mathrm{Li}}$) may exist in appreciable concentrations that could give rise to photorefraction. Annealing our samples temporarily increases quality factors and reduces photorefraction, indicating that diffusion of mobile species such as Lithium may indeed play a role in long-term stability of our devices. These results suggest that simple fabrication modifications can help reduce the leaky dielectric nature of our integrated films, while posing questions about the fundamental limits of this platform for integrated photonics.

SESSION EL06.09: Breaking News
Session Chairs: Peter Qiang Liu and Xi Wang
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3022

1:30 PM EL06.09.01

Bioinspired Artificial Photonic Synapses Based on Polycrystalline *β*-Ga_2O_3 for Neuromorphic Applications Youngbin Yoon, Yongki Kim, Wansik Hwang and Myunghun Shin; Korea Aerospace University, Korea (the Republic of)

Recently, artificial intelligence technology that mimics the efficient information processing mechanism of the human brain has emerged as a core technology for big data processing. In particular, a neuromorphic computing chip can directly implement the human brain structure and computational process in hardware, enabling efficient low-power intelligent computation at high speeds. This enormous potential of neuromorphic computing has prompted a worldwide increase in research to realize the technology. More recently, complex biological activities and perceptions, such as memory and forgetting processes, classically conditioned learning experiments, and artificial sensory functions, have been emulated using neuromorphic artificial synaptic devices, including memristors and field-effect transistors (FETs). The biological nervous system represents associative learning through sensory systems. To comprehensively mimic brain functions, artificial synaptic devices integrating sensing and processing functions must be developed. Vision plays a vital role in organisms' reactions to the external environment, primarily because more than 80% of the information acquired through the sensory organs is obtained through vision. In addition to visible light, various animal species contain photoreceptor cells that can absorb ultraviolet (UV) light in the retina and transduce it into cellular signals. For example, bees can be trained to search for sugar water because of their UV-sensitive visual and nervous systems. In the dim Arctic twilight, reindeer use their ability to sense contrast in the UV to locate plants, including lichen and moss, and effectively evade predators (wolves and polar bears). Since humans cannot perceive UV light, the development of UV neuromorphic sensors complements our understanding of UV light and can be utilized in a variety of applications, such as chemical/biological sensors, on-chip optical communications, ultraviolet astronomy, and early warning systems. In particular, the incorporation of light into the operation of synaptic FETs can expand the bandwidth and effectively improve the interconnection problem of synaptic devices. Synaptic devices of oxide semiconductors are stimulated by deep UV signals because of their large optical bandgaps. Among them, gallium oxide (Ga_2O_3), which has an ultra-wide bandgap of 4.9 eV is particularly noteworthy. The ultra-wide bandgap provides a controllable number of large memory (storage) states. Moreover, Ga_2O_3 is suitable for optical device applications because of its almost direct bandgap properties and can also be utilized in synaptic devices that respond to optical stimuli. In this study, β-Ga_2O_3-based synaptic phototransistors were fabricated for the first time. Optical and electrical spikes stimulated the Sn-doped 100-nm thick polycrystalline β-Ga_2O_3 synaptic FETs. The device mimicked crucial synaptic functions, such as EPSCs, IPSCs, PPF, SNDP, SRDP, and STDP using two types of stimuli (optical and electrical). With light stimulation, a linear increase in synaptic weight (current) was confirmed owing to the PPC effect in the device that was fabricated with a back-gate structure. Synaptic reinforcement and inhibition were achieved by gate dielectric (SiO_2) interfacial states induced by gate voltage control. We confirmed the modulation of weights through the synergistic effect of excitatory and inhibitory synapses and mimicked the associative learning process, an expected neurological behavior. Moreover, convolutional neural network (CNN) simulation was used to perform National Institute of Standards and Technology (MNIST) handwritten digit images pattern recognition to further demonstrate the applicability of the synaptic β-Ga_2O_3 phototransistor in the neuromorphic field and achieved using the proposed optimized training method.

1:45 PM EL06.09.02
Emerging Glassy and Phase-Change Chalcogenide Thin Films with Unconventional Bonding Mechanism for Adaptive Photonic Devices Anthony Albanese[1], Jean-Baptiste Dory[1], Jean-Yves Raty[2], Martina Tomelleri[1], Meryem Ibnoussina[3], Jean-Baptiste Jager[4], Anthonin Verdy[1], Francesco d'Acapito[5], Magali Tessaire[1], Aurélien Coillet[3], Benoît Cluzel[1] and Pierre Noé[1]; [1]Univ. Grenoble Alpes, CEA, LETI, France; [2]CESAM-Physics of Solids, Interfaces and Nanostructures, Belgium; [3]ICB, UMR CNRS 6303, Univ. Bourgogne Franche-Comté, France; [4]Univ. Grenoble Alpes, CEA, IRIG, France; [5]CNR-IOM-OGG c/o ESRF – The European Synchrotron, France

Chalcogenide materials have attracted much attention over the years due to their wide range of applications. Among them, some compounds such as Ge-Sb-Te based alloys exhibit a unique portfolio of properties, which has led to their wide use for non-volatile memory applications such as optical data storage or more recently resistive phase-change memory [1,2]. In addition to a high IR transparency window and high optical nonlinearities [3], some chalcogenide glasses such as Se-based compounds exhibit an unusual conductivity behavior under high electric field, called ovonic threshold switching (OTS) effect [4]. Recently, we showed that some As-free $GeSb_wS_xSe_yTe_z$ chalcogenide compounds exhibit outstanding reconfigurable linear and nonlinear properties when deposited in thin films. All films were obtained by industrial magnetron co-sputtering deposition.
First, the linear and non-linear optical properties of innovative $GeSe_{1-x}Te_x$ thin films in the amorphous phase as-deposited as well as after annealing crystallization are studied. These alloys belong to the GeSe-GeTe pseudo-binary line located between the covalent GeSe compound and the "metavalent" GeTe phase-change material (PCM). They are considered very promising candidates for high temperature non-volatile resistive memories [5], emerging all-optical neuromorphic circuits and IR photonic applications. These new PCM compounds offer promising properties for optical switch applications requiring high refractive index contrast upon crystallization with limited optical losses, especially at 1.55 µm. In addition, the amorphous films exhibit good thermal stability up to crystallization occurring above 300 °C [5], as well as a high nonlinear refractive index offering promising opportunities for nonlinear NIR-MIR on-chip devices. Second, exceptional n_2 values are obtained for all as-deposited $GeSb_wS_xSe_yTe_z$ films in the NIR-MIR range. These values are 2 to 3 orders of magnitude higher than those found in SiN_x thin films, which are considered today as the reference material for on-chip nonlinear NIR photonic applications. A dramatic change in the Kerr index as a function of the composition of the $GeSb_wS_xSe_yTe_z$ chalcogenide alloys is also observed and related to changes in the amorphous structure. The origin of the very high local electronic polarizability, related to highly polarizable structural motifs in the amorphous lattice, can be linked to the enhanced optical nonlinearities of the material [6]. These highly polarizable patterns are reminiscent of "metavalent" bonding, the unique bonding mechanism that causes the huge optical and electrical contrast between the amorphous and crystalline states of phase change materials.
In summary, some innovative As-free $GeSb_wS_xSe_yTe_z$ chalcogenide compounds exhibit outstanding linear and nonlinear optical properties that are behind their promising potential for reconfigurable and on-chip NIR-MIR applications. This results from the formation of particular structural patterns leading to a specific bonding mechanism that gives rise to their huge polarizability. These results pave the way to control and enhance the unique optical properties of chalcogenides in thin films.

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2:00 PM EL06.09.03
Broadband Total Absorption of Light Nina Vaidya[1], Eric Plum[1], Anton N. Vetlugin[2] and Nikolay I. Zheludev[1,2]; [1]University of Southampton, United Kingdom; [2]Nanyang Technological University, Singapore

We report a new light absorption device that - in principle - can absorb light completely across the entire electromagnetic spectrum by utilizing its spatial coherence and we provide proof-of-concept experimental demonstration of such a device. Complete absorption of broadband light is key for several technologies including photovoltaics, energy conversion, quantum and stealth technologies.

We demonstrated *broadband* coherent perfect absorption through experimental results. Constructive interference of counterpropagating waves on a thin film with appropriate optical properties (e.g. chromium or graphene film of appropriate thickness with 50% absorption) enables complete (deterministic) absorption of light, down to the single-photon level. We, recently, succeeded in demonstrating experimentally how this discovery can be utilized to realize a compact device that perfectly absorbs broadband spectrum of light simultaneously- by broadband constructive interference of light we achieved perfect absorption in nanometer scale thin films. When the optical path lengths were not matched, the reflectivity spectrum oscillated between coherent absorption and coherent transmission. With alignment, the bandwidth of coherent absorption increased, and became very large when the path lengths were matched. In this case, we observed only 9% reflectivity across the studied wavelength range of 1540 to 1620 nm, implying >90% absorption. Changing one effective optical path length by about half a wavelength switched between coherent absorption and coherent transmission of the Cr film, i.e., between a perfect absorber and a mirror. We also note that perfect absorption of s-polarization coincides with perfect transmission of p-polarization and vice versa.

The thin film can be made photoactive (using 2D transition-metal dichalcogenides, semiconductors thin films, or organic-inorganic mixed films like perovskites) so that it not only absorbs all the light but also produces electricity/detects. Several permutations of optical designs including 2D and 3D structures, tessellated arrays, scaling, broadband light sources, polarizers, and various absorbing thin film materials are being investigated to develop the demonstration further and to optimize the concept for specific applications.

The recent results are noteworthy as the first demonstration in the field – of *broadband* coherent perfect absorption in a single compact device. This demonstration will help pave the way forward to go beyond the ergodic light trapping limit and the Shockley–Queisser limit to create highly efficient ultrathin absorbers, solar cells, and detectors; and forms building blocks for future adaptive nanophotonics as well.

2:15 PM EL06.09.04
Tunable Infrared Metasurface of Quasi-Metal Transparent Conductive Oxide for Thermal Management Applications Thu H. Le[1] and Ngoc Lam Huong Hoang[2]; [1]National Institute of Advanced Industrial Science and Technology (AIST), Japan; [2]Vietnam National University, Hanoi University of Science, Viet Nam

This study reports a novel class of transparent conductive oxide (TCO) of TiO_2:Nb that exhibits the carrier density comparable to metals for infrared plasmonic applications. Recently, TCOs have emerged as alternative plasmonic materials to replace noble metals, owning to their CMOS compatibility, tunability of optical and structural properties, etc. The plasmonic properties of TCOs are determined by their carrier densities, however, most of the studies, so far, reported the carrier densities (~10^{20}/cm^2) much lower than those in nobel metals (~10^{22}/cm^2). It consequently limits the realization and improvement of plasmonic properties in TCOs. In this study, we demonstrate a new method to significantly increase the carrier density in transparent conductive oxides by doping of a small amount of silver (Ag) into conductive oxide thin film (TiO_2:Nb), while maintaining the crystalline structure and the visible transparency of TiO_2 film. The tunability of optical properties of Ag-Nb co-doped TiO_2 in mid-infrared regime was charaterized by ultrafast transient infrared spectroscopy. Thin films were fabricated by co-sputtering Ag and TiO_2:Nb (9% Nb) targets at appropriate ratios. After deposition, the amorphous films underwent the annealing process at 350-400^{o}C in vacuum. This thermal treatment induced the diffusion and the ion exchange of Ag during the crystallization of Nb-doped TiO_2, resulting in the co-doping of Ag of Nb into the anatase structures of TiO_2. The doping of Ag improves the carrier density while has subtle effect on the visible transparency TiO_2 films. The Hall measurement results of 100 nm-thick Ag-Nb co-doped TiO_2 films show carrier density at 2.1×10^{22}/cm^2. This value is two-order larger than reported TCOs and at the same level with nobel metals. The film exhibits the transparency of 85% in the visible regime, which is comparable to TiO_2:Nb without Ag doping. The plasmonic properties of Ag-Nb co-doped TiO_2 were investigated by fabricating metasurface of nanostructures on thin films and characterizing their optical properties. For example, nanorod structures fabricated on a 100 nm-thick Ag-Nb co-doped TiO_2 thin film, with different rod sizes. The corresponding transmittance spectra reveal distinct plasmon dips in the infrared regime, and the decreasing resonant wavenumbers with larger rods, that clearly indicates the plasmonic property in Ag-Nb co-doped TiO_2. Moreover, the plasmon resonance can also be tuned by the doping level of Ag. The achieved plasmonic property can be attributed to the extremely high carrier density and its controllability by Ag doping levels. We also demonstrated the dynamic tuning and switching of optical properties of Ag-Nb co-doped TiO_2 metasurface by thermal and electrical triggers. We observe redshifts of localized surface plasmon resonances arising from a change of the plasma frequency of Ag-Nb co-doped TiO_2, which is governed by the conduction band non-parabolicity. Herein we have demonstrated a simple method of Ag doping for TCOs thin film and demonstrated a novel class of quasi-metal TCOs that exhibit distinquished plasmon properties and tunability in mid-infrared regime. The tunability of optical properties in mid-infrared promises their wide applications for effective usage of solar energy, such as smart windows that allow us adjust light and thermal at ultra-low energy consumption. This work also demonstrates a new scheme to control infrared plasmons for optical switching, telecommunications and sensing.

2:30 PM BREAK

3:30 PM EL06.09.05
All-Dielectric High-Q Thermo-Optically Tunable Transmissive Metasurfaces Ruzan Sokhoyan, Claudio Hail, Morgan D. Foley, Meir y. Grajower and Harry A. Atwater; California Institute of Technology, United States

We theoretically demonstrate all-dielectric low-loss active metasurfaces, which can dynamically manipulate the wavefront of the transmitted light in the near-infrared wavelength range. Our active metasurfaces feature an array of amorphous silicon (a-Si) pillars on a silica (SiO_2) substate, which support supercavity resonances with quality factors (Q-factors) as high as 9800, as well as lower-Q resonances. We show that the considered supercavity mode is also supported by an isolated pillar with the highest achievable quality factor of 676. We observe that the quality factor of the supercavity mode increases by a factor of 14 when the metasurface elements are arranged in a metasurface array.
Next, we propose a metasurface geometry and a realistic interconnect architecture, which enable thermo-optic dynamic beam steering and dynamic beam switching with switching times as low as 7.3 μs. In the proposed metasurface implementation, the top and bottom 50 nm of Si are n-doped with a carrier density of 6×10^{18} while the carrier density of the lightly doped Si core is 3.2×10^{17} cm^{-3}. By applying voltage between the top and bottom doped Si layers, we flow a current between the doped layers through the lightly doped a-Si layer. The induced current raises the temperature a-Si pillars by means of Joule heating, resulting in a modified refractive index of a-Si. To realize dynamic beam switching or beam steering in transmission, we utilize modest refractive index modulation of amorphous Si ranging between $\Delta n = 0.0026$ to $\Delta n = 0.006$, depending on the specific implementation. In our proposed metasurface structures, we benefit from both relatively low-Q modes as well as high-Q supercavity mode supported by an individual a-Si pillar. We use full wave optimization to obtain high directivity steered beam using the particle swarm optimization algorithm. We show that that that our full wave optimization approach increases the directivity of the steered beam as compared with the case when the intuitive forward design approach is used.
We observe that both the high-Q and lower-Q modes can steer the beam for two orthogonal incoming polarization directions at two different wavelengths, indicating that with an appropriate interconnect design, the proposed metasurface can potentially be used for two-dimensional beam steering.
It is also worth mentioning that, so far, most of the active metasurfaces enabling dynamic wavefront shaping operate in reflection. On the other hand, active metasurfaces operating in transmission can readily be integrated with chip-scale light sources, yielding ultra-compact wavefront shaping devices.

3:45 PM EL06.09.06
Filterless Narrowband Si/organic Integrated Photodetector for Sensitive Near-Infrared Detection Zhuhua Xu and Guodan Wei; Tsinghua-Berkeley Shenzhen Institute, China

Narrowband photodetector (PD) has attracted intensive attention for full-color imaging and visible-blind near-infrared (NIR) detection in image sensing, optical communication .They requires a strongly peaked response centered around a certain “design wavelength” since the wavelength selective light detection could increase the sensitivity, color separation and resolution of image sensors. However, it always remains a great challenge to reach narrowband PDs for commercialzed Si photodetectors due to its absorption limition. For narrowband photodetection application in night-vision imaging and security, Si photodetectors have to integrated complex **optical filters**, resulting increased manufacturing cost and architectural complexity. Even the quality of imaging sensing could be affected. Numerous efforts have been explored with limited success on searching solutions for narrowband NIR detection. Herein, we have explored unique silicon nanograting structure on top of the regular Si substrate in combination of very thin organic layer, obtaining filterless NIR narrowband photodetectors as narrow as **26 nm**. The ultrafast response time could be reached in micro seconds. This unique Si nanograting/organic bulk heterojunction has facilitated the charge collection narrowing of the external quantum efficiency of the NIR photodetectors. To our best knowedge, this has been the **very first narrowest** NIR Si photodetectors, which could open up a new window for commerciated application for multicolor imaging and autonomous mobiles.
The narrowband detection capability of the PD can be attributed to the following reasons: 1) The periodic neat nanograting Si structure can generate optical diffraction and a wide reflection peak; 2) The organic film have a transmission spectrum that strongly overlaps with the absorption spectrum of the

nanograting Si underneath, which could ensure the wavelength onset of the resonant enhancement absorption peak; 3) The as-obtained organic layer forms a nanograting structure for strongly localized optical field and the strong optical interference that has greatly contributed to the narrow NIR photoresponse; 4) The effective potential barrier could be formed after introducing the appropriate organic layer, which greatly suppresses dark current; 5) The interface of the nanograting Si and the organic layer has provided energy favorable sites for effective charge transfer, enhanced charge collection efficiency, and therefore 40-fold higher photoresponse than that of the nanograting Si PD.

SESSION EL06.10: Virtual Session I: Adaptive Nanophotonics
Session Chairs: Fei Ding, Min Seok Jang, Xi Wang and Jinghui Yang
Tuesday Morning, April 25, 2023
EL06-virtual

8:00 AM *EL06.10.01
Optically-Controlled Dielectric Metasurfaces for Dynamical Dual-Mode Modulations on Terahertz Waves Lei Zhou; Fudan Univ, China

Dynamically controlling terahertz (THz) waves with an ultra-compact device is highly desired, but previously realized tunable devices are bulky in sizes and/or exhibit limited light-tuning functionalities. Here, we experimentally demonstrate ultra-fast dynamical light modulations with a dielectric metasurface in mode-selective or mode-unselective manners, through optically pumping the system at different wavelength. Coupled-mode-theory analyses, in good agreement with both experiments and simulations, reveal that the physics is governed by distinct wavefunction overlapping between resonance modes and field patterns of pumping light penetrating inside the system at different wavelength. We then design/fabricate a dielectric metasurface and experimentally demonstrate that it can dynamically control the polarization state of incident THz wave, dictated by the strength and wavelength of the pumping light. Our studies reveal that the pump wavelength can be a new external knob to dynamically control THz waves, which may inspire the realizations of many tunable meta-devices with diversified functionalities. As an illustration, we finally numerically demonstrate the pump-wavelength-controlled optical information encryption based on a carefully designed dielectric metasurface.

8:30 AM *EL06.10.02
Plasmon-Empowered Electrically Tunable Metasurfaces Sergey I. Bozhevolnyi; University of Southern Denmark, Denmark

Optical metasurfaces (OMSs) represent subwavelength-dense planar arrays of nanostructured elements designed to control local phases and amplitudes of scattered optical fields, thus being able to manipulate radiation wavefronts at a subwavelength scale. In the past decade, many configurations involving different physical mechanisms have been developed, and numerous diverse applications have been demonstrated, including free-space wavefront shaping, versatile polarization transformations, optical vortex generation, optical holography and many others [1]. However, to date, most reported OMSs are static, featuring well-defined optical responses determined by OMS configurations that are set during fabrication, although, for more intelligent and adaptive systems, dynamic OMSs with externally controlled functionalities are in high demand. Realization of dynamic adaptive OMSs is, at the same time, very challenging because of the high density of array nm-sized elements that are also arranged in nm-thin planar configurations, circumstances that limit severely the interaction volumes.

In this talk, I present recent results that we obtained with two different configurations for realizing electrically controlled OMSs operating in reflection: piezoelectric micro-electro-mechanical systems (MEMS) integrated with gap surface-plasmon (GSP) based OMSs [2] or Fabry-Perot resonant OMSs [3] and resonant configurations based on thin electro-optic crystal layers sandwiched between nanostructured electrodes [4,5]. Their operational principles are described, and the main experimental results obtained are presented. Furthermore, new developments and functionalities demonstrated will be presented at the conference.

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9:00 AM *EL06.10.03
Direct Coupling for Compact Integrated All-Optical Reservoir Computing Ivan Boikov[1], Daniel Brunner[2] and Alfredo de Rossi[1]; [1]Thales Research & Technology, France; [2]CNRS & University Bourgogne Franche-Comté, France

We propose a highly compact Reservoir Computer (RC) implementation on integrated platform based on evanescently coupled nonlinear optical microresonators acting as neurons. We discuss how basic parameters of system impact RC properties, suitability of microresonator types and semiconductor platforms and scalability of reservoir with number of neurons. We compare impact of two-photon absorption, free electron dispersion and Kerr effect on RC properties. Finally, we demonstrate RC operation on a common benchmark of Mackey-Glass prediction task and an applied task of optical data recovery. Such RC was capable of performing autonomous computation at GHz frequency range in real-time, while requiring several mW of optical power and footprint on the order of 0.001 mm^2, excluding readout. We found that all three nonlinearities positively contributed to computing performance.

9:30 AM *EL06.08.01
Active THz Topological Photonics for 6G and Beyond Ranjan Singh; Nanyang Technological University, Singapore

Global digitalization and the recent rise of artificial intelligence-based data-driven applications have directed their vectors towards terabits per second (Tbps) communication links. The fast-evolving 5G communication network cannot fulfill this demand due to several technological challenges, including bandwidth scarcity, which has stimulated innovative technologies with a vision of 6G communication. Semiconductor and emerging quantum material-driven Terahertz (THz) micro-nanotechnologies have been identified as a critical candidate for the emerging 6G communication with the potential to provide ubiquitous connectivity and remove the barrier between the physical, digital, and biological worlds. Nonetheless, the existing THz photonic on-chip communication devices suffer from backscattering, bending loss, limited data speed, and lack of active tunability. Here, I will describe active on-chip THz photonic topological devices consisting of low-loss, broadband single channel 160 Gbit/s interconnect devices and critically coupled high-*Q* cavities built on Silicon Valley-Hall Photonic Crystal. Silicon topological photonics will pave the path for augmentation of CMOS-compatible hybrid electronic-photonic driven terahertz technologies, vital for accelerating the development of 6G and 7G communications.

SESSION EL06.11: Virtual Session II
Session Chairs: Fei Ding and Xi Wang
Tuesday Morning, April 25, 2023
EL06-virtual

10:30 AM *EL06.11.01
Abstract Presented (ON-DEMAND ONLY) Controllable Doping of Noble Metals in Disordered Inorganic Solids—An Alternative Way for Tunable Nanophotonics Cheng-Wei Qiu and Zhiyuan Yan; National University of Singapore, Singapore

Phase transitions among amorphous, quasicrystals and crystals states are ubiquitous in nanoscale and bulky materials, manifested in alloys, 2D materials, phase change materials, thermoelectric and semiconductors. Here we report a phase-transition-assisted gradient and reversible doping approach for solid thin films that enables the dopants to be gradually doped into the host and reverted to their pristine positions. We demonstrate thermally tunable high-resolution and large-scale colour images on Si wafer within 1 minute using this approach. Our findings provide a distinct post-production modification of optical, electrical, mechanical, and thermal properties of inorganic solids, and that would be useful for dynamic and tunable nanophotonics.

11:00 AM *EL06.11.02
Learning from Failure—Improving Cycling Endurance of Optical Phase Change Materials Juejun Hu; Massachusetts Institute of Technology, United States

Chalcogenide phase change materials (PCMs) are truly remarkable compounds whose unique switchable optical and electronic properties have fueled an explosion of emerging applications in electronics and photonics. Key to any application is the ability of PCMs to reliably switch between crystalline and amorphous states over a large number of cycles. While this issue has been extensively studied in the case of electronic memories, current PCM-based optical devices show limited endurance. To understand the failure mechanisms limiting endurance of PCMs specifically in photonic devices, we have developed an on-chip micro-heater platform and an automatic multi-modal characterization system to analyze cycling performance of optical PCMs. Our work revealed directional elemental segregation over extended cycles, and identified morphological instability as a new premature failure mode unique to photonic devices. Reversible switching of large-area PCM devices over 10,000 cycles was demonstrated.

SYMPOSIUM

April 11 - April 26, 2023

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SESSION EL07.01: Synthesis and Functionalization I
Session Chairs: Lorenzo Mangolini and MingLee Tang
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3007

10:30 AM *EL07.01.01

Low Pressure Dusty Plasmas Synthesis of Silicon Nanocrystals for Photonic Applications Uwe R. Kortshagen; University of Minnesota, United States

Chemically reactive nonthermal plasmas at low pressure are an interesting medium for the growth of nanocrystals. Molecular precursors are dissociated by electron impact reactions and the resulting molecular fragments and radicals, many of them charged, nucleate to form clusters and nanocrystals. Energetic surface reactions can heat these initial clusters to temperatures that exceed the gas temperature by hundreds of Kelvin. This enables plasmas to form crystalline nanoparticles even of materials with very high melting points. The unipolar negative charging of nanoparticles in the plasma virtually eliminates particle aggregation, leading to very monodisperse size distributions. Furthermore, plasma synthesis is an all-gas-phase method that does not require solvents or ligands and is thus a relatively sustainable synthesis method. In this presentation, we will discuss the plasma synthesis of silicon quantum dots with diameters on the order of ~3 nm for luminescent applications as well as the synthesis of larger silicon nanocrystals, 60-200 nm in diameter, that show interesting scattering behaviors.

Plasma-synthesized silicon quantum dots have shown good luminescence properties with photoluminescence quantum yields of up to 60%. To attain such high quantum yields, passivation of surface defects is required that has traditionally been achieved by hydrosilylation reactions. However, hydrosilylation requires organic solvents which partly offsets the sustainability advantage of plasma synthesis. Here, we report on recent progress in performing the surface functionalization in the gas phase right after the synthesis step. We discuss various methods to attach organic ligands to the surfaces of silicon quantum dots while in flight in the afterglow of the synthesis plasma.

One application of luminescent silicon quantum dots is in luminescent solar concentrators (LSCs). These are semitransparent waveguides that are doped with silicon quantum dots. The silicon dots absorb solar radiation primarily in the blue range of the spectrum and reemit it in the near-infrared. Waveguiding concentrates this radiation on small solar cells that can be edge or surface mounted. We discuss results of a numerical model that investigates the application of silicon LSCs to greenhouses and demonstrate that LSC roof panels have the ability to enable net-zero-energy greenhouses in certain climates.

In the final part of the presentation, we discuss recent progress in the plasma synthesis of larger, highly monodisperse silicon nanocrystals with diameters of 60-200 nm. These nanocrystals exhibit intriguing optical scattering through overlapping electric and magnetic dipole modes. We show that ensembles of silicon nanocrystals produced by plasmas show scattering behavior that is essentially consistent with single particle scattering models due to their very narrow size distribution.

This work was supported by the Army Research Office MURI grant W911NF-18-1-0240.

11:00 AM EL07.01.02
Ge-Based Nanowires of Metastable Composition: Hyper-Doping and Alloy Formation Sven Barth[1], Raphael Behrle[2], Masiar Sistani[2], Jos Haverkort[3] and Michael Seifner[4]; [1]Goethe University Frankfurt, Germany; [2]TU Wien, Austria; [3]TU Eindhoven, Netherlands; [4]Lund University, Sweden

This contribution will address the formation of nanowires and nanorods of metastable composition and demonstrate the significant changes in physical properties associated with their composition.[1] All the growth studies are carried out either in solution or by gas phase techniques using the metal to be incorporated in the Ge host lattice as a growth seed. This approach allowed the formation of highly crystalline, metastable Ge$_{1-y}$Ga$_y$ (y~0.03%) as well as Ge$_{1-x}$Sn$_x$ (x=0.13-0.28) nanowires and nanorods at low temperatures.[2-4] The materials have been characterized by different analytical methods including TEM, EDX, Raman spectroscopy as well as XRD. Generally, a homogeneous incorporation of unusually high contents of Sn and Ga in the Ge lattice has been observed. The high incorporation efficiency also alters the physical properties significantly. While hyperdoped Ge$_{0.97}$Ga$_{0.03}$ shows quasi-metallic behavior in temperature dependent transfer characteristics, Ge$_{0.81}$Sn$_{0.19}$ reveals still semiconducting behavior in equivalent experiments. Moreover, the formation of Ge$_{1-x}$Sn$_x$ with x>0.09 causes the transformation to a direct bandgap material, while the solid solubility limit according to the binary phase diagram (~ 1 at% Sn in Ge) has to be overcome. The efficient absorption and emission in the mid-IR range (<~0.55 eV) makes Ge$_{1-x}$Sn$_x$ very attractive for CMOS-compatible optoelectronics based purely on group IV elements. The high crystal quality of CVD-grown, epitaxial Ge$_{0.81}$Sn$_{0.19}$ nanowires can be illustrated.

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11:15 AM EL07.01.03
Vanadium-Related Electro-Luminescence from Vertical 4H-SiC PiN-Diode at Elevated Temperature Koichi Murata[1], Shin-Ichiro Sato[2], Satoshi Asada[1], Seiichi Saiki[2], Yuta Masuyama[2], Takeshi Ohshima[2] and Hidekazu Tsuchida[1]; [1]Central Research Institute of Electric Power Industry, Japan; [2]National Institutes for Quantum Science and Technology, Japan

Introduction

Quantum-sensing technology has gained increasing appeal to detect magnetic and electric fields and measure temperature with high sensitivity in a range of fields, including biomedical and space applications. The negatively charged nitrogen-vacancy defects in a diamond are the most well-known spin defects and widely studied. Although silicon carbide (SiC) has great potential for quantum sensing, several spin defect candidates have been reported [1]. These include vanadium (V^{4+}) in its neutral state in 4H-SiC, which shows photoluminescence (PL) and a wavelength of 1.3 μm in the optical telecom O-band (original band) [2, 3]. In addition, V-doped 4H-SiC materials exhibit high thermal stability against thermal post-processes up to 1973 K [2], although current-driven electroluminescence (EL) of V-doped 4H-SiC has not yet been studied. In this report, we will present EL from a vertical PiN-diode with a V-doped n-layer above room temperature.

Experiment

A V-doped 4H-SiC epitaxial layer was grown in a CVD reactor using liquid VCl$_4$ as the V dopant source [2]. A 120 μm-thick V-doped n-layer (N: 1 × 10^{15} cm^{-3}, V: 2 × 10^{14} cm^{-3}) was grown on a commercial n$^+$ SiC (0001) substrate, while a 1.5 μm-thick aluminum-doped p-type layer was grown on the n-type layer to form a vertical PiN diode structure. The comb-shaped electrode was fabricated on the p-anode and the EL was recorded under a forward bias. Deep level transient spectroscopy (DLTS) was employed to study V-related trap levels in the diode.

Results & discussion

Applying a forward current saw a clear EL appear, with peaking at 1.28 μm (hν = 0.97 eV) and a spectral shape showing positive agreement with the PL spectra obtained from V-doped n-type epilayers [2, 3]. It corresponds to the intra-3d-shell transition of V^{4+}. The EL intensity intensified as the forward current was increased, while the luminescence profile remained unchanged. The EL is also observable, even at temperature over 523 K, with no significant shift in the luminescence peak. These results demonstrate the potential of V-doped 4H-SiC based PiN diodes to function as infrared emitters at elevated temperature. The EL mechanism was also considered. Incorporated V atoms act as amphoteric defects and form two trap levels of $V^{3+/4+}$ acceptor (Ec - 0.97 eV) and $V^{4+/5+}$ donor (Ec - ~ 1.5 eV) in the 4H-SiC band gap. Within this device, the $V^{3+/4+}$ peak was confirmed on a DLTS spectrum taken under reverse bias. The $V^{3+/4+}$ peak originates from the transition between negatively charged V^{3+} and neutral V^{4+} by thermal emission. The Fermi level in the n-type layer is located well above the $V^{3+/4+}$ trap level, indicating the V^{3+} is a steady state in the n-type layer in the PiN diode at the temperature range of this study. Accordingly, the transition from V^{3+} to V^{4+} is essential and has two possible origins: (i) hole-capturing at V^{3+} and (ii) excitation of trapped-electron in V^{3+} by the energy from an electron-hole pair recombination of 4H-SiC. Given that the $V^{3+/4+}$ trap level acts as an effective carrier recombination center and minority carrier lifetimes in V-doped n-type layers are determined by V concentration [2], the origin (i) would be enhanced under a forward bias. Besides, extra excitation energy of > 0.97 eV is necessary for the intra-3d-shell transition of V^{4+}. The possible energy source for this process would originate from the electron-hole pair recombination of 4H-SiC. The luminescence mechanism discussed above supports V-doped 4H-SiC has a potential as infrared emitters operating at elevated temperature. Furthermore, electrical control of the charge states of V could be useful for quantum-sensing.

Acknowledgement
This presentation is based on results obtained from a NEDO Feasibility Study Program (Uncharted Territory Challenge 2050).

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11:30 AM EL07.01.04
Hexagonal SiGe Phase Revealed by Nano-XRF and XLD XAS Madeleine Han[1], Jaime Segura-Ruiz[1,1], Gema Martinez-Criado[1] and Erik Bakkers[2]; [1]European Synchrotron Radiation Facility, France; [2]Technische Universiteit Eindhoven, Netherlands

Highly crystalline hexagonal $Si_{1-x}Ge_x$ nanowires (NWs) are tunable light emitting semiconductors that opens the silicon technology to photoelectronic applications. Under perpendicular crystallographic orientations, by using a hard X-ray nanobeam it is possible to probe axial vs radial coordination environment and detect any preferential order modulation that impacts the anisotropic optical response. This proposal aims to record XEOL-detected X-ray linear dichroism (XLD) microscopy around Ge atoms in $Si_{1-x}Ge_x$ alloyed NWs to illustrate 2D projections of the optical anisotropies that relies on different short-range structural orders.
Although silicon is a critical material in semiconductor industry, its indirect electronic band gap structure makes silicon an inefficient light emitter, limiting its applications. Cubic Si has the lowest conduction-band minimum close to the high-symmetry X-point and a second-lowest minimum at the L-point. On the other hand, cubic Ge also has an indirect bandgap, but its lowest conduction-band minimum is located at the L-point. Thus, by modifying the crystal structure from cubic to hexagonal, the symmetry along the <111> crystal direction can be changed. As a consequence, for hexagonal Ge the band-folding effect results in a direct bandgap at the Γ-point with a magnitude close to 0.3 eV. However, the goal of achieving efficient light emission from group-IV materials in silicon technology has been elusive for decades. Recently, Fadaly et al. demonstrated efficient light emission from direct bandgap hexagonal Ge and SiGe NWs[1]. These findings were possible thanks to the growth of Ge-rich $Si_{1–x}Ge_x$ alloys around a thin (about 35 nm in diameter) wurtzite gold-catalysed GaAs NW that is lattice-matched to Ge. These NWs have shown a sub-nanosecond, temperature-insensitive radiative recombination lifetime and an emission yield similar to that of direct-bandgap III–V semiconductors. Moreover, by controlling the composition of the hexagonal $Si_{1–x}Ge_x$ alloy, the emission wavelength can be continuously tuned over a broad range, while preserving the direct bandgap structure. Therefore, such results represent a huge step in the silicon technology and a thorough investigation could provide further insights into their singular physical properties. However, it is hard to filter out the SiGe phase from GaAs phase by XRD technique. They are expected to present the same hexagonal structure and close lattice parameters due to the close element number of Ga (31) and As (33) compared with Ge (32). So far , nanoXRF and nanoXAS have proven to be a valuable tool to image different types of semi-conductor alloy NWs[2,3]. Here in we propose to combine the power of these two approaches with elemental and polarization selectivity via X-ray linear dichroism (XLD) at the Ge K-edge to explore in details the property-function relationships in these novel SiGex alloyed NWs.

1. Fadaly, E. M. T. *et al.* Direct-bandgap emission from hexagonal Ge and SiGe alloys. *Nature* **580**, 205–209 (2020).
2. Troian, A. *et al.* Nanobeam X-ray Fluorescence Dopant Mapping Reveals Dynamics of in Situ Zn-Doping in Nanowires. *Nano Lett.* **18**, 6461–6468 (2018).
3. Martínez-Criado, G. *et al.* Exploring single semiconductor nanowires with a multimodal hard X-ray nanoprobe. *Adv. Mater.* **26**, 7873–7879 (2014).

11:45 AM EL07.01.05
Photon Up-Converting Silicon Quantum Dots via Gas-Phase Synthesis and Grafting Joseph Schwan[1], Kefu Wang[2], MingLee Tang[2] and Lorenzo Mangolini[1]; [1]University of California, Riverside, United States; [2]The University of Utah, United States

Due to their non-toxic composition and high performance, upconverting silicon quantum dots (SiQDs) are becoming interesting for applications ranging from photovoltaics to bioimaging.[1] This study utilizes a one-step gas-phase method of silicon nanocrystal synthesis and surface-grafting of alkyl ligands to produce monodisperse silicon with uniform partial surface functionalization. The novel technique employed is a non-thermal plasma for SiQD synthesis, followed by functionalization within the plasma afterglow through the introduction of ligand saturated hydrogen.[2,3] This method allows for precise control over the SiQD size as well as the ligand species and amount being grafted to the surface. Partial surface functionalization with alkyl ligands allows for indirect control over subsequent 9-ethylanthracene (9EA) transmitter group surface coverage. Upon 9EA quantification through absorption measurements, transmitter molecule surface coverage effects are directly studied. Further analysis by FTIR enabled the quantification of alkyne surface coverage relative to unoccupied SiQD surface sites, allowing investigation into alkyne-length solubility relations. Meanwhile, emission measurements provided relations between ligand length, SiQD size, and transmitter coverage to photoluminescence and upconversion quantum yield. We have carried out experiments with 1-hexene, 1-octene, and 1-dodecene, demonstrating differences in surface coverage required for colloidal stability and the effects this coverage has on subsequent 9EA attachment and photon upconversion. Additional experiments optimizing SiQD size and alkyl surface coverage for upconversion were also conducted. Conditions enabling upconversion quantum efficiencies reaching 17% were thus achieved under minimal 1-dodecene grafting to maintain solubility, allowing for 3 9EA per SiQD.

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SESSION EL07.02: Surface Chemistry
Session Chairs: Lorenzo Mangolini and Sean Roberts
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3007

1:30 PM *EL07.02.01
Surface Functionalization of Silicon—Introducing Spectroscopic Labels, Monolayer Control for Ultra-Shallow Doping, and Providing Surface Passivation for Atomically-Precise Processes Andrew Teplyakov; University of Delaware, United States

Over the last several decades, chemistry for surface functionalization of silicon went through a number of directional changes that were largely dictated by the technology development. Some of the recent work in our group has been targeting modification of silicon surfaces that could be done in solution or in high vacuum, meaning that the silicon surfaces used should be sufficiently robust to withstand chemical modification conditions. Hydrogen and halogen terminations have been well documented for single crystalline surfaces, such as Si(100) and Si(111). However, if Si(111) has demonstrated overall well-ordered and chemically defined surface structures, Si(100), which is the surface mostly used in applications, has always been difficult to prepare and characterize. This presentation will cover the solution reactions of boron trichloride, boric acid and 4-fluorophenylboronic acid studied in order to understand the interaction of these molecules with hydrogen- and chlorine terminated Si(100) surfaces. These reactions will also be compared with the chemistry of nitrogen containing molecules (such as ammonia and hydrazine) in solution and at gas/solid interface. Parallels and major differences between the chemistry of (100) and (111) crystal faces of silicon will be examined. The reactions of the same surfaces with metalorganic precursor molecules will be presented to evaluate the role of minority sites (defects) in atomically-precise processing. Selected chemical modification pathways will be compared between flat silicon surfaces and nanomaterials.

2:00 PM *EL07.02.02
Tailoring Silicon Quantum Dot Photophysics Using Surface Chemistry and Doping Enabled by Gas-Phase PECVD Growth Nathan R. Neale; National Renewable Energy Laboratory, United States

We have been exploring the effects of surface chemistry and doping on the photophysics of silicon quantum dots (QDs) prepared by nonthermal plasma-enhanced chemical vapor deposition (PECVD) growth. In this presentation, we will describe the PECVD synthesis of silicon quantum dots (Si QDs) that provides the ability to incorporate high concentrations (~10^{20} cm^{-3}) of either p-type (B:Si) or n-type (P:Si) dopants. We also can use this synthetic technique to prepare co-doped QDs containing *both* P and B atoms in the same PB:Si QD. Whereas the optical absorption of singly P:Si and B:Si QDs exhibit plasmonic features characteristic of a high concentration of dopants, the co-doped PB:Si QDs instead exhibit photophysics that resemble those of intrinsic Si QDs, for example emission lifetimes of ~100 ms, but with size-dependent optical transitions that are tunable even *below* the energy of bulk Si (1.12 eV). We also will describe surface chemistry strategies made possible by the highly reactive hydride-terminated surfaces of these QDs that provide further tunability of their photophysics that could potentially enable their use in novel optoelectronic devices.

2:30 PM EL07.02.03
Silicon Quantum Dot-Molecular Hybrid System with C-C and Si-Si Binding Bridges for Efficient Photon Upconversion Kefu Wang[1], Nguyen Nhien[2], Joseph Schwan[3], Minglee Tang[4], Lorenzo Mangolini[3] and Timothy Su[3]; [1]University of Utah, United States; [2]University of california, Riverside, United States; [3]University of California, Riverside, United States; [4]The University of Utah, United States

Si quantum dots (QDs) holds great applicative potential in optoelectronic devices and bio-fluorescent agents due to their biocompatibility compared to conventional toxic Group II-VI and III-V metal-based quantum dots. [1] Recently, Si QDs have shown excellent photon upconversion property and a high photon upconversion efficiency of 7% was obtained for Si QD - 9-ethylanthracene (Si:9EA) system. [2] In addition, it has been reported that sigma Si-Si bonds exhibited comparable electron/ hole conductivity compared to C=C bonds. [3] This motivated us to investigate the binding group between Si QDs and molecular transmitters to facilitate triplet energy transfer so as to improve photon upconversion efficiency. In this work, we successfully attached silyl anthracene transmitter to Si QD surface with Si-Si bond employing di-tert-butyl peroxide as the radical initiator. Si-anthracene system with three different binding group (-CH$_2$-CH$_2$-; -Si(Me)$_2$-Si(Me)$_2$-; -Si(Me)$_2$-Si(TMS)$_2$-) between Si QDs and anthracene molecules were compared to investigate how they affect triplet energy transfer and photon upconversion. We found all three Si-anthracene systems showed high photon upconversion exceeding 5%, indicating the efficient triplet energy transfer between Si QD and anthracene transmitter for these binding bridges. Compared to Si-anthracene system with C-C binding bridge, Si-anthracene system with Si-Si binding bridge exhibited a red-shift and broader triplet excited states absorption. Overall, this work shows efficient triplet energy transfer and photon upconversion efficiency in silicon quantum dot-molecular hybrid system for both C-C or Si-Si binding bridges, which might shed light on controlling energy or charge transfer at nanoscale interfaces for optoelectronic applications.

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3:15 PM *EL07.02.05
Friend or Foe—Unraveling the SiO Evolution Reaction Jonathan Veinot; Univ of Alberta, Canada

Silicon and silica-based materials are ubiquitous in 21st century technology. Whether as nanoparticles or integrated circuits, these systems are essential to a wide array of modern semiconductor applications. While the Si-SiO$_2$ interface is often presumed to be stable, the Veinot group recently encountered a previously overlooked/underappreciated reaction while exploring a widely employed silicon nanoparticle preparation. At high temperatures, silica can be reduced by silicon, resulting in the evolution of silicon monoxide (SiO) gas. Under appropriate conditions, this competing reaction eliminates all silicon nanoparticles from the synthesis. To better understand and exploit this reaction, we investigated the SiO evolution reaction and its impact on silicon nanoparticle synthesis. As our understanding of silicon monoxide improved, we were inspired to explore this reaction as a new pathway for Si-SiO$_2$ interface manipulation. This presentation will outline the insights gained during our studies and outline the challenges and opportunities presented by the silicon monoxide evolution in the context of Si nanomaterial design and preparation.

3:00 PM BREAK

3:45 PM EL07.02.06
Wet Chemical Processing to Form Nanotrenches along Step Edges on a Vicinal Si(111) Surface Composed of Terraces and Atomic Steps Kenta Arima, Zhida Ma, Tetsuro Takeuchi, Ryuto Hashimoto, Rongyan Sun and Kazuya Yamamura; Osaka University, Japan

We aim at forming ultrathin Si ribbons from a silicon-on-insulator (SOI) layer possessing a vicinal surface by total wet chemical processing. To test this concept, we used a p-type Si(111) wafer of which surface is misoriented in the <11-2> direction at an angle of 0.2°. After a cut sample was wet cleaned, it was immersed in water with an ultralow level of dissolved O_2 molecules, which is referred to as the first LOW (Low dissolved-Oxygen Water) treatment. LOW was obtained by adding the deoxygenation agent ammonium sulfite monohydrate to deionized water [1] in which the O_2 concentration was less than 2 ppb. The first LOW treatment formed a Si(111) surface composed of flat terraces and biatomic steps. Then it was immersed in LOW containing Ag^+ ions at a concentration of 5 ppm, which is referred to as the second LOW treatment. We have found that Ag atoms were selectively reduced at the edges of atomic steps on Si(111) to form Ag nanowires, as reported by another group [2]. Finally, the Si sample with Ag nanowires was immersed into a mixture of HF and H_2O_2. An atomic force microscopy (AFM) image reveals that the self-assembled Ag nanowires after the second LOW treatment were replaced by almost continuous nanotrenches [3]. This is probably because the Ag nanowires acted as a catalyst to enhance chemical etching of the Si surface underneath. The height and width of the trenches were in the range of 1.1–1.4 nm and 16–19 nm. By applying this sequence for a thin SOI layer, we expect to form Si ribbons of which width and thickness are both controlled in a self-assembled manner. We also present very recent results to form and image a staircase Si structure on an SOI layer at the boundary of a buried SiO_2 and the SOI.

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4:00 PM EL07.02.07
Non-Hydrogen Peroxide Plasma Activated Water—An Efficient Way of Surface Modification of Semiconductor Nanostructures Pavel Galar, Filip Matejka and Katerina Kusova; Czech Academy of Sciences, Czechia

The development and application of nanomaterials is one of the most impacted trends in the current science and also industry. The reason of its attractiveness is the possibility to significantly tune the properties of bulk materials by limiting their dimensions and using various surface termination or encapsulation strategies. Silicon nanocrystals (SiNCs) are one group of materials which gain significant interest. Even though Si is an indirect semiconductor, SiNCs show relatively high light emission efficiency with size tunable spectral position, good stress resistance and also surface reactivity. A wider application of SiNCs is, however, limited by the absence of a cheap and simple method for their surface termination and modification together with significantly low water dispersibility.

We have recently shown that non-thermal plasma can be effectively used for tuning of the SiNCs surface chemistry through plasma activated liquids (PAL).[1] The liquid activation is realized through treating a liquid by an electric discharge, resulting in the generation of reactive species in the liquid based on the chemical composition of the liquid, surrounding atmosphere and also properties of the used discharge. The most common PAL is plasma activated water (PAW), which is a well-known agent in medicine, agriculture and related field, because of its antibacterial, antifungal and disinfection properties. The limiting parameter of common PAW for nano-semiconductor surface treatment is the presence of a high concentration of hydrogen peroxide, which not only damages the nanocrystals, but also blocks any other surface termination except for oxidation. To overcome this effect, we have developed a technique for the preparation of PAW very low in hydrogen peroxide and containing a high concentration of nitrogen radicals (HiN:PAW). The technique is based on the application of transient spark discharge and semi-closed atmosphere at ambient conditions. Using a specific ratio between the electric pulse period and the peak current, the discharge is able to generate plasma containing a high concentration of nitrogen atoms in air, resulting in the suppression of peroxide generation in favor of nitrites and nitrates in HiN:PAW. The treatment of SiNCs by HiN:PAW for about 30 minutes resulted in nitrogen-based surface termination, manifested by a significant increase in their photoluminescence quantum yield (more than 10 times) and an increase in their dispersibility in water. The modification is stable for more than a month. While the first effect increases the prospective utilization of SiNCs in light conversion and generation and imagining technology, the latter makes them interesting for further applications in hybrid technologies, where water-based chemical processes are involved, such as the preparation of electrodes for lithium batteries. Analogical treatment can also be effectively applied to other kinds of semiconductor nanoparticles, which makes HiN:PAW a novel, cheap, easy and effective way of surface termination of semiconductor nanoparticles.

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4:15 PM EL07.02.08
Interfacial Strain Fields for Nano-Carrier-Confinement and Efficient Bandgap Emission in Silicon Under 980-nm Laser Excitation Sufian Abedrabbo[1], El Mostafa Benchafia[1], Ali Abdulla[1], Anthony T. Fiory[2] and Nuggehalli M. Ravindra[2]; [1]Khalifa University of Science and Technology, United Arab Emirates; [2]Integron Solutions LLC, United States

Ordinary Czochralski silicon (CZ-Si) is known to be inferior in radiative recombination at the bandgap. Interfacing CZ-Si with sol-gel based silica coatings improves the bandgap emission significantly by introducing random strain fields; such results have been reported in several publications and presentations in the literature. In all previous work, the emission band can be modeled by a combination of uncorrelated electron-hole and phonon three particle process. In this work, we report an enhancement in carrier recombination from p-Si photoluminescence that is unorthodoxly dominated by excitonic carrier recombination. The nano-region carrier-confinement results in photons of energy hn with intensity of spectral form $e^{1/2}$ associated with correlated carrier recombination, where e = hn - E_B + E_{exc} + E_{TO}, E_B is the band gap, E_{exc} is the exciton binding energy, and E_{TO} is the transverse optical phonon energy.

SESSION EL07.03: Novel Applications
Session Chairs: Matthew Panthani and MingLee Tang
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3007

8:30 AM *EL07.03.02
Luminescent Silicon Nanocrystals—From Single Quantum Dot to Light-Converting Applications Ilya Sychugov; KTH Royal Institute of Technology, Sweden

Fundamental photophysical properties of Si quantum dots (QDs) were investigated on a single-particle level to understand the mechanism of light conversion [1-3]. Emission, absorption and lifetime data were obtained for individual silicon nanocrystals with either oxide or ligand passivation. In comparison with theory we found that core-related luminescence from Si QDs emanates from an indirect-bandgap state for all practical size range of Si QDs. Small intermixing of direct-bandgap character due to quantum confinement effect takes place, but relevant only for higher energy states pertinent to the light absorption process. Quantum size effect from Si bandgap (1.1 eV) up to 2 eV has been clearly demonstrated by observation of sharp emission linewidths in a broad energy range [3].

Despite partly forbidden character of the recombination process, luminescence from Si QDs may still possess high quantum efficiency when a defect-free core with proper surface passivation realized. We have demonstrated a new synthesis method, which can reduce pre-cursor cost by an order of magnitude from the established HSQ-based method [4]. Si QDs prepared in this way have near-unity internal and > 50% external (quantum yield) quantum efficiency. They also possess a large Stokes shift, which suppresses re-absorption of the emitted light of importance in a number of applications.

One such application is a semi-transparent photovoltaics for glazing in building-integration. It is based on a luminescent solar concentrator concept, where high efficiency and a large Stokes shift are necessary requirements for nanophosphors [5-6]. In this configuration absorbed solar light is re-emitted and a large fraction of it is guided by total internal reflection to the edges for collection by standard solar cells. As a proof-of-concept we fabricated 20x20 cm^2 prototypes, where Si QD-doped polymer layer is sandwiched between glass plates in a triplex geometry. Such "solar windows" feature high transparency (>80%), low haze (<3%), high color rendering index (~ 88) and, at the same time, deliver up to 0.6 W of electrical peak power under one sun [7-8]. Another application is in bio-labeling, where long lifetime of Si QD emission (~ us) makes them sensitive to surface chemistry. It was shown previously that the presence of nitrogen moieties on nanocrystal surface may introduce a fast, ~ ns, recombination channel, which can take over carrier recombination from the QD core. Here we used this effect to monitor amino acids in the cell, where their binding of Si QDs manifested in shifted luminescence from near-infrared to blue and drastically reduced the lifetime, acting as an efficient amino acid probe in live cells [9].

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9:00 AM *EL07.03.01
Designing Hybrid Silicon Interfaces for Photon Up- and Down-Conversion Sean T. Roberts; The University of Texas at Austin, United States

Organic compounds that undergo singlet fission or its inverse process, triplet fusion, have emerged as promising materials for designing systems that efficiently convert light of one color into another by redistributing the energy of individual photons. However, to achieve these functions, these materials need to be partnered with a long wavelength light absorber. Due to its prominent role in microelectronics, photodetection, and solar energy harvesting, silicon is a natural target material to partner with organic singlet fission and triplet fusion compounds. In this presentation, I will describe work by my group done in collaboration with others to prepare heterojunctions wherein covalent bonds are used to anchor organic singlet fission and triplet fusion compounds to silicon to enable energy exchange between these materials. In particular, I will showcase recent work wherein we have achieved strong-coupling between acene molecules and silicon. This strong coupling produces excitonic states with mixed molecule:silicon character that straddle their interface and can serve as effective doorways for shuttling energy between silicon and its environment. We have used these states to prepare silicon nanocrystals that fuel photon upconversion, converting green photons to blue ones with better than 17% efficiency as well as silicon surfaces wherein spatially separated acene molecules form spatially-delocalized 2D excitonic states via intermolecular interactions that are fueled by coupling to the underlying silicon lattice.

9:30 AM EL07.03.04
EL07.03.04 Universality of Photoluminescence Lifetimes in Slowly Emitting Silicon Quantum Dots Katerina Kusova[1], Tomas Popelar[1], Pavel Galar[1], Filip Matejka[1] and Paola Ceroni[2]; [1]Czech Academy of Sciences, Czechia; [2]University of Bologna, Italy

Silicon quantum dots (SiQDs) are a class of light-emitting materials with very low inherent toxicity and broad spectral tunability. SiQDs are being developed for several decades and a wide range of synthesis techniques are available now. Generally speaking, several modes of light emission from SiQDs have been reported in the literature, covering an extremely wide range of photoluminescence lifetimes from hundreds of microseconds to ten nanoseconds. In this contribution, we focus on the "traditional", first-reported mode of light emission featuring slow (tens to hundreds of microseconds) emission tunable from the red to the near infrared spectral range, originating in the lowest excited transition of the quantum-confined states in the QD. Using our characterization of SiQD samples prepared by various techniques and a wide compilation of literature data, we observe striking similarities in the lifetimes of differently prepared samples and propose that all these fabrication techniques yield SiQDs with fundamentally similar properties. Our analysis provides us with a tool for the determination of radiative and slow non-radiative lifetimes of these samples, which is, unlike complicated measurements of internal quantum efficiency yielding the same quantity, extremely easy to apply. We also differentiate between fast and slow non-radiative pathways and discuss the importance of the radiative and both the fast and the slow non-radiative pathways in the assessment of the overall emission properties of slowly emitting SiQDs.

9:45 AM EL07.03.05
Nanograin Network Memory with Reconfigurable Percolation Paths for Synaptic Interactions Hoo-cheol Lee[1], Jungkil Kim[2], Ha-reem Kim[1], Kyung-Ho Kim[3], Kyung-Jun Park[1] and Hong-Gyu Park[1]; [1]korea University, Korea (the Republic of); [2]jeju national university, Korea (the Republic of); [3]Chungbuk National University, Korea (the Republic of)

The development of memory devices with functions that simultaneously process and store data is required for efficient computation. To achieve this, artificial synaptic devices have been proposed because they can construct hybrid networks with biological neurons and perform neuromorphic computation.

However, irreversible aging of these electrical devices causes unavoidable performance degradation. Although several photonic approaches have been suggested to control the currents, photonic suppression of current levels and switching of analog conductance remain challenging. Here, we present a nanograin network memory using reconfigurable percolation paths in a single Si nanowire consisting of solid core/porous shell segments. The unique electrical and photonic control of current percolation paths in the Si nanograin networks enabled the analog and reversible adjustment of the persistent current level, exhibiting memory behavior and current suppression in this single nanowire device. In addition, the synaptic behaviors of memory and erasure were demonstrated through potentiation and habituation processes. Notably, photonic habituation was achieved using laser illumination on the porous shell, with a linear decrease in the postsynaptic current. Furthermore, synaptic elimination was emulated using two adjacent devices interconnected on a single nanowire. Therefore, electrical and photonic reconfiguration of the conductive paths in Si nanograin networks will pave the way for next-generation nanodevice technologies.

10:00 AM BREAK

10:30 AM *EL07.03.06
Lead-Free Infrared Photodetectors with III-V and IV Materials Pan Xia, Margherita Biondi, Tong Zhu, Bin Sun and Edward H. Sargent; University of Toronto, Canada

Infrared photodetectors are vital for multi-detection applications, including cameras, security systems, and LiDAR. Low-toxicity, lead-free infrared photodetectors have significant applications in consumer electronics and industry. III-V and IV group materials stand out due to their ability to absorb visible to mid-infrared light, being heavy-metal free, and their high carrier mobility. This work introduces the investigation of III-V and IV group materials in infrared photodetectors in two aspects: 1) photophysical study of III-V group colloidal quantum dots (CQD), and the optimization of their photodetectors; 2) application of hybrid III-V and IV group materials in photodetectors.
In recent years, several synthesis and passivation approaches for typical III-V group-InAs quantum dots (QDs) have been explored. InAs CQD-based photodetectors have been reported to achieve good detectivity and fast response at room temperature [1,2]. This work reports that improvement of the surface passivation of InAs CQD enables photodetectors with low dark current and good detectivity across a spectrum of wavelengths. In addition, the hybrid of IV with III-V materials as photodetectors is being studied for better detectivity and a wider detection range.

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11:00 AM *EL07.03.07
Photoinduced Disordering and Recovery in Colloidal Silicon Nanocrystals Richard D. Schaller[1,2]; [1]Argonne National Laboratory, United States; [2]Northwestern University, United States

Low toxicity silicon nanocrystals offer potential for use in applications that range from bio-labeling to solar energy conversion and LEDs. Small particles present reduced melting points and highly active surfaces that raise possibilities of loss of crystalline structure upon excitation as phonons are generated. We probe behavior of few-nanometer colloidal silicon particles and in particular focus on how the lattice responds to controlled fluence optical excitation. Using transient X-ray diffraction using optical excitation enabled by Beamline 11-ID-D at Argonne's Advanced Photon Source, we correlate development of transient signals with number of photons absorbed to arrive at excitation densities that demonstrably disorder the initially crystalline lattices. Electronic consequences of this disordering are examined.

11:30 AM EL07.03.08
High Hole Mobility in Two-Dimensional Germanane Thin Films Yumiko Katayama, Daiki Kobayashi, Yuhsuke Yasutake, Susumu Fukatsu and Kazunori Ueno; The University of Tokyo, Japan

Germanane (GeH) is a hydrogen-terminated layered crystal of germanium and is expected to be a direct bandgap semiconductor with high electron mobility [1]. Our group reported an electric double-layer transistor on a GeH thin film with the ambipolar transport characteristics and the Hall mobilities of electrons and holes at 120 K, 6500 cm^{2}V^{-1}s^{-1}, and 570 cm^{2}V^{-1}s^{-1}, respectively [2]. However, due to the high contact resistance between electrode and GeH, the transport properties below 120 K remained unexplored. In this study, we report unexpectedly high hole mobilities of GeH thin films exceeding 67 000 cm^{2}V^{-1}s^{-1} at 15 K, which was achieved by optimizing the electrode materials and crystal growth conditions.
The GeH thin films were prepared by the topotactic transformation of epitaxial CaGe$_2$ films on a Ge (111) grown by solid-source molecular beam epitaxy (MBE) with a base pressure better than 2x10^{-8} Pa. A Ge buffer layer and a Zintl-phase CaGe$_2$ film were grown on the nominally undoped Ge (111) substrate. The GeH films were obtained by immersing the CaGe$_2$ films in concentrated aqueous HCl for 1~4 days at -18 °C, and then by rinsing in isopropanol at room temperature. Pt electrodes, in a Hall-bar configuration, were formed by sputtering through a stencil mask. The transport properties were measured on a Quantum Design physical properties measurement system.
The sheet resistance, Rs, of the GeH film showed a peak approximately at 250 K. Below 250 K, Rs decreased with decreasing temperature from ~1.5 kΩ at 250 K to ~50 Ω at 30 K, which indicates metallic conduction, whereas it showed semiconducting behaviors above 250 K. From the Hall measurement, the majority carriers were confirmed to be holes at low temperature while they were electrons at high temperatures above 250 K. Rs above 250 K was likely to be dominated by conduction through the Ge substrate and the buffer layer. At 200 K, the Hall resistance showed nonlinear dependence on the magnetic field, which can be understood in terms of two-carrier transport including the holes from the GeH film and the electrons from the Ge layer. Because the magnetic-field dependence of the Hall resistance becomes linear at low temperature, the contribution of the Ge layers can be ignored below 200 K. That the carriers are holes at low temperatures was also confirmed by the Seebeck coefficients. The hole concentration decreased with decreasing temperature from 2×10^{17} cm^{-3} at 200 K to 3×10^{16} cm^{-3} at 15 K. Meanwhile, the Hall mobility increased with decreasing temperature from 2×10^3 cm^{2}V^{-1}s^{-1} at 200 K to 6.7×10^4 cm^{2}V^{-1}s^{-1} at 15 K. At 15 K, the magnetoresistance ratio reached 6,500 % at 7 T and Shubnikov-de Haas oscillation was observed. The sheet carrier density by assuming a spherical Fermi surface was estimated to 2.8×10^{11} cm^{-2}, which is in good agreement with the Hall carrier density of 3.0×10^{11} cm^{-2} at 15 K. These results indicate the possibility of single-band conduction originating from the light-hole band in GeH.
Our results showed that two-dimensional hydrogen-terminated layered germanium prepared by topotactic reaction exhibits unprecedented high hole mobility and well-resolved Landau levels at 15 K. Further attempts at even lower temperatures would allow the first observation of the quantum Hall effect in this novel layered system.

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11:45 AM EL07.03.09
Self-Switching Diode Effect in Electrostatically Gated Silicon Nanowire Geometric Diodes Kelly White, Gordon Rogelberg, James Custer and James Cahoon; The University of North Carolina at Chapel Hill, United States

High frequency rectifying diodes are essential for microwave and terahertz detection systems, with important applications in security, healthcare, and high-speed communication. Geometric diodes are an emerging class of electrical diodes that have unique advantages as high frequency rectifiers, without a dependence on minority carriers and with simpler device fabrication using lower cost materials. They operate on the principle of ratcheting by converting a fluctuating, unbiased force into unidirectional electron motion. Silicon nanowire geometric diodes are morphologically asymmetric silicon nanostructures that function as electron ratchets at room temperature and have been shown to rectify frequencies up to 40 GHz, with a theoretical cut-off frequency above 1 THz. While these devices are considered quasi-ballistic rectifiers, their electrostatic effects, particularly at the nanowire surface, have a significant impact on diode performance and are largely unexplored. Here, we synthesize silicon nanowire geometric diodes using dopant-encoded VLS growth and dopant-selective etching and fabricate wrap-around gated single-nanowire devices to precisely control nanowire surface charge. Electrical characterization of single-nanowire devices demonstrates tunability of diode polarity, current magnitude from 1 nA to 10 µA, and DC asymmetry from 1 to 400 with gate voltage. Through finite-element modeling, we clarify the asymmetric bias-induced barrier lowering mechanism that enables electron ratcheting in these gated nanostructures and is indicative of self-switching diode devices. Notably, we observe this same mechanism and similar current and DC asymmetry results in simulations of ungated silicon nanowire geometric diode devices with sufficiently large trap densities at the nanowire surface. When we consider the surface trap states, the resulting surface charge acts like a wrap-around gate with a fixed voltage. These results demonstrate the creation of a novel silicon nanowire-based self-switching diode and the possibility for simplifying fabrication through surface modification to tune nanowire surface trap density.

SESSION EL07.04: Modelling
Session Chairs: Uwe Kortshagen and MingLee Tang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3007

2:00 PM *EL07.04.03
Strong Coupling Physics and Nanoscale Photoreactivity Joel D. Eaves[1,2], R. P. Cline[1,2,3], Sean T. Roberts[4], Lorenzo Mangolini[5] and Ming Lee Tang[6]; [1]University of Colorado, United States; [2]University of Colorado Boulder, United States; [3]National Renewable Energy Laboratory, United States; [4]The University of Texas at Austin, United States; [5]University of California, Riverside, United States; [6]The University of Utah, United States

Recently, experimentalists have built new interfaces consisting of organic molecules covalently bound to inorganic solids. Covalent bonding between the molecule and the solid allows for stronger and more tunable electronic coupling between the localized electronic states, typical of the molecule, and the delocalized states of the solid. These systems can exhibit much stronger coupling than is typical in either the molecule or solid alone, and that coupling can be controlled using simple linking chemistries. In this talk, I will discuss how strong electronic coupling allows one to tune the onset of the absorption maximum and how coherences between molecules at the surface, mediated by strongly coupled bulk electronic states, can influence photoreactivity. Preliminary results suggest that these strong coupling physics might be a vital step in the development of new multielectron redox catalysts.

2:30 PM BREAK

3:00 PM EL07.04.04
Theory of Optically Detected Magnetic Resonance of a Silicon Vacancy in SiC Nanoparticles—A Quantum Sensor of Magnetic Fields David Fehr and Michael Flatté; University of Iowa, United States

Magnetometers are used in virtually every aspect of our lives: from navigation, the detection of submarines and underwater debris, archaeological and geological surveys, to our mobile phones and in the exploration of our solar system [1-2]. Recently, solid-state magnetometers have stimulated particular interest due to their smaller size, weight, and power (SWaP) compared to existing magnetometers [3], and their potential to self-calibrate [4]; two attractive features which improve the efficiency of any device carrying a magnetometer, especially spacecraft. However, extensive research must be completed to optimize this new technology for widespread commercial use, and a detailed theory is the first step in this process.

Silicon Carbide nanoparticles containing defects with optically addressable spin states are available in a variety of sizes and crystal structures [5-8]. This creates the perfect playground for optimizing the spin-photon interaction for the purpose of quantum sensing of magnetic fields. In this work we model optically detected magnetic resonance (ODMR) of the silicon vacancy (V_{Si}) in silicon carbide,
a budding candidate for solid-state quantum magnetometry, using Lindblad master equations. The silicon vacancy can be thought of as a $S = 3/2$ synthetic atom, and its spin states are sensitive to magnetic fields via the Zeeman effect. In ODMR, magnetic resonances of the Zeeman field are detected by extrema in the normalized photoluminescence signal when a transverse microwave field is applied. The photoluminescence is calculated from the steady-state density matrix populations and compared to recent experimental results [9-11].

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3:15 PM EL07.04.05
Cross-Correlated Quantum Thermometry Using Diamond Containing Dual-Defect Centers Madhav Gupta, Tongtong Zhang and Zhiqin Chu; The University of Hong Kong, Hong Kong

The contactless temperature measurement at micro/nanoscale is vital to a broad range of fields in modern science and technology. The nitrogen vacancy (NV) center, a kind of diamond defect with unique spin-dependent photoluminescence, has been recognized as one of the most promising nanothermometers. However, this quantum thermometry technique has been prone to a number of possible perturbations, which will unavoidably degrade its actual temperature sensitivity. Here, for the first time, we have developed a cross-validated optical thermometry method using diamond containing both NV centers and Silicon Vacancy (SiV) centers. Particularly, the latter has been intrinsically immune to those influencing perturbations for the spin-based approach, hence serving as a real-time self-calibration system. As a proof-of-the-concept demonstration, we have shown a trustworthy temperature measurement under the influence of the randomly changing magnetic fields. This multi-modality approach allows a synchronized cross-validation of the measured temperature, which will be meaningful for micro/nano scale measurements in complicated biosensing environments such as inside a living cell. Additionally, we propose to build on our previously developed method[1] of using high quality salt-assisted air-oxidized (SAAO) nanodiamonds (NDs)[2] as CVD seeds to grow diamond particles, for synthesizing nanodiamond crystals having a co-existence of NV and SiV defect centers. This will provide a high performance all-optical thermometer as an independent temperature validation/self-calibration mechanism with nanoscale spatial resolution. This has a wide variety of practical applications requiring high spatial resolution, such as performing quantum thermometry in living cells.

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3:30 PM EL07.04.06
Understanding Stability in Ge-Sn Surfaces and Nanoparticles with First-Principles Calculations Katelyn P. Nelson, Mattea Miller, Deep M. Patel and Luke T. Roling; Iowa State University, United States

Group IV semiconductors have demonstrated promise as candidates for next-generation low-temperature optical computing and communications technologies due to their promising optoelectronic properties. In particular, the bandgap of Ge can be tuned and made direct through the incorporation of Sn, motivating the study of Ge(Si)Sn nanomaterials and surfaces. However, the development of practical devices utilizing these elements is limited by the incorporation of Sn in high quality and uniform synthesizable materials. In this presentation, we will share our recent computational insights into fundamental properties governing the stability of Sn in Ge surfaces and nanoparticles.

Using density functional theory (DFT) calculations, we show that the stability of GeSn systems changes non-monotonically with Sn content. The incorporation of Sn depends strongly on morphology, considering both {111} and {100} crystal orientations; structure, considering extended surfaces and nanoparticle models of varying sizes; surface termination, considering a range of terminating species including H, halogens, and alkyl groups; and atomic-scale arrangements of Sn and Ge atoms. Our calculations predict improved Sn incorporation in {100}-terminated nanocrystals compared to {111}-terminated structures, enabled by the increased geometric freedom imparted to the larger Sn atoms at the more open {100} surfaces. The nature of the surface termination strongly influences atomic arrangements at the surface, with stronger-binding species (e.g., -Cl) exhibiting significantly different stabilization of Ge and Sn and thereby affecting the preferred segregation of components within surfaces and nanoparticles. Our results also suggest that the relative stability of nanoparticles depends on the nanoparticle size, though the nature of the size effects depend on surface termination (species and geometry). We finally show the effects of applied strain on the stability of Sn in surfaces, including in the presence of adsorbates. These fundamental insights suggest possible routes toward the synthesis of GeSn materials with tunable and high Sn content.

SESSION EL07.05: Poster Session
Session Chairs: Lorenzo Mangolini and MingLee Tang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL07.05.01
Surface Termination of Plasma Synthesized Silicon Nanocrystals using Plasma-Activated Liquids Filip Matejka[1,2], Pavel Galar[1,2], Josef Khun[2] and Katerina Kusova[1]; [1]Czech Academy of Sciences, Czechia; [2]University of Chemistry and Technology, Czechia

In the last decades, nanoparticles of a broad variety of materials, mainly semiconductors, made a breakthrough impact on science and industrial development. The main glamor of nanostructured materials is due to the alteration of their original bulk properties. Nano-scaled materials report a higher surface-to-volume ratio, leading to a crucial impact on the surface effects. Moreover, with sizes less than a dozen of nanometres, the quantum confinement of the wavefunctions is manifested. In the case silicon in the form of nanocrystals (SiNCs), these effects lead to the lighting up of the normally dull bulk material. The relatively high light emission efficiency of SiNCs is accompanied by wide spectral tunability from visible to near-infrared (IR)spectral regions. The peak emission and intensity of photoluminescence (PL) is dependent on the size, defects, and surface termination. However, the limitations of further applications of the SiNCs are their methods of synthesis and methods of surface termination. So far, especially the existing termination methods are low yield, expensive, complex, and not environmentally friendly.

In this work, we apply non-thermal plasma (NTP) for both the synthesis and the subsequent surface modification. In the case of the synthesis, the NTP low-pressure method generates SiNCs with a highly reactive hydrogen-terminated surface; due to the synthesis from silane gas, with a low number of defects, leading to initial high PL intensity. Additionally, the mean size of the NCs and therefore their PL peak emission is finely tuneable from 700 nm to 950 nm. The yield of this method is high, in micrograms per minute.

The reactive hydrogen surface can be modified by several methods. The most common method for carbon termination creating C:SiNCs is hydrosilylation, which is costly on time, (reaction time up to 12 hours) and on energy, due to the long reaction time and high boiling points of organic liquids. Hence, we introduce an innovative approach of the NTP treatment of liquids, the so-called plasma activation (PAL). The NTP treatment provides a gentle interaction with the liquid, using reactive species generated by the discharge from the surrounding atmosphere (can be applied in air, or in a closed-space inert atmosphere), using by two needle electrodes. The reactive species then react with the molecules of the liquid, creating a reactive environment for the SiNCs with enough energy to exchange the surface bonds. In our study, we focused on organic liquids (PAOL), whose molecules report dipoles, leading to a better interaction of the discharge with the liquid phase (e.g., Ethanol, Acetic Acid, Octanol, etc.). For the PAOL treatment, the closed chamber reactor constantly flushed with Ar was designed to prevent the the interaction with humid air, suppress flammability, and establish stable discharge conditions. Despite that, the overall PAOL process can be done in less than an hour of reaction time. The PAOL treatment produced a stable (for more than 72 days) enhancement of the quantum yield (QY) and PL properties (intensity increment more than 25 times and slight blue-shift) and better dispersibility (proven by DLS measurements). The surface bonding was studied by IR spectroscopy and PL measurements.

An analogical PAL treatment can be also applied to inorganic liquids. In our recent work, we showed that plasma activated water (PAW) can successfully enrich the surface termination of SiNCs with nitrogen-based species. In this on-air process, the creation of the intermediary phase above water is needed, therefore the settings of the shape of the reactor, volume of water, and discharge are crucial to generate PAW without hydrogen peroxide, which kills the SiNCs PL, simultaneously exhibiting a high concentration of nitrogen species. This treatment leads to stable enhancement of QY (up to 10 times) and water dispersibility of SiNCs, making them more attractive for further applications.

5:00 PM EL07.05.02

Improving the Dispersion of Silicon/Silicon Dioxide Quantum Dots Adriana Chapa[1,2], Kristine Q. Loh[1], Vivian Ferry[1] and Uwe Kortshagen[1]; [1]University of Minnesota, United States; [2]The University of Texas Rio Grande Valley, United States

Through the years there has been a growing need for renewable energy sources. Luminescent Solar Concentrators (LSCs) are semitransparent devices that generate renewable electricity. LSCs are composed of a transparent polymer waveguide with embedded luminescent nanocrystals. Silicon Quantum Dots (Si QDs) are semiconductor nanocrystals that broadly absorb UV light and photoluminese near-infrared light. Si QDs are suitable for LSC applications as they are nontoxic and made from an abundant element.

This work focuses on developing a method to disperse core/shell Si/SiO2 QDs in a solvent. Various aspects of the dispersion were studied by experimenting with different ligands, pH levels, and solvents. We tested two different ligands, (3-Glycidyloxypropyl) trimethoxy silane (GPTMS) and polyethylene glycol, two different pH level additives, ammonium hydroxide (NH4OH) and hydrochloric acid, and different solvents including ethanol, H2O, and toluene.

The dispersions were characterized using Fourier transform infrared (FTIR), UV-Visible, and photoluminescence (PL) spectroscopies. First, the ligands GPTMS and polyethylene glycol (PEG)-silane were tested. The solution contained 100 µL of HCl, 1.5 mL of ethanol and 0.3 mL of H2O. The dispersion of the Si/SiO2 with GPTMS and HCl settled faster than the Si/SiO2 with PEG-silane and HCl dispersion. Using UV-Vis, the Si/SiO2 with GPTMS absorbance is higher than the absorbance of the Si/SiO2 with PEG-silane due to scattering from the larger agglomerates that settled. The samples in HCl were more stable than ones using ammonium hydroxide. FTIR measurements confirmed that the Si/SiO2 QDs were coated with PEG-Silane.

Lastly the dispersions were characterized using photoluminescence spectroscopy. The Si/SiO2 QDs in toluene and Si/SiO2 QDs in PEG-silane show that the solutions can have similar photoluminescence intensities even though the toluene dispersion sample agglomerates. Si/SiO2 QDs in H2O agglomerate faster relative to the QDs in ethanol. In conclusion, using PEG-silane as a ligand in an acidic environment with a polar solvent led to a stable, homogeneous mixture with a high photoluminescence intensity.

5:00 PM EL07.05.03

Fast Photoluminescence and Energy Transfer in Silicon Quantum Dots Tomas Popelar[1], Katerina Kusova[1] and Paola Ceroni[2]; [1]FZU - Institute of Physics of the Czech Academy of Sciences, Czechia; [2]Università di Bologna, Italy

Si nanocrystals (SiNC) can be relatively efficient light emitters despite their indirect bandgap. Their attributes (e. g. light-emission efficiency) depend heavily on surface passivation. Various schemes were exploited over the years, however, the functionalization with diphenylanthracene (DPA) is quite new in the SiNC field. To investigate the role of DPA we compared the samples with DPA covalently attached to SiNCs (SiDPA), samples passivated with dodecane (SiDDE) and also the mix of SiDDE with various concentrations of DPA. This enabled us to properly characterize the energy transfer between the DPA molecules and SiNCs.

Apart from the classical methods of optical spectroscopy like absorption and time-resolved photoluminescence (PL) measurements, we also used the seldom utilized two-photon excitation to investigate the energy transitions in our samples in detail. This excitation theme interacts with the samples differently compared to the common one-photon excitation due to the different absorption coefficients of two-photon absorption. The samples exhibit typical two-part PL consisting of the fast (ns) blue band and slow (us) red band. By using the two-photon excitation, we observed the enhanced red PL compared to the blue PL and also completely different dynamics even in the case where the same energy transition was excited, i.e. the two-photon excitation scheme used the twice as long wavelength compared to the one-photon excitation. These new effects were observed even in the "classical" SiDDE sample showing that there are still issues to be resolved, particularly in the blue band area. Our usage of a femtosecond laser and optical parametric amplifier (output pulses with wavelengths between 315 - 2000 nm and time-length 150 fs) with streak camera with ps time-resolution for detection enabled us to analyze the individual decay channels and determine the "transition energy" connected to the switching PL dynamics among other effects.

5:00 PM EL07.05.04

Study of Ignition Condition of Non-Thermal Plasma Synthesized Silicon Nanoparticles Jakub Kopenec[1,2], Pavel Galar[1,2], Katerina Kusova[1] and Martin Muller[1]; [1]Institute of Physics the Czech Academy of Sciences, Czechia; [2]University of Chemistry and Technology Prague, Czechia

Silicon (Si) proved to be one of the essential elements of current electronics, energetics and of many other technological fields. When in the form of a nanostructure, e. g. as silicon nanoparticles (SiNPs) Si properties are altered by a complex synergy between quantum effects and an influence of high surface to volume ratio. In comparison with bulk Si, SiNPs show high surface reactivity, mechanical resistance and, despite being an indirect semiconductor, also effective light emission. The combination of Si original and nano-gained properties is beneficial for many optoelectronic, electronic, or biological applications. In addition to these applications, in Li-Ion technology is of special interest here, because silicon possesses the highest theoretical gravimetric (specific) capacity of all elements and in the form of a nanostructure, it is able to withstand extreme volume changes during the lithiation and delithiation proces.

In this study, we demonstrate the potential of SiNCs being used as an energy-storage material. One of the most perspective ways of high-gain synthesis of SiNPs is the utilization of non-thermal plasma. However, at specific synthesis conditions, the plasma-prepared SiNPs (nanoparticles in general) can be highly flammable. They can be ignited even by a weak laser with light intensity of units of mW/mm^2 or by temperatures above approximately 90°C. The origin of this effect is based on the presence of hydrogen in the synthesis chamber and its following efficient integration onto the SiNPs surface. Thus, after synthesis, SiNPs store significant amounts of energy (up to 7000 cal/g), which they release after being ignited. We observed a significant dependence of the ignition conditions on the crystallinity and size of SiNPs and also on the amount of additional hydrogen in the synthesis chamber. Infrared spectroscopy proved that it is the type of the bond ($Si\text{-}H$, $Si\text{-}H_2$, $Si\text{-}H_3$) that plays an important role in the stability/flammability of SiNPs. In particular, SiNPs containing SiH_3 structures on its surface were easier ignited in contrast to the ones containing SiH which were highly stable. The microscopic interpretation of this effect is presented. These findings are potentially important not only for applications in explosives, but they also point towards the possibility of using SiNPs as a hydrogen/energy-storing material.

5:00 PM EL07.05.05

Millimeter Wave to Terahertz Sub-5nm Nonlinear Optoelectronic CMOS Technolog—Performance Advantages Over Traditional CMOS-Based ASICs, SoC and Silicon Photonics James Pan; AELC, United States

Negative resistance millimeter wave semiconductor devices (including Tunnel, Gunn, IMPATT and, BARITT diodes) can generate high frequency microwave signals approaching the terahertz infrared regime for commercial telecommunications and military applications. These devices can be included in the drain or source regions of a MOSFET as one integral device to form Millimeter Wave to Terahertz Optoelectronic CMOS Transistors. Here, we will discuss the performance advantages of this novel technology: how it may even outperform traditional CMOS-Based RF ASICs, System on Chip (SoC), or Silicon Photonics due to reduced series resistance and capacitance. Critical RF parameters, such as cutoff frequency (ft and fmax), are improved due to the switching speed improvements from the photonic and millimeter wave generation process. The integrated device produces less heat and can be thermally more stable. Also, photonic millimeter-wave devices can be designed to handle pulsed laser and millimeter-wave signals simultaneously. Low operating voltages are possible due to the nature of the tunneling process and the close proximity of the components in the integrated device. We also show a path toward monolithic integration in a CMOS fabrication sequence. IMPATT and BARITT are reverse-biased diodes. Laser and LED are forward-biased diodes. The source or drain junction of a MOSFET is a reverse-biased diode. Photon and microwave generating diodes can be included in the drain or source regions of a MOSFET. Photon sensors can be fabricated in the substrate, well or drain regions. Millimeter wave diodes, laser or LED, Photon Sensors, and MOSFET are fabricated as one integral device to form the Millimeter-wave Photonic CMOS Transistors. A millimeter wave tunnel diode can be operated at a very low voltage, due to the tunneling process without thermal diffusion. Photonic Microwave CMOS functions with electric fields (it is a field effective device) compared with diode lasers, which rely on thermal diffusion and produce more thermal noises. With improved device models and circuit designs, nonlinear laser and millimeter wave communications can be a reality. The manufacturing costs for 3D All-Around-Gate FETs and Sub-5nm FINFETs can be very high.

The Milliwave Optoelectronic CMOS is 100% compatible to sub-5nm CMOS technology nodes, as the Laser, LED, and Microwave diodes are in the MOSFET or FINFET drain region - the gate and channel regions are not affected. The manufacturing cost for sub-5nm Millimeter Wave Optoelectronic CMOS is much lower, and the performance can be much higher.

Terahertz operations can be achieved using the Millimeter Wave Optoelectronic CMOS, with Microwave Diodes and Mid- or Far- Infrared QCL (Quantum Cascade Laser) in the CMOS drain regions.

The Transferred Electron Tunnel Millimeter Wave and Gunn Diodes present unique "Negative Resistance" characteristics under a certain bias conditions and internal electric fields, which may reduce the Rsd (series resistance), ft / fmax (cutoff frequency) and are suitable for high clock-speed operations.

In this report we will discuss the performance advantages and cost benefits of the technology. We will also look into various Microwave diodes, how they can be added to the sub-5nm CMOS, and what are the operating conditions, as one integral transistor.

5:00 PM EL07.05.06

Local Bandgap Measurement of Core/Shell Ge/GeSn Nanowires Employing Electron Energy Loss Spectroscopy in Scanning Transmission Electron Microscopy Milenka Andelic[1], Alexandre Pofelski[1], Sebastian Koelling[2], Simone Assali[2], Lu Luo[2], Oussama Moutanabbir[2] and Gianluigi Botton[1]; [1]McMaster University, Canada; [2]Polytechnique Montréal, Canada

Group IV $Ge_{1-x}Sn_x$ alloyed semiconductors have attracted a lot of attention because of their numerous applications in the field of monolithically integrated optoelectronic and photonic devices compatible for use on the Si platforms. Such applications include free-space data communications, night-vision sensors, biosensors, and materials for thermal imaging, which dominate in the short-wave infrared (SWIR: 1.5-3 um) and mid-wave infrared (MWIR: 3-8 um) and long-wave infrared (LWIR: 8-14 um) wavelength ranges [1], [2].

Core/shell Ge/GeSn structured nanowires (NWs) exhibit high tunability of electronic properties by varying two parameters, Sn content and lattice strain. Furthermore, these free-standing core/shell Ge/GeSn NWs grown on Si wafers tend to accommodate more elastic strain which is relaxed at the sidewall facets of the wires. In this research, a GeSn shell has been grown around the colloidal-nucleated Ge core using the chemical vapour deposition (CVD) technique. The variation in Sn content incorporated in GeSn alloy strongly affects the electronic bandgap energy and optical transitions, such as the plasmonic oscillations and interband transitions. By increasing the Sn content in the $Ge_{1-x}Sn_x$ shell, the bandgap is expected to experience a transition from indirect to direct bandgap, progressively narrowing down. For high enough Sn concentration, the electronic structure would eventually exhibit an effective negative bandgap, essentially an indirect semimetal behaviour [3].

Here we investigate the behaviour of electronic band structure and bandgap energy demonstrating the potential of high-resolution electron energy loss spectroscopy (EELS) in a monochromated scanning transmission electron microscope (STEM). Spatial locality is essential in the bandgap measurement of these NWs as EELS can provide a wealth of information on various features in the low-energy range, showing the effect of localized defect states that may be present in the bandgap energy onset. Other transitions, such as collective plasmon oscillations and single-electron transitions that depend upon the position of electronic levels within the band structure, are observed and will be discussed. [4]

References:
[1] Moutanabbir, O., Assali, S., Gong, X., O'Reilly, E., Broderick, C. A., Marzban, B., ... & Nam, D. (2021). Monolithic infrared silicon photonics: the rise of (Si) GeSn semiconductors. *Applied Physics Letters*, *118*(11), 110502
[2] Luo, L., Assali, S., Atalla, M. R., Koelling, S., Attiaoui, A., Daligou, G., ... & Moutanabbir, O. (2022). Extended-SWIR Photodetection in All-Group IV Core/Shell Nanowires. *ACS Photonics*, *9*(3), 914-921.
[3] Assali, S., et al. "Growth and optical properties of direct band gap Ge/Ge0. 87Sn0. 13 core/shell nanowire arrays." Nano letters 17.3 (2017): 1538-1544.
[4] Acknowledgment: This work was carried out at the Canadian Centre for Electron Microscopy, a national facility supported by the Canada Foundation for Innovation under the MSI program, McMaster University, Defence Canada (Innovation for Defence Excellence and Security, IDEaS), and NSERC.

SESSION EL07.06: Synthesis and Functionalization II
Session Chairs: Lorenzo Mangolini and Pan Xia
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3007

8:30 AM *EL07.06.01
Microwave-Assisted Solution Synthesized Germanium Nanocrystals Susan M. Kauzlarich; University of California, Davis, United States

Ge is one of the quintessential semiconductors being considered in nanoform for optoelectronic applications. Ge alloys have been shown to have potential for energy storage as a Li ion battery anode and energy conversion as a catalyst. Ge has several advantages over Si or SiGe alloys including superior charge carrier mobilities, low dopant activation temperatures, and a smaller band gap. We have recently employed a two-step microwave-assisted reduction of GeI_4 in oleylamine to prepare monodispersed Ge NCs from 10 -20 nm in diameter. The as-synthesized Ge NCs showed high crystallinity with single crystal nature as indicated by powder X-ray diffraction, selected area electron diffraction, and high-resolution transmission electron microscopy. Solutions involved in this two-step reaction were investigated with ^{1}H NMR spectroscopy and high-resolution mass spectrometry to better understand the reaction pathway. I will present new insights gained from this chemical route that may impact the nanoparticle synthesis of other covalently bonding semiconductors.

9:00 AM *EL07.06.02
Functional Silicon Nanoparticles with Sizes Ranging from Single Nanometers to Sub-Micrometers Hiroshi Sugimoto; Kobe University, Japan

Si forms not only the backbone of microelectronics technology but also gains in significance for photonics when its size is down to nanoscale. Depending on its size (1-1000 nm), Si nanostructures exhibit different optical responses. In this presentation, we show the optical properties of Si nanoparticles with two different size regimes. For sub-10 nm in size, so-called quantum dots (QDs), the quantum confinement effect enables the efficient photoluminescence (PL) and facilitate the applications as light emitters. The properties can be also controlled by doping impurities. Here we present a comprehensive study on colloidal Si QDs codoped with boron (B) and phosphorus (P).[1,2] We show the detailed structural and optical characterization and demonstrate that the codopants modify the electronic structures of Si QDs and introduce donor and acceptor levels in the band gap of Si QDs. This enables the optical transition with the energy below bulk Si bandgap (~1.1 eV). We will demonstrate the potential applications of codoped Si QDs in photonics and biomedical fields. The second part of the presentation focuses on Si nanoparticles with 100-250 nm in diameter that exhibit electric and magnetic Mie resonance in the visible to near-IR range due to the high refractive index of Si, which can be utilized as optically resonant antennas. We develop monodispersed Si nanoparticles in solution and show the structural colors by size-dependent Mie resonances. We also discuss optical functionalities and Mie-resonance-enhanced light matter interactions in different materials such as emitting lanthanoid ions and two-dimensional materials.
[1] Nano Lett., 16, 2615 (2016). [2] Nano Lett., 18, 7282 (2018). [3] Adv. Opt. Mater., 8, 2000033 (2020). [4] Nano Letters, 20, 7737 (2020). [5] ACS Photon., 8, 1794 (2021). [6] ACS Photon., 9, 1741 (2022).

9:30 AM EL07.06.03
Tunable, High Intensity Photoluminescence from Si/SiO_2 Core/Shell Quantum Dots *via* High-Pressure Water Vapor Annealing Kristine Q. Loh, Vivian Ferry and Uwe Kortshagen; University of Minnesota, United States

As non-toxic, abundant, and low-cost luminophores, silicon quantum dots (Si QDs) can suit myriad applications, from luminescent devices to biological imaging. Nonthermal plasma-assisted decomposition of silane gas is an efficient, sustainable, and controllable method for synthesizing Si QDs. However, as-synthesized, Si QDs have a high dangling bond defect density and require additional passivation for widespread utilization. Liquid-based passivation methods, such as thermal hydrosilylation, can organically cap Si QDs but cannot prevent oxidation upon exposure to ambient air. Native oxidation can passivate the Si QDs through the formation of a silica (SiO_2) shell and ensure long-term air stability but occurs over at least one month. Therefore, we use high-pressure water vapor annealing (HWA) to quickly obtain Si/SiO_2 core/shell quantum dots with tunable, high-intensity photoluminescence (PL) that results in long PL lifetimes and comparable PL quantum yields (PLQY).

HWA is a scalable method that was used to oxidize plasma-synthesized Si QDs with high-pressure steam within a few hours, including heating and cooling time. A high-pressure vessel with both pressure and temperature gauges was loaded with the Si QDs and a controlled amount of deionized water that tuned the pressure of the saturated steam. The vessel was heated between 250 and 300 °C using a thermal sand bath. After ten minutes at its equilibrated pressure, the vessel was vented to atmospheric levels. The vessel was then left to cool to room temperature. The dry Si/SiO_2 QDs were extracted and dispersed in toluene for characterization.

We first show the influence of additional hydrogen gas injection in synthesizing the Si QDs and demonstrate that contrary to previous reports, no additional gas injection in the plasma afterglow led to more stable silica shells. In varying the hydrogen gas flow rate from 0 to 100 sccm, the more hydrogen gas injection, the lower the intensity of the more thermally stable, network-structure silica peak in the measured Fourier-transform infrared (FTIR) spectra. The Si QDs synthesized without hydrogen gas had the highest PL intensity as well.

Then, we show that varying the applied pressure to oxidize Si QDs made using only argon and silane gas can tune the PLQY. We measure both steady-state and time-resolved PL (TRPL) to find that increasing the pressure from seven to 17 bar leads to blue-shifted PL and a 10% reduction in the PLQY. A stretched exponential function was used to fit the TRPL decay and extract lifetimes and dispersion factors. The lifetime also decreases with increasing pressure by 70 µs, but the dispersion factor increases from 0.81 to 0.87. When higher pressures are applied, the silica shells are also fully thermally relaxed. FTIR spectra show the presence of characteristic peaks for Si QDs oxidized in a humid environment. Furthermore, with increasing applied pressure, the peak wavenumber of the Si-O-Si bond increases as well. At an applied pressure of 17 bar, the peak wavenumber reaches 1080 cm^{-1}, which exceeds that of thermally grown silica.

Lastly, we report the influence of silica shell thickness. Thicker shells made using larger Si QDs oxidized with optimized HWA conditions led to a stable PLQY of over 40%. After three months of storage in room air, the PLQY plateaued at 35%. Si/SiO_2 QDs with thicker silica shells also had longer lifetimes (240 µs) and higher dispersion factors (0.85 – 0.9). Compared to other passivation methods, HWA can effectively passivate Si QDs within a much shorter time span and only using water. Using HWA, the PL of Si/SiO_2 QDs can be tuned to meet various design requirements by controlling the applied pressure.

9:45 AM EL07.06.04
Group IV Nanosheets with Surface and Composition Tunable Optical Properties Matthew G. Panthani; Iowa State University, United States

We present our recent efforts in synthesizing 2D Group IV nanosheets derived from layered Zintl phases. This presentation will focus on synthesis of layered/2D silicon (often referred to as silicane, siloxene, or layered polysilanes), as well as other 2D Group IV (comprised of Ge, and Si_XGe_{1-X})[1,2] nanosheets, with precise control over their size and surface chemistry. Using NMR, IR spectroscopy, and atomic pair distribution function analysis we gain insight in their local coordination and long-range order. The optical properties of the nanosheets are sensitive to the structure and interfacial chemistry, which we explain using DFT simulations of electronic band structures. Using ultrafast spectroscopy, we find evidence of a "fast" (few ns) optical transition in 2D Si nanosheets, with a temperature dependence may imply that we observve direct bandgap photoluminescence. Finally, we show the thermal stability of 2D silicon nanosheets, demonstrating their structure and photoluminescence are stable to temperatures beyond what they would experience in real applications.

References
[1] Ryan et al, "Silicene, siloxene, or silicane? Revealing the structure and optical properties of silicon nanosheets derived from calcium disilicide." (2020) *Chemistry of Materials* 32(2), 795-804.
[2] Ryan, Roling, Panthani. "Anisotropic Disorder and Thermal Stability of Silicane."(2021) *ACS Nano* 15(9),14557-14569.

10:00 AM BREAK

10:30 AM *EL07.06.05
Functionalized Silicon Nanoparticles—Gram-scale Synthesis and Optical Properties Han Zuilhof; Wageningen University, Netherlands

Silicon nanoparticles (Si NPs) are highly attractive materials for typical quantum dots functions, such as in light-emitting and bioimaging applications, owing to silicon's intrinsic merits of minimal toxicity, low cost, high abundance, and easy and highly stable functionalization. Especially non-oxidized Si NPs with a covalently bound coating serve well in these respects, given the minimization of surface defects upon hydrosilylation of H-terminated Si NPs. However, to date, methods to obtain such H-terminated Si NPs is still not easy. Herein, we report a new synthetic method to produce size-tunable robust, highly crystalline H-terminated Si NPs (4 – 9 nm) using microwave irradiation within 5 min at temperatures between 25 – 200 degrees C, and their further covalent functionalization. The key step to obtain highly fluorescent (quantum yield of 7 – 16%) green-red Si NPs in one simple step is the reduction of triethoxysilane and (+)-sodium L-ascorbate, yielding routinely ~1 g H-Si NPs via a highly scalable route in 5-15 min. Subsequent functionalization via hydrosilylation yielded Si NPs with an emission quantum yield of 12-14%. This approach can be used to easily produce high-quality H-Si NPs in gram-scale quantities, which brings the application of functionalized Si NPs significantly closer.

11:00 AM EL07.06.06
Si-Ge-Sn Alloys Grown by CVD for Applications in Optics, Electronics and Thermoelectrics Omar Concepción Díaz, Prateek Kaul, Oliver Krause, Jin-Hee Bae, Thorsten Brazda, Andreas Tiedemann, Qing-Tai Zhao, Detlev Grützmacher and Dan M. Buca; Forschungszentrum Juelich, Germany

The experimental demonstration of an Sn-based optically pumped laser grown on Silicon by chemical vapor deposition (CVD)[1], the research of group-IV Sn-based semiconductors has exponentially increased. Direct bandgap GeSn alloys offers a unique solution for monolithic integration of photonics in the current CMOS technology. The impediment in reaching room temperature electrically pumped laser based on SiGeSn/GeSn alloys is the low capacity of dissipation of heat[2], reason why new designs are investigated to date. At the same time, the poor heat dissipation has aroused the interest of the scientific community in the field of thermoelectric. Studies have shown that group-IV Sn-based materials can be tailored to offer very low thermal conductivity[3]. In the field of electronics, the high mobility associated with the direct bandgap of Si-Ge-Sn alloys boosts the present field-effect transistor (FET) devices' performance[4].

The content of Sn in the alloy is directly defining the material properties and through this the specific application. While Sn contents above 14 at.% are best used in photonics and thermoelectric, lower Sn contents, <10 at.%, are sufficient to improve nanowire FET devices. However, due to the low solid solubility of Sn of below 1% and the large lattice mismatch between the lattice constants of these elements, such high Sn concentrations are a challenge[6]. Its application to the design of layered heterostructures with multiple Sn contents is even more challenging considering also the low thermal stability of Sn alloys.

In this work, a simple and novel methodology to control the incorporation of Sn in the alloy is discussed. Starting for a reference growth conditions that offer high crystalline quality, keeping the process temperature and the reactor pressure constant, as well as the flow of the gas precursors, the total flow of the carrier gas (N_2 or H_2) is varied. In this way, the gas velocity and the partial pressure of the precursors changes, thus gas phase reactions are modified with impact on the surface kinetics allowing to control the Sn concentration in the films, offering a simple path towards high-quality GeSn/SiGeSn heterostructures. The method is applied for a precise control of the Sn concentration in different heterostructures. Examples of structures used for applications in electronics (MOSFETs,), photonics (Lasers), and thermoelectric (lattice thermal conductivity) are presented and discussed.

11:15 AM EL07.06.07
Near-Field Ultrafast Nanoscopy of Carrier Dynamics in Semiconductor Nanowires Jingang Li, Rundi Yang and Costas Grigoropoulos; University of California, Berkeley, United States

Carrier distribution and dynamics in semiconductor materials often govern their physical properties that are critical to functionalities and performance in industrial applications. Many techniques have been developed to resolve the charge transport and carrier dynamics in semiconductor nanostructures for the design of future electronic and photonic devices. Conventional pump-probe microscopy has limited spatial resolution due to optical diffraction. Recently, ultrafast infrared-terahertz nano-spectroscopy was developed through the integration of scanning near-field optical microscopy and pump-probe optics. However, given the limited photon energy, the efforts have been primarily focused on studying carrier dynamics in narrow bandgap semiconductors or graphene plasmons.
Here, we report near-field ultrafast optical nanoscopy in the visible-near-infrared spectral region to access the carrier dynamics in silicon, one of the most prevalent materials in current semiconductor technology. Our pump beam has a wavelength of 400 nm (3.1 eV), which is sufficient to excite carriers in common optoelectronic semiconductors, including silicon (bandgap of 1.12 eV) and GaAs (bandgap of 1.42 eV). By combining ultrafast nanoscale measurements and theoretical modeling, we unravel the local photocarrier recombination dynamics in silicon nanowires. Moreover, we demonstrate the spatial mapping of carrier lifetime in silicon with a sub-50 nm resolution. Our results provide the capability to probe carrier behaviors in nanoscale materials and devices, which is of great significance to understanding the optoelectronic properties and practical functionality of semiconductor nanostructures.

SESSION EL07.07: Virtual Session
Session Chairs: Lorenzo Mangolini and MingLee Tang
Wednesday Morning, April 26, 2023
EL07-virtual

10:30 AM *EL07.07.01
Silicon Photocatalysts for Solar-Driven Hydrogen Production Isabel Curtis, Sarrah Putwa and Mita Dasog; Dalhousie University, Canada

Hydrogen is an important feedstock for various chemical processes and a promising green energy source. Sustainable and affordable production of hydrogen is extremely important for extensive commercialization of fuel cells and to reduce our reliance on steam-methane reforming which has a high carbon footprint. Technoeconomic analyses have shown that solar driven water-splitting using suspended particulate photocatalyst is a simple and cost-effective way to produce hydrogen. Nanoscale Si is an attractive photocatalyst for this process given its abundance, biocompatibility, favorable conduction band edge position for water reduction, and their solar light absorption properties. High surface area Si nanoparticles can be prepared using magnesiothermic reduction reaction. In the last five years, our research group has identified that the magnesiothermic reduction reaction parameters strongly influence the physical properties of the resulting Si particles and their catalytic performance. This presentation will summarize which Si properties are important for photocatalysis and how the reaction conditions can be chosen to maximize the hydrogen evolution rates under solar illumination. Further, the influence of photocatalysis setup and its effect on hydrogen production rates will also be discussed.

11:00 AM EL07.07.02
Colloidal Synthesis, Energy Gap Tuning and Carrier Dynamics of Ge-Si-Sn Nanoalloys with Visible to Near IR Photoluminescence Drew Spera, Griffin Spence, David Pate, Corentin Villot, Umit Ozgur, Ka Un Lao and Indika U. Arachchige; Virginia Commonwealth University, United States

Group IV semiconductor quantum dots have gained noteworthy interest in optoelectronic applications due to their high natural abundance, low-cost of elemental components, and low-to-non-toxicity. A number of chemical syntheses for colloidal Si and Ge quantum dots have been reported and new methods continue to appear. However, these methods generally lack the wide tunability of nanocrystal size and consequently absorption and emission energies resulting in minimal exploration of photophysical properties. To address this issue, we have recently studied the incorporation of elemental Si and Sn into Ge nanocrystals to produce homogeneous $Ge_{1-x-y}Si_ySn_x$ ternary alloy and quantum dots that exhibit size and composition-tunable absorption and emission across visible to near-infrared spectrum. Herein, the physical characterization of the quantum-confined and non-quantum-confined $Ge_{1-x-y}Si_ySn_x$ alloys using powder X-ray diffraction, transmission and scanning electron microscopy, energy dispersive spectroscopy, steady-state and time-resolved absorption and emission spectroscopy, and computational electronic structure calculations will be presented. The effect of synthetic parameters on nanocrystal size, shape, composition, absorption and emission energy, and carrier dynamics will be discussed in light of their application in silicon-based visible to near-infrared optoelectronics.

11:15 AM *EL07.07.03
Light Management in Si Nanocrystal-Based Solar Concentrators Vivian Ferry; University of Minnesota, United States

Luminescent solar concentrators, semi-transparent panels that harvest diffuse, high-energy sunlight, shift the spectrum to more optimal wavelengths, and focus that emitted light onto small-area solar cells. I will discuss the design of luminescent solar concentrators for both architectural and agrivoltaic applications, the fabrication of nanocrystal composites with excellent optical properties, and the use of photonic strategies to direct light within the concentrator to overcome losses.

One recent design I will discuss is the bilayer luminescent solar concentrator, which combines CdSe/CdS core/shell nanocrystals in one layer with Si nanocrystals in a bottom layer. While either layer can act directly as an LSC, combining them both broadens spectral coverage and allows the CdSe/CdS layer to sensitize the Si nanocrystal absorption: light emitted by the CdSe/CdS layer is reabsorbed and emitted by the Si nanocrystals, where it propagates to the edge of the concentrator with minimal parasitic losses. Variation of the relative concentrations of these nanocrystals in the concentrator tunes the transmission spectrum. Integration of various photonic structures into the LSC design is also beneficial for reducing escape cone losses and ensuring that the luminescent light reaches the edge, or that the transmitted light is appropriately outcoupled from the concentrator.

SYMPOSIUM

April 11 - April 27, 2023

Symposium Organizers
Jun Chen, University of California, Los Angeles
Sohini Kar-Narayan, University of Cambridge
Yong Qin, Lanzhou University
Xudong Wang, University of Wisconsin--Madison

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SESSION EL08.01: Bioinspired and Biomaterials for Triboelectric Nanogenerator
Session Chairs: Jun Chen and Xudong Wang
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3008

10:30 AM *EL08.01.01
Biomaterials-Based Wearable Triboelectric Sensors Wenzhuo Wu; Purdue University, United States

The capability of sensor systems to efficiently scavenge their operational power from stray, weak environmental energies through sustainable pathways could enable viable schemes for self powered health diagnostics and therapeutics. Triboelectric nanogenerators (TENG) can effectively transform otherwise wasted environmental mechanical energy into electrical power. However, obstacles hindering the development of efficient triboelectric devices based on biocompatible materials continue to prevail. I will discuss our recent progress in designing and engineering biomaterials for biocompatible, wearable triboelectric devices. Such wearable devices are conformable to human skins and can sustainably perform non-invasive functions by harvesting the operation power from the human body. The gained fundamental understanding and demonstrated capabilities enable the rational design and holistic engineering of novel materials for more capable biocompatible triboelectric devices that can continuously monitor vital physiological signals for creating unprecedented diagnostic tools for diagnosis, interpretation, and prediction of human status in ubiquitous resource-constrained conditions.

11:00 AM EL08.01.02
Soft Triboelectric Pressure Sensor with Spiking Calibration Signal Chankyu Han, Jungrak Choi and Inkyu Park; KAIST, Korea (the Republic of)

Soft triboelectric pressure sensors are growing interest due to increasing demand for various sensors for human-machine interaction and growing global energy concerns. However, signals of triboelectric sensors are significantly affected by miscellaneous factors such as environment and user motion. It is because the surface charge density of triboelectric layers depends on those factors. Although there have been a few attempts to compensate for the change in surface charge density, they were either limited to the change by a specific factor or had considerably limited pressure resolution. None of them could directly calculate current surface charge density to eliminate diverse factors including humidity, time decay and warm-up time while providing continuous pressure information. Here, we propose a triboelectric self-powered pressure sensor with a unique spiking calibration system to directly calculate and compensate for the change in surface charge density.
The sensor generates two output signals: open-circuit voltage and spiking calibration voltage. While open-circuit voltage provides continuous pressure information, it is affected by the change in surface charge density just as in conventional triboelectric sensors. Contrarily, the spiking calibration voltage conveys discrete pressure information without the influence from the change in surface charge density. The spiking calibration voltage is generated based on geometrically switchable operation. A mechanical beam and a parallel-line patterned electrode were designed and fabricated to work as an electrical switch such that the connection depends only on the geometrical state of the sensor. Since closing the switch results in abrupt current spike to flow, a series of voltage spikes are observed with respect to applied pressure. The magnitudes of spikes were not affected by the speed of motion from 0.1mm/s to 5mm/s, and the direction of spikes indicates the direction of pressure change. For triboelectric layers, porous polyurethane and porous ethylene vinyl acetate were utilized due to their softness, high triboelectric performance and cheap price.
Simultaneous analysis of the two signals gives an estimation of current surface charge density in real-time. By comparing the change in the open-circuit voltages between two consecutive spiked moments, current surface charge density can be calculated, which can be further utilized to compensate its change. Triboelectric sensor signals varied by a factor of over two for same pressure due to change in humidity (from relative humidity of 20% to 80% at 22°C) or applying successively higher pressure (up to 13kPa). Nevertheless, our sensor system could successfully eliminate the effect of the change in surface charge density by directly calculating and calibrating it.
Furthermore, the sensor was integrated to a robotic arm to harvest crops in their own optimal growing environmental conditions to demonstrate its possible usage in smart farming robots. As demonstration, a gripper on the robotic arm was feedback controlled to harvest, transport and release a cherry tomato and lettuce with optimal relative humidity of 50% and 75% at 24°C, respectively. While both crops were grabbed with a same target pressure, the open-circuit voltages at the target pressure differed due to different optimal growing humidity conditions. Although conventional triboelectric sensors would have failed to pick them up due to either overestimation or underestimation of pressure, our sensor system could successfully harvest both crops due to its accurate pressure measurements based on the spiking calibration system.

11:15 AM *EL08.01.03
Bioinspired Triboelectric Surface with the Improvement of Nanogenerator Durability for Gait Analysis Zong-Hong Lin[1,2]; [1]National Taiwan University, Taiwan; [2]National Tsing Hua University, Taiwan

Real-time gait analysis is crucial for diagnosis and rehabilitation monitoring of neuromuscular ailments. However, the existing wearable sensors for gait analysis suffer from the drawbacks of bulky, short-term stability and professional operator requirement, which restrict their applicability outside clinical settings. Here, a solid-liquid contact-based triboelectric nanogenerator is developed with soft, flexible and stretchable properties. The device is mainly composed of liquid metal and Ecoflex with biomimic shark skin microstructured surface. The unique surface property prevents the adhesion of liquid metal during sensing and facilitates real-time monitoring of signals and long-term operation stability. The as-designed low-cost, highly scalable self-powered sensor, which is also compatible with diverse detection strategies, provides an on-demand user-friendly point-of-care gait detection and rehabilitation monitoring system with significant applications in personalized health care and sports science.

11:45 AM EL08.01.04
Bio-Triboelectric Wearable Sensors with Enhanced Tribo-Negativity Pedro Henrique de Souza Barbosa[1,2], Robert Ccorahua Santo[1,2] and Wenzhuo Wu[1,2,3]; [1]Purdue University, United States; [2]Flex Lab, United States; [3]Regenstrief Center for Healthcare Engineering, United States

Herein, we have engineered a simple, low-cost, and scalable process to manufacture a biobased triboelectric sensor with enhanced electrical outputs. Our method, based on blade coating, allows us to uniformly modify the thickness of the dielectric layer, which allow us to correlate the processing parameters and performance of our device. Our triboelectric sensor is made from a blend of all-natural compounds and lignin biomass, resulting in an increased tribo-negativity and biodegradability. Recent advances in bio-derived triboelectric sensors are limited by the tribo-positive characteristics of the related materials with respect to human skin. Our lignin-based triboelectric sensors exhibit improved charge transfer when used against the skin, making it sensitive even to subtle mechanical stimuli. We further demonstrated the application of our self-powered wearable device to continuously monitor physiological signs, such as the pulse wave, with high fidelity. Such capability enables the decoding of cardiovascular information around-the-clock sustainably for continuous diagnostics of health status.

SESSION EL08.02: Bio-Related Applications of Nanogenerators

Session Chairs: Sihong Wang and Wenzhuo Wu
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3008

1:45 PM *EL08.02.01
Stretchable and Self-Powered Bioelectronics for Achieving Sustainable Interfacing with the Human Body Sihong Wang; University of Chicago, United States

The vast amount of biological mysteries and biomedical challenges faced by humans provide a prominent drive for seamlessly merging electronics with biological living systems (e.g. human bodies) to achieve long-term stable functions. Towards this trend, one of the key requirements for electronics is to possess biomimetic form-factors in various aspects and continuous energy supply for achieving long-term compatible and sustainable operations. This goal conjunctionally relies on two aspects. First, the entire electronic systems (including the power sources) are desired to have similar mechanical (i.e., soft and stretchable) properties with the skin and biological tissues, so as to improve the wearing comfort, suppress invasive reactions, and enhance the signal quality. Second, the power sources of the electronics, which have been conventionally served by rigid batteries, should be sustainable and maintenance-free, ideally with an unlimited lifetime. In this talk, I will introduce our innovative use of polymer chemistry and engineering for achieving stretchable triboelectric nanogenerators that can efficiently harvest energy from human body movements, as well as our developments of stretchable electronic devices, sensors, and light-emitting devices, for ultimately producing fully integrated systems for human-body interfacing.

2:15 PM EL08.02.02
Tellurene-Based Wearable Biosensor for Real-Time Longitudinal Monitoring of Neurotransmitters in Human Sweat Ruifang Zhang[1,2] and Wenzhuo Wu[1,2,3]; [1]Purdue University, United States; [2]Flex Laboratory, United States; [3]Regenstrief Center for Healthcare Engineering, United States

Metabolic biomarkers provide direct indicators of physical and mental health status. However, the state-of-the-art tools for measuring metabolites in body fluids are expensive, time-consuming, and often require invasive procedures to collect the samples. Non-invasive wearable sensors for measuring metabolites in sweat, the most accessible human secretion, are promising alternatives to costly diagnostic tools. Moreover, existing wearable sensors have limited sensitivity, selectivity, and lifetime for measuring disease-specific metabolic markers (e.g., neurotransmitters) from human sweat. Wearable sweat sensors that can monitor the dynamics of neurotransmitters directly from human sweat have yet to be developed. Here we report a novel wearable biosensor based on tellurene for selective and sensitive detection of dopamine (DA) and norepinephrine (NE) in human sweat for the first time. We demonstrated for the first time the successful sensing and quantification of DA and NE concentrations in real human sweat samples using tellurene sensors. We also evaluated and validated the concentrations of neurotransmitters in human sweat using high-performance liquid chromatography/mass spectrometry (HPLC/MS) for the first time. Our technology could create unprecedented diagnostic tools for improving the experience and outcomes of patient care. The development of non-invasive wearable sensors capable of longitudinal measurement of disease-specific metabolic markers from sweat will positively impact erroneous or delayed diagnoses, enable affordable and ubiquitous diagnostic tools, and foster data-driven precise mobile health monitoring with translational applications in patient care and beyond.

2:30 PM EL08.02.04
Frequency-Dependent Performance of Biocompatible Triboelectric Nanogenerators for Ultrasound-Powered Implantable Devices Kalliope Margaronis; University of Cambridge, United Kingdom

Triboelectric generators rely on contact-generated surface charge transfer between materials with different electron affinities, converting mechanical energy into useful electricity. They could potentially be used as power sources for implantable medical devices, which currently mostly run on batteries. Implantable medical devices are an important area of modern medicine, with tens of millions of people living with an implanted medical device, such as cochlear implants and pacemakers. Replacing batteries in implanted medical devices with triboelectric energy harvesters could negate the need for battery replacement surgeries, and could also provide a more convenient, efficient and reliable way of powering such devices.
Two of the main hurdles to consider before replacing batteries with triboelectric nanogenerators (TENGs) are power output and biocompatibility. In order to optimise the performance of a TENG, materials with high surface charge density must be used. Nanostructuring the surface of a material increases its surface area, allowing for greater charge density and therefore larger electrical output. With these considerations poly-L-lactic acid (PLLA) and polytetrafluoroethylene (PTFE) have been investigated as possible biocompatible materials to use in an implanted TENG. We have recently shown that tribopositive PLLA nanotubes grown by melt-press template wetting can be fabricated and optimised for higher triboelectric output through control of polymer crystallinity [1]. As a counter material for TENG applications, PTFE is a highly tribonegative material which, like PLLA, is already widely used as a biocompatible material in the biomedical industry. We therefore investigate the performance of TENGs based on combinations of nanostructured PLLA and PTFE. Importantly, as TENG devices can be actuated at different frequencies, the frequency response of these devices is also presented in this work, with a view to power implantable devices using ultrasound, which represents a low-loss form of energy transfer through human tissue.

[1] Kalliope Margaronis *et al* 2021 *J. Phys. Mater.* **4** 034010

3:00 PM BREAK

SESSION EL08.03: Bioinspired and Biomaterials for Piezoelectric Nanogenerators

Session Chairs: Sihong Wang and Wenzhuo Wu

Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3008

3:30 PM *EL08.03.01
Biomolecule-Based Piezoelectric Nanomaterials and Their Energy Harvesting Application Rusen Yang; Xidian University, United States

Biomolecule-based materials can enable technological innovations by virtue of their intrinsic bioactivity and physical properties. Since the discovery of the quantum dots made out of diphenylalanine (FF) peptides, biomaterials have long been explored as biological semiconductors. Their insulating nature with ultra-wide gaps limited their study to mainly optical properties and a conventional electronic device is still to be seen. Piezoelectricity was found in FF peptides and many other biomolecular materials such as virus, amino acids, wood, silk, hair, cornea, tendon, and bone. Relatively low piezoelectric constants and the difficulty of achieve uniform polarization are common in biomaterials. Designing tailored biomaterials is essential to better understand these materials, achieve desired properties, and fulfill their application potential. Herein, the electronic structures, dielectric, piezoelectric and elastic properties of biomaterials is revealed by the first-principle calculation. We demonstrate a physical property-enhanced strategy by taking advantage of the hydrogen-bonding networks of double-layer amino acid crystals with their molecular side chains. We based on the Stranski-Krastanov (S-K) growth mode and propose a mechanism for the growth of ordered amino acid array structures via physical vapor deposition. The growth mode not only explains the formation of uniform and controllable morphology of amino acid structures but also leads to the significant enhancement of their piezoelectric properties. The biomaterials with excellent thermostability and piezoelectricity are employed in nanogenerators with much improved performance, demonstrating their potential for eco-friendly energy harvesting devices.

4:00 PM EL08.03.02
Orientation-Controlled Crystallization of γ-Glycine Films with Enhanced Piezoelectricity Jiajie Sui[1], Jun Li[1], Long Gu[1], Connor A. Schmidt[2,3], Ziyi Zhang[1], Pupa Gilbert[2,3] and Xudong Wang[1]; [1]University of Wisconsin, Madison, United States; [2]University of Wisconsin–Madison, United States; [3]Lawrence Berkeley National Laboratory, United States

Glycine, the simplest amino acid, is considered a promising functional biomaterial owing to its excellent biocompatibility and strong piezoelectricity comparable to conventional soft piezoelectric materials. Practical applications require great flexibility and strong out-of-plane piezoelectricity in glycine films, in which the piezoelectric polar <001> direction aligned with the film thickness direction. Based on the recently-developed solidification approach of aqueous polyvinyl alcohol (PVA) and glycine solution, in this work, we demonstrate that the crystal packing direction of as-synthesized film is determined by glycine crystal nuclei orientation. This alignment was possible because crystal orientation follows those of the nuclei, which is determined by the surface curvature at the nucleation site, which was confirmed by the contact angle-related crystal orientation tuning. From cleavage features in cross-sectional SEM images, the films synthesized on each substrate have different incline angles responding to their contact angle. Typically, larger surface curvature from a larger contact angle leads to greater out-of-plane piezoelectric performance. Inspired by this, we further confined the local nucleation kinetics by introducing a wall around the liquid precursor film thereby the surface curvature along the edge was inverted from positive to negative. Changes in surface curvature suppressed the nucleation at the edge area and forced initial nucleation to the middle of the film, where the surface was flat. Therefore, the (001) surface of glycine nuclei became parallel to the film surface, so as the entire film grown thereafter. Tuning the piezoelectric <001> polar direction of γ-glycine crystal to the thickness direction enhanced the out-of-plane bulk piezoelectricity, with an average d_{33} of ~ 6.13±1.13 pC/N. This value was more than 20% higher than the d_{33} of films nucleated from the edge, where their <001> directions were tilted away from the normal direction. This work demonstrated a promising approach to improving the bulk piezoelectricity of glycine films by nucleation kinetics control. This strategy may inspire crystal orientation control in advanced manufacturing processes of amino acid- or polypeptide-based bio-crystals with enhanced properties.

SESSION EL08.04: Materials Innovations in Nanogenerator Development

Session Chairs: Miso Kim and Sihong Wang
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3008

8:30 AM *EL08.04.01
Vacuum and Plasma Synthesis and Processing of Surfaces, Multifunctional Thin Films and 3D Nanoarchitectures—A Platform for the Development of Energy Harvesting Systems Xabier Garcia-Casas, Javier Castillo-Seoane, Laura Montes, Jaime Del Moral, Francisco Aparicio, Ali Ghaffarinejad, Lidia Contreras-Bernal, Jorge Gil-Rostra, Jorge Budagosky, Carmen Lopez-Santos, Juan Sanchez-Valencia, Angel Barranco and Ana Borras; ICMSE (CSIC-US), Spain

Plasma processing and synthetic routes are called to be a game-changer in the realization of environmentally friendly, low-energy consuming, and scalable key enables technologies for nanomaterials development and their practical implementation in devices. In this presentation, we will demonstrate the application of vacuum and plasma-assisted deposition techniques to process surfaces and thin films and to develop complex nanowires (NWs) and nanotubes (NTs) with a core@multishell morphology where each shell adds functionality or multifunctionality to the system. The steps required for the implementation of these nanomaterials as supported or in-device applications will be presented. The universal character of vacuum and plasma methods allows for the deposition of an unprecedented variety of possibilities, including, organic (small-molecules, organic nanocomposites, polymeric layers), inorganic (metal and metal oxides), hybrid (hybrid perovskite) materials acting as conducting, semiconducting, dielectric, photo-absorbent, piezoelectric or plasmonic components in a radial configuration. Clues to foster reliable and robust low-dimensional materials will be presented. Finally, we will share the results and advances accomplished during the last years in the field of energy harvesting (solar cells,[1-4] piezoelectric and triboelectric nanogenerators[5,6]), photoelectrocatalysis, superwettable surfaces [7], anti-icing,[8-10] and the development of semitransparent nanoelectrodes[11].

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9:00 AM EL08.04.02
Ferroelectricity-Modulated Flexible Lead-free Halide Perovskite-based Tribovoltaic Nanogenerator for Mechanical Energy Harvesting Feng Jiang[1,2], Yihui Zhang[3] and Pooi See Lee[2]; [1]Institute of Flexible Electronics Technology of Tsinghua, Zhejiang, China; [2]Nanyang Technological University, Singapore; [3]Applied Mechanics Laboratory, Center for Flexible Electronics Technology, Tsinghua University, China

With the emergence of artificial intelligence, Internet of Things (IoT), and big data, the requirements for device miniaturization, self-powered smart sensors, as well as distributed and wearable power sources, have proliferated dramatically. Tribo- and piezo-electric nanogenerators (TENG and PENG), serving as efficient, low-cost, and distributed energy techniques, enable the energy conversion from low-frequency mechanical energy to electricity, and provide us an opportunity to harvest wasted mechanical energy from the environment or human motion. However, these two technologies are still limited by their large impedance, pulsed electrical signals, as well as the low current output. To solve these potential challenges, a new strategy, tribovoltaic nanogenerator (TVNG), has been proposed, which can directly convert the mechanical energy into direct current (DC) electricity. The DC signals stem from the dynamic Schottky or P-N junctions where the non-equilibrium carriers will continuously diffuse and drift at the conductor/semiconductor or semiconductor/semiconductor interface under the built-in electric field. This new approach not only generates continuous DC output, but also exhibits unique advantages such as high current density, low matching impedance, and continuous power output, providing a new strategy for the future development of sustainable and self-powered energy technology.

In our work, a lead-free (DF-CBA)$_2$CuCl$_4$ halide perovskite was adopted to construct an Al/(DF-CBA)$_2$CuCl$_4$ Schottky junction DC TVNG. Compared to other semiconductor materials, halide perovskites display promising advantages, such as solution-based preparation method, tunable bandgap, photovoltaic as well as ferroelectric properties, which promote the electrical performance of TVNGs. In addition, this copper-based halide perovskite is more eco-friendly, safer than the lead/cadmium/chromium-based perovskites and more stable than the tin/ germanium-based ones, which is significant for their potential applications in the sustainable power sources and wearable materials. Most importantly, the (DF-CBA)$_2$CuCl$_4$ exhibits unique multiaxial ferroelectricity and low coercive field, so its surface charge and work function can be tuned via the external poling process, enabling the TVNG device with excellent electric performance modulation. This work not only offers an insight into the unique coupling between ferroelectric polarization and tribovoltaic effect, but also proposes a ferroelectricity-induced strategy that can modulate the electric output performance of TVNG devices, paving a new avenue for the development of high-performance TVNG devices.

9:15 AM EL08.04.03
Imidazolium-functionalized Ionic Polyurethanes based Self-Healable Triboelectric Nanogenerator with Enhanced Performances Hyeonseo Joo and Ju-Hyuck Lee; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

Triboelectric nanogenerator (TENG) is one of the promising energy harvesting technologies which converts ambient mechanical energy to electrical energy. In order to advance in next-generation soft electronic devices, the TENG is required to be flexible, stretchable, and biocompatible. In addition, the ability of autonomously self-healing after mechanical damage is highly desired for durability and stable production of electrical energy. Thermoplastic polyurethane (TPU), a multi-block copolymer composed of hard and soft segments, can control its electrical and mechanical properties through chemical modification. Also, TPU has advantages such as elasticity, flexibility, and mechanical strength. Therefore, a lot of research on self-healing polyurethane TENG based on disulfide bond, and borate bond has been reported so far. However, research on materials that can simultaneously increase output as well as self-healing is still needed. So, in this study, we synthesized imidazolium-based ionic polyurethane to fabricate high output performance and self-healable TENG. Imidazolium-based ionic polyurethane was intended to have biocompatible properties using polycaprolactone diol and hexamethylene diisocyanate. In addition, using imidazolium ionic liquids diol, an ionic polymer composed of a polymer backbone and an ionic liquid (IL) species was prepared for each repeating unit. As a result, the IL moieties consisting of loosely bound bulky cations and anions can form the electrostatic interaction to form self-healing TENGs. If there is a small scratch on the TENG, it will heal and return to its original state after about an hour. Even in an entirely cut state, it can be fully healed after 24 hours at a temperature of 50 degrees and has the same mechanical properties as before. IL not only affects self-healing, but also greatly affects TENG output performance. ILs could form the electrical double layer (EDL) by their high capacitance and mobile ions. So, we checked the output change while gradually increasing the proportion of imidazolium ionic liquids. As a result, it was confirmed that (1,1) has the highest output. In addition, we confirmed that when the molecular weight of PCL was lowered, and a fluorine unit was included under the (1,1) condition, the output was dramatically increased, resulting in a maximum 650 V and 47 μA output. Finally, the power density is 13.5 times greater than when imidazolium ionic liquids are not included, resulting in 1243 $\mu W/cm^2$. So, this imidazolium-based ionic polyurethane TENG demonstrated a possibility of high output performance and self-healable TENG for electronic devices.

9:30 AM EL08.04.04
Liquid-Metal Nanogenerator Fiber for Harvesting Mechanical and Electromagnetic Energy and as Self-Powered Sensors Ying-Chih Lai; National Chung Hsing University, Taiwan

Future wearable technolgies and personal electronics can be benefit from e-textiles that simultaneously possess high elasticity and multiple capabilities such as energy harvesting and sensing. In this talk, we will present an intrinsically stretchable liquid-metal nanogenerator fiber that can harvest both mechanical energy (e.g. from the body) and electromagnetic energy (e.g. from nearby electronics such as laptops, cell phones, transformers). Furthermore, to the best of our knowledge, this is the first single energy-harvesting fiber that simultaneously possesses inherent elasticity and extraordinary stretchability with the ability to harvest two sources of energy (that are mechanical and electromagnetic Energy). This is also the first report of fibers that convert dielectric-loss from electronic devices to electricity. In addition to converting multiple sources of waste energy into electricity, the fibers can act as self-powered tactile and biomechanical sensors. The fibers consist of hollow elastomeric fiber filled with liquid metal. The fibers harvest energy by the combination of triboelectricity (160 V/m, 5 μA/m, and ~360 μW/m) and induced electrification of the liquid metal (8 V/m (60 Hz), 1.4 μA/m, and ~8 μW/m). We characterize the fibers and demonstrate their utility for powering electronics and sensing biomechanical information. These fibers are further demonstrated as completely soft and stretchable components for human-machine interfaces, including keypads and wireless music controllers. The findings of this work provide new advancements in stretchable/wearable energy and sensing technologies, which are both timely and could advance a wide range of emerging wearable technologies and personal electronics.

9:45 AM EL08.04.05
Scalably Manufactured Tellurium Nanowires for Wearable Piezoelectric Devices Meng Hao Lee and Wenzhuo Wu; Purdue University, United States

Scalable synthesis of low-dimensional nanomaterials provides a route for practically using these emerging materials. We demonstrate scalable solution synthesis of tellurium nanowires (TeNW) and explored their application for wearable piezoelectric devices. The process can achieve thin TeNW with a small diameter and uniform distribution (avg. diameter ~8±3 nm). We further demonstrated the integration of the wearable TeNW-based devices for pulse sensor with excellent sensitivity. Our result presents a facile approach of large-scale, high throughput synthesis of piezoelectric nanomaterials for wearable applications.

10:00 AM BREAK

SESSION EL08.05: 3D Structured Nanogenerators
Session Chairs: Ana Borras and Zong-Hong Lin
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3008

10:30 AM *EL08.05.02
Additive Manufacturing of Tribovoltaic Direct-Current Generator for Self-Powered Sensing Jun Liu; University at Buffalo, The State University of New York, United States

Tactile sensing is crucial for implementing future intelligent devices for the applications of wearable electronics, biomedical implant, and future robotics. Particularly, the ability to measure and distinguish real-time multidirectional mechanical stimuli remain as a challenge for slip detection and self-adaptive manipulation of unknown objects in robotic applications. Tribovoltaic direct-current (DC) generator is emerging as a promising solution for high-efficient mechanical energy harvesting due to its unique advantage of high current density compared to traditional triboelectric or piezoelectric approaches. Meanwhile, the DC generation itself can be utilized as an effective mechanism for high-performance sensing. In this talk, I will discuss our recent progress in designing and additive manufacturing of tribovoltaic direct-current generator (e.g., 3D printed, woven, etc.) for self-powered sensing applications, and provide perspective about the main challenges and future direction for implementing the technique for future applications.

11:00 AM *EL08.05.05
Self-Powered Flexible Devices: Piezo-Sensor and MicroLED Keon J. Lee; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

This seminar introduces two recent progresses of self-powered flexible devices; piezo-sensors and microLED.

The first part will introduce flexible inorganic piezoelectric membrane that can detect the minute vibration of membrane or human skin that expands the application of self-powered acoustic sensor and blood pressure monitor. Speaker recognition has received spotlight as a next big thing of voice user interface such as personalized voice-controlled assistant, smart home appliance, biometric authentication. The conventional speaker recognition was realized by a condenser type microphone, which detects sound by measuring the capacitance value between two conducting layers. The condenser type microphone, however, has critical demerits such as low sensitivity, high power consumption, and an unstable circuit due to the large gain amplification. Speaker recognition also suffers from a low recognition rate, caused by limited voice information and optimal algorithms for a simple and accurate process. Herein, we reported a machine learning-based acoustic sensor by mimicking the basilar membrane of human cochlear. Highly sensitive self-powered flexible piezoelectric acoustic sensor (f-PAS) with a multi-resonant frequency band was employed for voice recognition. The speech waveforms were recorded by the multi-channel f-PAS and converted into frequency domain signals by using Fast Fourier Transform to obtain the characteristics of voice frequency. Convolutional Neural Network (CNN) were utilized for speaker recognition, resulted in a 97.5% speaker recognition rate with the 75% reduction of error rate compared to that of the reference MEMS microphone.

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SESSION EL08.06: Piezoelectric Materials and Piezotronics
Session Chairs: Xudong Wang and Haixia Zhang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3008

1:30 PM *EL08.06.01
Analytical and Numerical Models of Zinc Oxide Nanowire-Based Nanogenerators Guylaine Poulin-Vittrant, Emmanuel Dumons, Kevin Nadaud and Louis P. Tran-Huu-Hue; GREMAN CNRS UMR 7347, France

Piezoelectric nanogenerators integrating piezoelectric-semiconducting nanowires are multilayer and composite devices [1], making their theoretical study a challenge. The active piezoelectric layer is similar to a 1-3 composite piezoelectric transducer [2], which offers the advantage to enhance the electromechanical coupling compared to a full piezoelectric layer from the same material. This composite consists of a piezoelectric nanostructured layer surrounded by an insulating and soft polymer matrix, which is destined to isolate electrically the nanowires from each other, and to protect them from damage or ageing. As nanogenerators are designed to harvest mechanical energy from human movements, or forces in natural environment (water, wind), or industrial vibrations, the mechanical excitation is rarely purely sinusoidal. This seminar will introduce the simulation tools, which are analytical [3,4], numerical [5,6], or mixed [3,7], that have been developed to estimate the electrical power harvested by a zinc oxide (ZnO) based nanogenerator, for a given dynamic applied force. Moreover, the different physical phenomena influencing the conversion efficiency will be presented, for instance the surface (acceptor) traps which compensate the negative effect of the free charge carriers. Finally, the sensitivity of the harvested energy will be explained relative to the different model parameters, which may be geometrical or physical properties. Some design trends will be proposed, regarding the strategic parameters to optimize in order to enhance the nanogenerator performance.

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2:00 PM EL08.06.02
Strain-Correlated Piezoelectricity in Quasi-Two-Dimensional Zinc-Oxide Corey Carlos, Ziyi Zhang, Yizhan Wang and Xudong Wang; University of Wisconsin--Madison, United States

Flexible, wearable, and human-compatible electronics are helping shape a future of integrated nanotechnologies. As such, piezoelectric and semiconducting materials have drawn intense interest by many research groups for the excellent potential to advance the field of wearable devices. Moreover, two-dimensional (2D) nanomaterials, valued for their enhanced mechanical, electronic, and structural properties, have moved to the forefront of compliant electronic devices. Therefore, a thorough understanding of the interfacial charge distribution is required when utilizing flexible piezoelectric semiconductors, such as zinc-oxide (ZnO). We present a method for monitoring the piezoelectric response of nanometer-thick 2D ZNO nanosheets (NS) grown via Ionic Layer Epitaxy (ILE). The direct piezoelectric effect, and the coupling of electronic dipole polarization to lattice strain within ZnO-NSs, is monitored *in situ* via piezo force microscopy (PFM). Using PFM we illustrate the effects of modulating strain in piezoelectric nanomaterials and its role in the polarization charge distribution across the surface of the 2D ZnO-NS. Subsequently, we show that the strain configuration (either tensile or compressive) can dramatically influence the measured piezoelectric coefficient (d_{33}) of the 2D ZnO-NS. Our results illustrate the critical need for understanding the interdependent roles of static piezoelectric charges, semiconducting properties, and strain, for future flexible devices.

2:15 PM EL08.06.03
High-Performance Piezoelectrocatalytic Sensing of Uric Acid using Wurtzite Zinc Oxide Nanorods Jing Jiang[1] and Wenzhuo Wu[1,1,2]; [1]Purdue University, United States; [2]Regenstrief Center for Healthcare Engineering, United States

Piezoelectricity in nanostructured semiconductors provides a novel way to efficiently engineer the catalytical performance for applications in biotechnological, agricultural, and pharmaceutical areas. Here, a low-cost, high-performance piezoelectrocatalytic sensor for the detection of uric acid (UA), an important pathophysiological signal molecule in the human body, is designed and demonstrated based on the principles of piezoelectrocatalysis. Vertical wurtzite ZnO nanorods (ZnO NRs) are grown on graphene oxide (GO) to realize the piezo-electrochemical detection of UA. The electrocatalytic efficiency is significantly boosted by the lowering of the electron transfer barrier at the ZnO NRs-electrolyte interfacedue to the piezoelectric polarizations. The enhancing mechanism of the piezo-potential during the electrochemical oxidation of UA on the ZnO NRs surface is unveiled and discussed. Such low-temperature, facile preparation of the ZnO NRs welcomes a cost-efficient mass production and a direct integration into human electrochemical wearables, whose performance can be modulated readily with a low mechanical budget generated from the human body.

2:30 PM EL08.06.04
Investigation into Ultra-Low-Power Capacitive Piezo-tronic Force Sensor Yu-Liang Hsiao, Chen Jang, Yi-Miao Lin, Chao-Hung Wang and Chuan-Pu Liu; National Cheng Kung University, Taiwan

With the rapid rise of the Artificial Intelligence and Internet of Things (AIoT), developing ultra-low-power devices is essential to future advanced technology. State-of-the-art piezo-tronic force sensors rely on the current changes manipulated by the piezo-potential built at the Schottky interface, which enables fast response and high sensitivity characteristics. However, a relatively high reading bias is necessary for achieving high performances, normally larger than 0.5 volts depending on the threshold voltage of the Schottky diode. In this study, we demonstrate a novel capacitive piezo-tronic force sensor that allow to operate at an ultra-low reading bias or even nearly 0 bias condition. The capacitive piezo-tronic force sensor directly detects the capacitance changes induced by the piezo-charges, instead of current changes. The changes of the capacitance directly reflect the perturbation of the effective depletion width, rather than the built-in potential, and it shows a consistent trend in wide operation voltage ranges including V_{op}~0V. This enables the ultra-low-power capability because it circumvents the necessity of turning on the diode. To deeply investigate the working mechanism, a force-dependent capacitance-voltage (C-V) characteristic was performed to explore the effective depletion width changes induced by piezo-charges. In addition, a dynamic response of the capacitive piezo-tronic force sensor also exhibits ultra-low-power capability, which is free of triboelectric interference. Based on this experimental study, it provides a design guideline for ultra-low-power thin-film-based capacitive piezo-tronic/piezo-phototronic devices in the future.

2:45 PM EL08.06.05
Piezo-Gated Thin Film Transistor—A Novel Device to Develop a Unique Multi-Axial Smart Strain Sensor and the Synergistic Interaction of Piezo-Gating Effect and Thermoelectric Effect Jit Dutta and Chuan-Pu Liu; National Cheng Kung University, Taiwan

The piezo-gating effect plays a pivotal role to develop piezotronic devices exclusively based on carrier modulation inside the piezoelectric semiconducting material. In earlier studies, the piezotronic devices were extensively developed based on the Schottky barrier height modulation at the interface with the electrode. Therefore, we have created an ohmic junction-based piezo-gated thin film transistor (PGTFT) using ZnO as a model material to eliminate the Schottky barrier height modulation and show the dual mode (depletion and accumulation) function of a PGTFT device for the first time. To obtain the dual mode operation, two configurations of the PGTFTs with Top and Bottom electrode subjected to the compressive force shows the opposite trends in I-V signals, which was further validated by analytical modeling and simulation data. This technique further evaluates and distinguishes the piezoresistive effect from the piezo-gating effect for the first time.Furthermore, utilizing this phenomenon we have developed a double-sided four-electrode-based flexible PGTFT, allowing to not only detect the total amount of strains but also distinguish between bending force (upward/downward) and normal force (tensile/compressive). Thus, we were able to first develop such a smart strain sensor using the piezo-gating effect to capture more information in one single device. Foremost, we also combine the piezo-gating effect with the thermoelectric effect to investigate the carrier dynamics of such effects and obtain a synergistic effect where the thermoelectric power factor was largely enhanced via incorporation of the piezo-gating effect. To examine such behavior, we have used the same PGTFT configuration and exerted a thermal gradient to the source and drain electrode interfaces to initiate the hot electron/hole flow and modulate that via strain-induced piezo-potential inside the channel.

3:00 PM BREAK

SESSION EL08.07: Hybrid Nanogenerators and Coupling Effects
Session Chairs: Zong-Hong Lin and Rusen Yang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3008

3:45 PM EL08.07.02
What is the Difference between Contact and Sliding? Tangential Forces are Important for Triboelectricity Karl Olson and Laurence D. Marks; Northwestern University, United States

Despite increasing research interest in triboelectricity, the electric charge transfer that occurs when two materials contact each other, the fundamental understanding of the subject is still limited, especially when at least one of the materials involved is insulating. When surface asperities of the rubbing materials contact each other, they deform, resulting in electromechanical effects that are large enough to cause charge transfer. Especially important is flexoelectricity, the coupling between electric polarization and the strain gradient, which can be very large due to the small size of the asperities [1].

Previously, we have modeled the electromechanics of simple single-asperity metal-semiconductor contacts [2]. Here, we extend this analysis to consider tangential forces as well as normal forces. Macroscopically, this roughly corresponds to sliding instead of simple contact and release.

Intuitively, one might suspect that sliding a balloon on hair causes more charge transfer than contacting and separating. Indeed, the results of our work suggest that in some cases, sliding forces can be more impactful than normal forces. The relative importance of normal forces and tangential forces to the electromechanics of contacting asperities is dependent on material parameters. This fundamental insight into the importance of the geometry of the contact force may be useful both in cases where charge transfer should be prevented to reduce dangerous sparks or where it is desired to power triboelectric nanogenerators.

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4:00 PM EL08.07.03
Coupling Triboelectric and Thermomagnetic Effects as a Novel Low-Grade Thermal Energy Harvesting Technology Catia Rodrigues[1], Ana Pires[1], Isabel Gonçalves[1], Andre Pereira[1], Joana Oliveira[2] and Joao Ventura[1]; [1]University of Porto - Faculty of Sciences, Portugal; [2]University of Porto - Faculty of Engineering, Portugal

Energy has been one of the major driving forces behind our societal development and economic growth. However, the resulting surge in energy demand has also led to the major environmental crisis we now face. Thus, new energy generation technologies able to convert low-grade thermal energy into electricity are urgent to tackle the continuous surge in energy demand. Here, a hybrid device that couples triboelectric and thermomagnetic effects to generate electrical power in the presence of small temperature gradients near room temperature was demonstrated [1]. Triboelectric nanogenerators (TENGs), appearing just in 2012 [2], are already one of the most promising mechanical energy harvesting technologies [3-5]. In this work, the thermomagnetic effect allowed us to induce the periodic and sustained motion of a second-order ferromagnetic material in temperature gradients below 30 °C. This mechanical motion was converted into electrical energy using a TENG. The applicability of this concept was demonstrated in a broad range of operating temperatures in both the cold (15 to 37 °C) and hot (60 to 90 °C) sides. Varying the temperature gradients with TENG assembled in the cold-side, a maximum power density of 18 mWm^{-2} was reached using a cold- and hot-sides temperature of 30 and 65 °C. When assembled in the hot-side, the TENG generated a maximum power density of 54.7 mWm^{-2} for cold- and hot-side temperature of ~20 and 65 °C. It was further shown that the electrical power generated by the hybrid TENG is more than 35× higher than that obtained by a conventional thermomagnetic generator. This work showed that TENGs is a high-efficient harvesting technology to use the temperature difference and vibration mechanical energy as electrical energy sources.

References:
1. C. Rodrigues et al., Advanced Functional Materials,32 (2022)
2. F-R. Fan et al, Nano Letters, 12 (2012).
3. C. Wu et al., Advanced Energy Materials, 9 (2019).
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5. C. Rodrigues et al., Nano Energy, 72 (2020)

4:15 PM EL08.07.04
Discovering Giant Magnetoelastic Effect in Soft Systems for Nanogenerators Xun Zhao; University of California, Los Angeles, United States

Magnetoelastic effect is usually observed in rigid bulky metal alloys. Very recently, we discovered giant magnetoelastic effect in a soft system composed of platinum-catalyzed silicone polymer matrix and neodymium-iron-boron nanomagnets. The soft composite system shows up to four times enhancement of the magnetomechanical coupling factor (T/Pa) than the traditional rigid counterpart owing to a distinct physical mechanism. The giant magnetoelastic effect was further coupled with magnetic induction to invent a soft magnetoelastic nanogenerator as an emerging approach to revive the community of biomechanical energy conversion that is challenged by low current, high internal impedance, and low water/humidity resistance for decent operation stability. This discovery established an alternative way for biomechanical to electrical conversion which could work stably on wet skin or in body fluids without reliance on any encapsulation. We studied its working mechanism by a wavy chain model based on the magnetic dipole-dipole interaction and demagnetizing factor. To facilitate practical applications, we explore their applications as bioelectronics for human-body-centered energy, sensing, and healthcare. For example, we invented a textile magnetoelastic nanogenerator, weaving the 1D soft nanomagnet fibers with conductive yarns, which could used for energy harvesting from human body and convert the arterial pulse into electrical signals.

4:30 PM EL08.07.05
How can the Surface Charge Effects be Advantageous for Enhancing the Piezo-Conversion Efficiency in GaN NWs? Noelle Gogneau[1], Pascal Chretien[2], Amaury Chevillard[1], Tanbir Sodhi[1,2], laurent Couraud[1], Laurent Travers[1], Jean-christophe Harmand[1], Francois Julien[1], Maria Tchernycheva[1] and Frederic Houze[2]; [1]Center for Nanosciences and Nanotechnologies, France; [2]Laboratoire de Génie électrique et électronique de Paris, France

The piezoelectric nanowires (NWs) are considered as promising nanomaterials to develop ultra-compact and high-efficient piezoelectric nanogenerators working under environmental mechanical deformations and vibrations (equivalent forces of few Newton in the 1-200 Hz frequency range) for supplying micro-sensors and medical implants. Especially sub-100 nm-wide NWs present the particularity to exhibit specific properties, non-existing or non-significant at micrometric scales, that can lead to a strong modulation/modification of their characteristics. Among these “new properties”, we can cite the exaltation of the piezoelectric coefficients, the formation of nano-contact at the NW/electrode interface allowing an enhanced energy harvesting, or the modulation of the free carrier concentration due to the surface charge (SC) effects. Regarding this last property, simulations have recently established that these SC effects can be advantageous for improving the piezoelectric response of the NWs, since they can limit, in given conditions, the screening by the free carriers of the piezoelectric charges. In-depth understanding of the relationship between these new properties and the piezoelectric conversion capacities of the NWs is now a prerequisite for further improving the device performances and thus approaching a future technological transfer.
To quantify experimentally the influence of the SC on the piezoelectric response of the GaN NWs, we have developed a new advanced nano-characterization tool based on AFM probing the piezo-conversion properties of NWs axially compressed with a well-controlled applied force. This unique technique, in addition to mimic the main deformations undergone by the nanostructures when they are integrated into a device, allow to measure simultaneously and thus correlate the output voltage generated by each NW of the array and its NW deformation rate. In other words, we can quantify the electromechanical coupling coefficient of each tested GaN NWs, one of the figures of merit of the piezoelectricity.
With this new system, we have measured the electromechanical coupling coefficient of GaN NWs characterized by an equivalent height and a diameter evolving between 20 and 110 nm. We established, for NW presenting the same compression degree, that the coupling coefficient is strongly affected by the surface charge effects. For large diameter (60 nm in the intrinsic doping conditions of our NWs), the SC have no effect on the piezo-conversion and thus this one is only controlled by the NW mechanical characteristics. By contrast, for lower diameters, the SC effects become favorable for piezo-conversion due to the strong reduction of screening effect of the piezo-charges into the fully depleted NWs. Thus, we observe an enhancement of the piezoelectric response of the NWs. Especially, we demonstrate that by finely architecting the NWs dimension, the SC effects can be advantageous for strongly improving the electromechanical conversion efficiency of GaN NWs up to 43,2%.

4:45 PM EL08.07.06
P-N Junction-Based Piezoelectric Smart Devices for Energy Harvesting and Self-Power Sensing Qinrong He, Xuan Li, Han Zhang and Joe Briscoe; Queen Mary University of London, United Kingdom

With increasing development of “Internet of Things” (IoT), it is particularly desirable to research flexible energy harvesters for the field of wireless, portable and monitoring fields, which can capture multiple forms of mechanical energy with enhanced energy conversion efficiency. Herein, textile and carbon fibres were used as flexible substrates to fabricate energy harvesters. P-N junction-based ZnO energy harvesters were designed to combine the advantage of ZnO piezoelectricity and the flexibility of textile and carbon fibres. PEDOT:PSS and CuSCN are used to reduce the external and internal screening effect by forming a P-N junction and surface passivation to enhance the performance, respectively.[1-2] PEDOT:PSS/CuSCN/ZnO structure was successfully fabricated on conductive Cu/Ni coated textile and carbon fibres. The textile-based device generated increasing output voltage from 0.2 V to 1.81 V as the shaking frequency increases from 19 Hz to 26 Hz, which was harvested to activate an LCD screen.[3] Carbon fibre-based devices generated increasing output voltage from 1.4 V to 7.6 V as the acceleration from an impacting force increased from at 0.1 m/s^2 to 0.4 m/s^2. Both of the above flexible devices exhibited high stability and durability under 26000 cycles test, and were also able to harvest energy from biomechanical forces such as impacting, flicking and gentle finger tapping . In addition, a carbon-fibre-based composite, carbon fibre-reinforced plastic (CFRP)-based self-power sensor was also fabricated, which exhibited output voltage from 0.27 V to 3.53 V under different impacting acceleration from 0.1 to 0.4 m/s^2 with good stability during a 26000 cycles test. The results provide an efficient method for future energy harvester and self-powered devices to harvest various mechanical source from the environment for portable electronics application.

Reference:
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SESSION EL08.08: Poster Session: Nanogenerator and Piezotronics I
Session Chairs: Xudong Wang and Wenzhuo Wu
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL08.08.04
Hybrid Energy Harvester Based on Perovskite Solar Cell and ZnO Piezoelectric Nanogenerator Yuan Zhang, Xuan Li and Joe Briscoe; Queen Mary University of London, United Kingdom

With the consumption of fossil fuels and the increasing awareness of environmental protection, more and more efforts are being put into the development of renewable and clean energy. Mechanical energy is the one of the most abundant and accessible energy sources, and has been widely harvested by large-scale technologies such as wind power or tidal stream generators. Piezoelectric nanogenerators (PENGs) provide a potential way to convert small

mechanical energy such as body motion or vibration into electricity, which can be used to power small portable electronics, medical bio implants, remote wireless sensors etc. Also, solar energy offers the potential to provide much higher power levels than motion since the sun delivers more energy to the earth in 1 h than the entire planet consumes in one year. However, light is not always available, nor is movement, therefore a hybrid energy harvester that can make use of both sources provide a more reliable and high-level of power for small, portable or self-powered devices.
Here, a combined solar and piezoelectric hybrid energy harvester (HEH) was designed, fabricated and tested, which combined a PENG and perovskite solar cell with the structure of PET/ITO/ZnO seed layer/ZnO nanorods/perovskite/hole transport layer/Au. Oscillation (NG) and illumination (PV effect) testing indicated that HEHs operated as kinetic and solar energy harvesters both separately and simultaneously. The length and diameter of ZnO nanorods, and the composition of perovskite were optimised to achieve the enhancement of both PV and NG output performance. The coupling effect between perovskite and piezoelectric ZnO nanorods, as known as the piezo-phototronic effect, was also investigated.

5:00 PM EL08.08.05
Manufacturing of Advanced Piezoelectric Nanogenerator by Functionalizing PVDF with $LiTaO_3$ and Multiwalled Carbon Nanotubes (MWCNTs) for Energy Harvesting and Sensing Applications Islam Uddin Shipu, Zaida Carballo, Rigobert Ybarra and Mohammed Uddin; The University of Texas Rio Grande Valley, United States

One of the freely available green energy sources that might be used to satisfy the small-scale energy need is mechanical energy. In order to capture mechanical energy, power the next generation of electronic gadgets, and health monitoring flexible piezoelectric nanogenerators made of light weight polymers and carbon nanotubes have drawn a lot of attention. Lithium tantalate ($LiTaO_3$) nanoparticles were prepared and utilized to create a flexible piezoelectric nanogenerator (FPNG). A compact piezoelectric nanogenerator that successfully transfers mechanical energy into electricity was then created using lightweight polyvinylidene fluoride (PVDF), multiwalled carbon nanotubes (MWCNTs), and $LiTaO_3$ nanoparticles. To create a piezoelectric composite film, $LiTaO_3$ nanoparticles were first prepared and loaded into poly vinylidene difluoride (PVDF) and multi-walled carbon nanotubes (MWCNTs). This piezoelectric composite film was then placed between two copper electrodes to create an flexible piezoelectric nanogenerator (FPNG). It was thoroughly examined and adjusted how the concentration of $LiTaO_3$ injected into PVDF and MWCNT affected the electrical performance of FPNG. 1.5%, 2.5%, 3%, and 5% $LiTaO_3$ were used to manufacture the flexible piezoelectric films and then the films' XRD, XPS, SEM characteristics were analyzed as well as the voltage and current were measured. Open-circuit voltage and short-circuit current measurements for the 3 wt% FPNG were ~70V and ~8µA respectively. The nanogenerator was further put to the test by combining it with common electronic parts including capacitors, bridge rectifiers, and 10 LEDs. By transforming human walking force into energy, multiple piezoelectric films can light a room even without electricity. The FPNG was used to harness diverse biomechanical energy. This FPNG was also employed as a sensor for in vitro and in vivo biological applications such as blood flow, respiration, and muscle contraction.

5:00 PM EL08.08.06
On the Effect of Dielectric Relaxation Mechanisms on the Performance of a Multi-layered Triboelectric Nanogenerator Xiaoyue Zhao and Zoubeida Ounaies; The Pennsylvania State University, United States

With the rapid development of the Internet of Things (IoT), a growing number of mobile electronics are being connected to the internet and working in an environment without human interventions. Therefore, there is a crucial need for an alternative energy technology that can harvest energy from ambient environment to self-power devices, due to the inadequacy of conventional energy sources. Among the many energy harvesting technologies, the triboelectric nanogenerator (TENG) is attracting attention recently since it is flexible, portable, cost effective and light in weight. TENGs utilize the triboelectric effect to generate electrical energy when two materials come in contact. The ubiquity of triboelectric effect makes TENG a potential energy source for many applications, such as wearable electronics, smart buildings, and implantable medical devices. Currently, TENGs are capable of milliwatt power; for this reason, their output needs to be enhanced to realize widespread adoption. Previous studies have found that the performance of TENGs can be improved by employing a muti-layer material configuration where each layer contributes to a unique part in the charge generation and transport mechanisms. This improvement cannot be explained using theory since the theoretical calculations of the power output assume that the charges are confined at the contact surface. Therefore, a comprehensive study of the mechanism behind the enhancement of triboelectric output for multi-layer materials is needed. In this work, layered materials of Polydimethylsiloxane (PDMS) and P(VDF-TrFE) are investigated and assessed against single layered PDMS as the control material. The number of layers, as well as the polarization and dielectric properties of P(VDF-TrFE) are tuned to maximize the triboelectric output. For example, a two-layer material consisting of PDMS and electrically poled P(VDF-TrFE) shows a 25% increase in the triboelectric output compared to a single-layer PDMS sample. The enhancement of the triboelectric output is then interpreted using dielectric spectroscopy. Specifically, the triboelectric output of the designed muti-layer material configuration along with the control TENG is quantified by measuring the open-circuit voltage and short-circuit current of the samples. In addition, the TENGs are characterized using dielectric spectroscopy to probe the charge transport, interfacial polarization, and other polarization effects in the multilayered materials. This study aims to relate the charge propagation and trapping to the change in the triboelectric output in multilayered dielectric materials. The findings will shed light on the mechanisms and contribute to the widespread adoption of TENG as an environmental-friendly energy technology for our society.

5:00 PM EL08.08.08
High Performance Mechanical Energy Harvesting from Ionomer Coated Carbon Nanotube Yarn Twist Gyu Hyeon Song, Jong Woo Park and Seon Jeong Kim; Hanyang University, Korea (the Republic of)

Mechanical energy harvesters such as piezoelectric, triboelectric are widely investigated to scavenge electrical energy from body movements to ocean waves. A high-power yarn-type mechanical energy harvester called "twistron" was reported in 2017. When stretching it, the increased twist reduces the effective surface area forming an electrical double layer capacitance (EDLC), and electricity is produced in proportion to the amount of EDLC change. By stretching with a sinusoidal applied strain, 140 mV of maximum open circuit voltage (OCV) and 250 W/kg of maximum peak power was obtained. Here, we increased the generated voltage from twistron by coating potential of zero charge (PZC) shifting materials. The shifted PZC increases the amount of intrinsic bias voltage (|OCV-PZC|) used for harvesting electricity. By coating the PZC shifting materials, the produced maximum OCV and peak power increased 1.63 and 4.06 times. Also, by comprising the yarn pair asymmetrically with pristine CNT and the PZC shifting materials coated CNT, the generated voltage can be the sum of the voltages from each electrode. Since the intrinsic bias voltage becomes negative, the direction of generated voltage becomes reversed for PZC-shifted materials coated CNT twistrons compared to pristine CNTs. These asymmetrically composing twistron yarn pairs were attached to joints such as the elbow, knee, and fingers in a form of textile, and energy harvesting from bending motions in seawater was demonstrated. Improved performance of twistron harvester was achieved by the simple coating of PZC shifting materials. Increased voltage without cell separation for serial connection is beneficial to be utilized in confined spaces.

5:00 PM EL08.08.09
Mover Electrode/Stater with Double Electrodes Triboelectric Nanogenerator with High Instantaneous Current Triggered by a Surficial Contact Electrode Haitao Wang[1], Yasuyoshi Kurokawa[1], Kazuhiro Gotoh[1], Shinya Kato[2], Jia-Han Zhang[3] and Noritaka Usami[1]; [1]Nagoya University, Japan; [2]Nagoya Institute of Technology, Japan; [3]Nanjing University, China

The conventional vertical contact-separation triboelectric nanogenerator (CS-TENG) and single-electrode triboelectric nanogenerator (SE-TENG) has attracted much attention due to practicality. In applications, although CS-TENG is always preferred than SE-TENG owing to the unique double-sided power generation layers, the top mover part and the bottom stator part should be connected by conductive wires, which lead to inconvenient control and unstable performance. On the contrary, in case of SE-TENG, the mover part is free to contact and separate with the stator part without connecting any conductive wires. However, the output is much lower than CS-TENG. Remarkably, a droplet-based electricity generator (DEG), which converts water-droplet energy into electrical energy, was invented in 2020. The DEG demonstrated several orders of magnitude higher instantaneous output than its counterparts. The DEG typically consists of tiny piece of top electrode and full coverage of bottom electrode, and a dielectric material between them. The core novelty lies in introducing a new bulk effect characterized by the formation of a closed loop between droplet, electrodes, and dielectric material. Charges flow directionally from a bottom electrode into the water contacted to the top electrode. In this study, inspired from the DEG, we introduce the mover electrode to DEG and call the device mover electrode/stater with double electrodes TENG (MESD-TENG). The MESD-TENG can achieve the same bulk effect in the case of solid-solid contact. The MESD-TENG was designed to meet the merits of CS-TENG, SE-TENG and DEG at the same time.
The MESD-TENG and CS-TENG were fabricated. In the case of the MESD-TENG, a fluorine-doped tin oxide (FTO)-coated glass (500 mm× 500 mm) was used as the top mover part. For a bottom stator part, the f(FEP) film (500 mm× 500 mm) was pasted on the another FTO-coated glass covered by FEP film. In this system, the top FTO acts as the tribo-positive layer and electrode simultaneously, the FEP film acts the tribo-negative layer, and the bottom FTO acts an electrode. The tiny piece of Al electrode was pasted on the FEP film. The size of the Al electrode is 10 mm × 5 mm. The Al electrode was connected to the bottom FTO electrode through external circuit. The bottom stater part was fixed and the top mover part was made moved iteratively by a step motor at 0.5 Hz. In the case of CS-TENG, FTO-coated glass (500 mm× 500 mm) was used as the top mover part. For a bottom stator part, the f(FEP) film (500 mm× 500 mm) was pasted on the another FTO-coated glass covered by FEP film. FTO in the top mover part was connected to the bottom FTO electrode through external circuit. The bottom stater part was fixed and the top mover part was made moved iteratively by a step motor at 0.5 Hz. The electrical output of them was measured by the electrometer (Keithley 6517b).
As a result, the MESD-TENG achieved a 15-fold enhancement of current and voltage of almost the same order of magnitude compared to the CS-TENG. For a more intuitive verification, we compared brightness when the same numbers of LED arrays (50 LEDs) are driven by the two devices of MESD-TENG and conventional CS-TENG under the same 0.5 Hz, and the results shows the LED arrays driven by MESD-TENG are lighted up much brighter than the other one. Therefore, this work provides an effective method to develop high-performance nanogenerators for further practical application.

5:00 PM EL08.08.10
Multi-Layered Triboelectric Nanogenerator for Human-Machine Interface Using an Artificial Synaptic Device Yong-Jin Park, Yun Goo Ro, Young-Eun Shin, Cheolhong Park, Sangyun Na, Yoojin Chang and Hyunhyub Ko; Ulsan National Institute of Science & Technology (UNIST), Korea (the Republic of)

Artificial synaptic device provides functions of sensing, short-term and long-term memory, which can find applications in various human-machine interfaces. Memory and sensing functions with low energy consumption are considered as a key of the neuromorphic system that is superior to high energy consuming von Neumann computing architecture. Triboelectric nanogenerator (TENG) provides spike-like impulses similar to the action potential propagation in the biological system, which can be utilized for the operation of artificial synaptic devices. Herein, we propose multi-layered TENG (M-TENG) capable of generating multiple spike impulses by a single mechanical stimulus based on tribo-positive microdome-patterned polydimethylsiloxane (PDMS) and tribo-negative 1H,1H,2H,2H-perfluorooctyltrichlorosilan (FOTS)-coated $BaTiO_3$/PDMS (FBP) composite films. While conventional triboelectric devices generate two spike peaks when the top and bottom triboelectric layers contact and separate with each other *via* contact electrification and electrostatic induction, our M-TENG can generate distinct multiple spikes corresponding to the number of layers under a single mechanical stimulus of the same applied force and frequency. Moreover, our M-TENG shows 1.33 times higher output charge compared to conventional single-layered TENG and the power density of 7.56 $\mu W/cm^2$ at 100 MΩ under the applied force of 19.6 kPa. For the application in artificial synaptic devices, M-TENG is coupled with organic electrochemical transistor (OECT), where multiple spikes generated from M-TENG are served as the gate voltage for the self-powered system. Our synaptic device exhibits continuous increase and gradual decay of post-synaptic current under several stimulations, leading to long-term plasticity (LTP). LTP is formed by paired-pulse facilitation (PPF) of excitatory post-synaptic current (EPSC). The efficiency of the triggered EPSC can be expressed by PPF index with different time intervals of stimulations. To further investigate human-machine interface using the artificial synaptic devices, a robotic hand is operated by training process mimicking memory consolidation.

5:00 PM EL08.08.11
Compressibility Effect of Charge Generating Layer on Output Performance of Triboelectric Nanogenerator Junho Jang[1], Chungryong Choi[2] and Jinkon Kim[1]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Kumoh National Institute of Technology, Korea (the Republic of)

Triboelectric nanogenerator (TENG) that can be used in next-generation wearable devices, have received great attention due to their simple device structure and low cost. Among many factors to affect the output of TENG, the compressibility of a charge generating layer becomes very important, because it influences the contact area as well as the number of induced charges. Nevertheless, it has been challenging to achieve high compressibility with conventional polymers due to the intrinsic entanglement of polymer chains. To significantly reduce the entanglement of polymeric materials for achieving low compressive modulus (E) or high compressibility, we chose bottlebrush polymers. Our study leverages bottlebrush elastomers, which suppress chain entanglements—an effect that significantly lowers various mechanical moduli compared to conventional linear polymer networks. We found that TENG output performance such as voltage, current and surface potential, are increased with decreasing E of the charge generating layer. When we used crosslinked bottlebrush poly(dimethyl siloxane) (PDMS) as a charge generating layer of TENG device, the output voltage (120 V) was more than twice larger than that (55 V) of conventional crosslinked PDMS without having bottle brush. These results demonstrate the power of controlling polymer architecture in the context of advanced electronic applications.

5:00 PM EL08.08.12
Development of Double Schottky Piezotronic Nano-newton Force Sensor based on Porous ZnO Nanorod Arrays Yi Miao Lin, Yu-Liang Hsiao and Chuan-Pu Liu; National Cheng Kung University, Taiwan

Force sensors based on piezotronic effect have received significant attention for the application in the internet of things, wearable electronics, biomedical engineering, and high-electron-mobility transistor due to their high sensitivity, fast response, and low energy consumption. The piezotronic force sensors rely on the current changes manipulated by the piezo-potential built at the Schottky interface, where most of them are working based on single-Schottky device, implying that the signals can only be read at either positive or negative bias. Contrarily, Double Schottky based piezotronic force sensors provide a possibility, allowing two modes both at positive and negative bias can be operated within one sensor unit for the advanced micro/nano electronic devices. Among the piezoelectric material, ZnO has been widely developedin applications such as sensors, photocatalysis, and energy harvesting because it is adaptable in multiple nanostructureswith piezotronics/ piezo-phototronic properties. In this study, intrinsic n-type ZnO and p-type Sb-doped ZnO nanorods were demonstrated to perform single and double Schottky piezo-tronic force sensor devices by applying ultra-low compressive force ranging from 20nN to 100nN with conductive atomic force microscopy (C-AFM). To improve the sensitivity of the force sensors, hydrogen annealing was performed to make porous structure to enhance the piezoelectricity of ZnO. To further clarify the contribution from porous structure, oxygen and argon annealing at different temperatures was performed to explore the influence of crystallinity, defects, and carrier concentrations on the sensitivity.In this study, the mechanisms of electrical transport of single and double schottky piezo-tronic force sensors have been comprehensively investigated.

5:00 PM EL08.08.13
Magneto-Responsive Switching of Liquid-Solid Triboelectrification for Self-Powered Magnetic Proximity Sensor Soyeon Yun[1], Kijung Yong[1] and Seunghyup Lee[2]; [1]POSTECH, Korea (the Republic of); [2]korea institute of Ceramic Engineering and Technology, Korea (the Republic of)

Water droplet-based triboelectric nanogenerators (WD-TENGs) harvest energy from triboelectrification between water drop and solid surface. WD-TENGs are highly advantageous to convert abundant rain drop energy.
This study proposed a new concept for switching of liquid-solid triboelectrification by introduction of a magnetocontrollable lubricant-infused layer as a triboelectric layer. This layer was composed of magneto-responsive micropillars and lubricating oil. The micropillars showed two different aligning structure states that determine the continuity of lubricant layer. As the direction of the applied magnetic field changes, vertically standing micropillars start to lie down and the continuous lubricant layer is generated. The lubricant layer works for preventing liquid-solid triboelectrification. Triboelectric switching resulted from reversible change between these two states. The electrical outputs showed a difference of nearly three times, so it could be clearly defined as ON and OFF states. The triboelectric switching cycles assured excellent reversibility and stability even after almost one hundred cycles.
The triboelectric switching has been analyzed in detail for factors that can affect the behavior of water droplets, such as the thickness of lubricant layer, drop height of water droplet and inclination angle of TENG.
Also, switching characteristics showed reversible wettability change and it was utilized to recover the performance of WD-TENG even under high humidity environment. Unlike most WD-TENGs, our device can avoid surface wetting problems and generate sustainable electrical power in extreme condition. To extend the usability, the proposed device could work as a self-powered magnetic proximity sensor. Our work presents a new idea of magneto-responsive triboelectric switching, extending the TENG applicablity in low-power-consumption applications such as no-extra power supply-need switches and self-powered sensors.

5:00 PM EL08.08.14
Sustainable Charged Composites with Amphiphobic Surfaces for Harsh Environment–Tolerant Non-Contact Mode Triboelectric Nanogenerators GiHyeon Han[1] and Jeong Min Baik[2]; [1]Ulsan National Institute of Science and Technology, Korea (the Republic of); [2]Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of)

Here, we report the harsh environment–tolerant and robust non-contact mode triboelectric nanogenerators based on sustainable charged TPU-SiO_2 and PDMS-PTFE composites with amphiphobic surfaces. In the composites, SiO_2 and PTFE particles are well-distributed with ethanol and n-hexane as dispersing agents, respectively. The PDMS-PTFE composites are then etched and fluorinated, resulted in the formation of the amphiphobic surfaces. As a practical non-contact mode application, a speed sensor fabricated using the two composites can stably detect a vehicle speed of 3.75 km/h when exposed to high humidity (~ 99 %) and various chemical oils. It also shows the enhanced charge retention characteristic of the composites by 6 times.

5:00 PM EL08.08.15
Real-time Observation of Ferroelectric Domains and Domain-Wall Motions in Plastic/Ferroelectric Crystal Films Itsuki Miyamoto[1], Satoshi Matsuoka[1], Jun'ya Tsutsumi[2], Jun Harada[3] and Tatsuo Hasegawa[1]; [1]The University of Tokyo, Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan; [3]Hokkaido University, Japan

Plastic/Ferroelectric crystals are a class of newly discovered ferroelectric molecular materials that attract considerable attentions as potential alternatives to widely used ferroelectric ceramics [1]. In the compounds, spontaneous polarization arises through the freeze of rotational motion of polar globular cations. Because of the solution processability and unique multiaxial ferroelectricity, the plastic/ferroelectric crystals are expected for device application by facile thin-film preparation. Among a variety of compounds reported so far, 1-azabicyclo[2.2.1] heptanium perrhenate (AH-R) exhibits 4-axis spontaneous polarization at room temperature and outstanding ferroelectric properties (P_s = 4.1 μC/cm^2, E_c = 2 - 4 kV/cm) even in bulk polycrystalline samples [2].

Herein we report ferroelectric domain structures and the response to applied electric fields in solution-processed AH-R crystalline thin films. We adopted birefringent field-modulation imaging technique, an optical imaging for observing ferroelectric domains via the Pockels effect under in-plane electric fields ($<< E_c$) [3,4]. We successfully observed various patterns of ferroelectric domains that are formed by three different types of domain boundaries in as-grown films. We then visualized step-by-step polarization orientation process by applying pulsed DC electric fields ($> E_c$) through the field-modulation imaging measurements. We found that the domain walls which involve lattice deformation and are nearly parallel to the external field begin to move along the direction perpendicular to the applied electric field. We finally observed that the polarization of entire area between electrodes is oriented to the same direction after several seconds.

We also performed a high-speed imaging experiment for observing periodic dynamics of domain wall motions during the polarization switching process under applying alternating (AC) electric fields. With gate bias control of the image intensifier installed in front of the image sensor, delay of the exposure to polarized light microscopy was swept so as to visualize the motion as a sequence of the images. We achieved visualization of smooth and repetitive behavior of the domain wall motions, where the striped domain walls perpendicular to the field are maintained while those parallel to the field move to expand the reversed domains. Based on the observations, we discuss motions of domain walls that drive the polarization reversal under electric fields. Such direct observation of domain behavior are expected to elucidate microscopic mechanisms of switching characteristics in multiaxial plastic/ferroelectric crystals.

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5:00 PM EL08.08.16
Progress Towards Piezoelectric (Ba,Ca)(Ti,Zr)O_3 Thin Film Using Wet Chemical Solution Deposition Hannes Rijckaert, Ewout Picavet, Isabel Van Driessche, Klaartje De Buysser and Jeroen Beeckman; Ghent University, Belgium

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

Since **BCTZ material offers promising piezoelectric properties**, making thin films of this material is of particular interest for use in various applications. Also, the integration of piezoelectric films on silicon (Si) or silicon nitride (SiN) based platforms is crucial for the miniaturization of electronic and photonic components. In this work, **wet chemical solution deposition (CSD) technique is introduced as a rapid integration** to develop a cost-effective, reproducible and high quality industrial pathway to piezoelectric BCTZ film on desired substrate. Therefore, the formulation of the environmentally friendly BCTZ precursor solution is highly important and must be stable prior to the CSD process with good wetting behavior and good homogeneity on desired substrate. Here we are able to develop **the environmentally benign BCTZ** inks based on the short carboxylic acid route as metal organic decomposition (MOD) method. These modified BCTZ inks can be deposited on several type of substrate such as $LaAlO_3$, $SrTiO_3$, Si, SiO2/Si and buffered Si using spin-coating or ink-jet printing techniques. After deposition, a comprehensive study of the thermal process is carried out to elucidate the nucleation and growth mechanism of the BCTZ film. This extensive study has led to **(*h*00) epitaxial BCTZ film with superior piezoelectric and ferroelectric properties on different substrates**. This approach presents some new specific challenges and opportunities to improve the functional and structural properties of epitaxial BCTZ films on different types of substrates prior to applications.

This newly developed approach will also simplify the cumbersome transfer of piezoelectric BCTZ film from single crystal substrate to flexible substrate, thus meeting the strict requirements for the **successful implementation of piezoelectric BXT material in several applications**.

5:00 PM EL08.08.17
Theoretical and Experimental Study of Self-Powered Piezoelectric Sensors Response to Applied Force Xabier Garcia-Casas[1], Jorge Budagosky[1,2], Francisco Aparicio[2], Juan Sanchez-Valencia[1], Angel Barranco[1] and Ana Borras[1]; [1]CSIC, Spain; [2]Universidad de Sevilla, Spain

Nanogenerators are devices that can effectively convert mechanical energy into electricity. Thus, nanogenerators can be implemented in self-powered sensors for many applications such as internet of things, environmental monitoring, health and medical monitoring and security. In this emerging context, providing a theoretical model and a mathematical representation that links the electrical output signal with the applied mechanical stimulus is a key point to understand and optimize this type of self-powered sensors.
In this communication, we present a theoretical description about the derivation of the output signal of a piezoelectric self-powered sensor. Our work is based on the constitutive differential equation derived from Maxwell's equations [1], in which a change in the effective surface charge $\sigma(t)$ due to a certain stimulus ($\sigma_p(t)$) produces a displacement current through the dielectric layers in the nanogenerator. Unfortunately, the closed analytic expression of the solution under an arbitrary time dependent function $\sigma_p(t)$ cannot be integrated. Thus, we propose it as an expansion series of the successive time derivatives or antiderivatives of the stimulus, in our case the applied force. This theoretical approximation allows us to distinguish and analyze two different regimes depending on the device and measurement configurations. In the first regime, the output signal is proportional to the force, and is observed for high impedance loads and top-bottom device configurations (lower impedance matching). In the second regime, the output signal is proportional to the time derivative of the force, and occurs for low impedance loads and laterally connected devices (higher impedance matching). For intermediate conditions, more terms of the function series need to be considered.
Our theoretical considerations were corroborated for real devices [2,3], which were manufactured and measured under these regimes and the results were compared with numerical simulations. Thus, the presented models provide an effective theoretical foundation for understanding and predicting the sensitivity regions of nanogenerators and self-powered sensors for practical applications.

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5:00 PM EL08.08.19
Triboelectric Properties of Electrospun Biomaterial Nanofibers Shivangi Agarwal, Robert Ccorahua and Wenzhuo Wu; Purdue University, United States

This research systematically explores the different characteristics and advantages of producing the biomaterial-based nanofibers using the manufacturing technique of electrospinning. This manufacturing method is further employed under various parameters including the ratio of the solvents, the temperature, the voltage, the distance of the collector, and the pumping rate. These parameters affect the structure of the electrospun fibers and hence their triboelectric properties. Next, this research compares the triboelectric properties of our electrospun fibers with those of other common processing methods used for biomaterials. Moreover, we evaluate the mechanical and optical properties of electrospun biomaterial fibers. These properties further improve the strength, durability, and triboelectric properties of the produced nanofibers. Depending on various conditions, we determine their advantages and applications in the textile industry. The results of this research would be helpful in producing/researching a better method for an environmentally friendly biomaterial-based triboelectric sensor that can be used in smart textiles for cardiovascular sensors and other applications.

5:00 PM EL08.08.20
Piezoelectric Nanogenerator Platform Integrating Laterally Grown ZnO Nanowires within Topographic Nanograting Electrodes Minwook Kim, Kwangjun Kim and Jong G. Ok; Seoul National University of Science and Technology, Korea (the Republic of)

Portable electronic devices such as personal healthcare sensors and smart wearable devices are of emerging demand, which require low power consumption and/or self-powering function in order for obviating extra batteries. Piezoelectric materials and piezo-driven nanogenerators for converting mechanical motion into electrical energy can provide a practical solution to this end. Among many piezoelectric materials, zinc oxide (ZnO) has been a workhorse for various piezoelectric devices because it is biocompatible, environmentally friendly, and can be engineered into various structural configurations in a relatively easy way. Among various structural forms of ZnO, 1D structures such as nanowire arrays are suitable for piezoelectric-based nanogenerators because they can generate piezoelectric voltage through higher elastic strain upon mechanical deformation. As a process for synthesizing ZnO nanowires, various methods such as chemical vapor deposition (CVD) and hydrothermal reaction can be used [1]. However, the CVD-based synthesis and the high-temperature synthesis of the Zn-salt-based ZnO seed layer, which require a high-temperature environment, introduce limitations in the substrate material, which poses a great obstacle to the development of flexible piezoelectric nanogenerators to maximize device displacement. Addressing this issue, it is highly requested to grow ZnO nanowires through seedless hydrothermal synthesis on metal thin films. This research develops a piezoelectric nanogenerator framework that integrates ZnO nanowires inside a laterally arrayed, topographic electrodes on flexible substrates. In more detail, a nanograting pattern with an aspect ratio of 1:1 was formed on a PET substrate by UV nanoimprint lithography, and glancing angle deposition (GLAD) was performed at an angle of 45° to selectively deposit a metal thin film on the nanograting pattern, especially on the sidewall region. Depositing Ag on one side and depositing Au on the opposite side, another GLAD was performed by using the catalytically inactive Cr layer at an angle of 80° to selectively deposit a Cr layer only on the top of the nanograting pattern. Following our previously developed recipe [2], ZnO nanowires were then grown selectively between the patterned valleys, forming numerous bridges. Bending of the ZnO nanowires laterally connecting the adjacent nanograting electrodes occurs according to the bending of the base substrate, and piezoelectric polarization occurs in the countless cross-linked structures. Considering the electron affinity of ZnO (4.5 eV) and work functions of Au (5.1-5.47 eV) and Ag (4.52-4.74 eV), the Schottky junction and Ohmic junction are formed in between ZnO-Au and ZnO-Ag interfaces, respectively. [3]. Due to the difference in the junction, a rectification action preferentially occurs at the ZnO-Au junction, which suggests that the device can also be used as a DC nanogenerator.

Acknowledgment
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SESSION EL08.09: Soft Piezoelectric Materials
Session Chairs: Guylaine Poulin-Vittrant and Rusen Yang
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3008

8:30 AM *EL08.09.01
Materials and Structural Design Approaches of Intelligent Piezoelectric Fibers for Self-Powered Sensing Miso Kim; Sungkyunkwan University, Korea (the Republic of)

Electrospun polymeric piezoelectric fibers have considerable potential for shape-adaptive mechanical energy harvesting and self-powered sensing in biomedical, wearable, and industrial applications. However, their unsatisfactory piezoelectric performance remains an issue to be overcome. While strategies for increasing the crystallinity of electroactive β phases have thus far been the major focus in realizing enhanced piezoelectric performance, tailoring the fiber morphology can also be a promising alternative. Here, we summarize a collection of advances that push the boundaries to achieve a drastic enhancement of self-powered sensing performance by tailoring both material and structural properties of electrospun piezoelectric polymer fibers at multi-scales. As one of the recent advances, we demonstrate a distinctive design strategy for fabricating P(VDF-TrFE) fibers with surface porosity under ambient humidity conditions via nonsolvent-induced phase separation (NIPS). The key aspect of this material design is the porosity engineering of electrospun piezoelectric polymer fibers. Considering the thermodynamic properties of the P(VDF-TrFE) polymer solution in combination with the kinetics of electrospinning, we successfully implemented surface porosity in the P(VDF-TrFE) fibers under ambient humidity conditions. Notably, electrospun P(VDF-TrFE) fibers with higher surface porosity outperform their smooth-surfaced counterparts with a higher β phase content in terms of output voltage and power generation. Further engineering structural morphology of piezoelectric materials from molecular to fiber and yarn structures will be discussed as a route to achieving improvement in the key figures of merit for energy harvesting and sensing, along with our unfolding new understanding of the underlying physics.

9:00 AM EL08.09.02
Control of Artificial Relaxor Behaviors in Ferroelectric/Dielectric Superlattices Zishen Tian[1,2], Michael Xu[3], Jieun Kim[1,4], Hao Pan[1], Djamila Lou[1], Xiaoxi Huang[1], James M. LeBeau[3] and Lane Martin[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Massachusetts Institute of Technology, United States; [4]University of Wisconsin–Madison, United States

Piezoelectric materials are an important class of functional materials, with applications ranging from sensors and actuators to energy harvesters and magnetoelectric devices. Understanding the structure-property relations and tuning the response of piezoelectrics is, thus, of great technological importance. Relaxor ferroelectrics such as $(1\text{-}x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-}(x)\text{PbTiO}_3$ and $\text{BaZr}_x\text{Ti}_{1\text{-}x}\text{O}_3$, in particular, have drawn considerable attention as high-performance piezoelectric materials due to their ultrahigh piezoelectric coefficients, but the complex structure-property relation in relaxor ferroelectrics remains underexplored. In general, it is thought that the chemical disorder of the cations generates random fields which are essential to the formation of relaxor-like polar order. Thus, manipulation of the chemical order should provide a pathway to control the relaxor-like polar order, and hence the dielectric and piezoelectric response of relaxors. In conventional relaxors based on solid solutions, however, the deterministic control of chemical order is challenging due to the inherent randomness, which calls for a new platform for unveiling the structure-property relations of relaxors.

Recently, fabrication of artificial relaxors based on superlattices has been proposed as a novel pathway to achieve the chemical-order control at unit-cell precision [1]. Here, $[\text{BaTiO}_3]_m/[\text{BaZrO}_3]_n$ superlattices, wherein the nanoscale-polar structures are confined in the ferroelectric BaTiO_3 layers, while the dielectric BaZrO_3 layers tune the spacing between neighboring layers of nanoscale-polar structures, are proposed and used as a model system to explore the effect of chemical-order control. $[\text{BaTiO}_3]_m/[\text{BaZrO}_3]_n$ superlattices (m, n = 4-12 unit cells) were fabricated via pulsed-laser deposition and characterized by X-ray diffraction and atomic-resolution microscopy. These studies confirm the production of high-quality heterostructures, wherein the BaTiO_3 and BaZrO_3 layers are coherently strained to each other with relatively sharp interfaces in between. Dielectric permittivity measurements revealed significantly enhanced in-plane dielectric-maximum temperature T_m^IP in the superlattices compared with the solid solution $\text{BaZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (from 173 K to ≥433 K), and a trend of higher T_m^IP in superlattices with larger BaTiO_3-layer thickness (from 433 K to ≥573 K as m increases from 4 to 12). Subsequent measurements of hysteresis loops and third-harmonic nonlinearity revealed relaxor-like behavior in the superlattices with the smallest BaTiO_3-layer thickness and ferroelectric-like behavior in the superlattices with larger BaTiO_3-layer thickness, with the crossover appearing between $m = 4$ and $m \geq 8$. Piezoelectric measurements along the out-of-plane direction revealed that the effective piezoelectric coefficient d_{33} is enhanced in superlattices with the smallest periodicity ($m = n = 4$, d_{33} = 7.8 pm/V) compared to both superlattices with larger periodicities ($m = n = 12$, d_{33} = 4.8 pm/V) and the solid solution (5.4

pm/V). Higher $BaTiO_3$ composition in the superlattice further enhances the piezoelectric response ($m = 12$, $n = 4$, $d_{33} = 12.3$ pm/V).

Altogether, these results suggest that an artificial relaxor phase can be achieved in ferroelectric/dielectric superlattices such as $[BaTiO_3]_m/[BaZrO_3]_n$, wherein the chemical order can be deterministically controlled and the relaxor behavior can be manipulated. Considering both the dielectric and piezoelectric response can be tuned by the chemical order, this provides a novel platform for exploring the complex structure-property relation in relaxor ferroelectrics, and opens up future opportunities for the design of high-performance piezoelectric superlattices.

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9:15 AM EL08.09.03
Synthesis of Ferroelectric PVDF-TrFE Nanoparticles for Ultrasound-Driven Electrostimulation Zulmari Silva, Yizhan Wang, Corey Carlos, Jun Li and Xudong Wang; University of Wisconsin--Madison, United States

P(VDF-TrFE) is a well-known ferroelectric co-polymer that can spontaneously present in its piezoelectric crystalline phase. The size and shape control in the nanoscale would open many opportunities in modern biomedical applications. In this work, we synthesized nanostructured P(VDF-TrFE) NPs through a self-assembly synthesis method which resulted in spherical NPs. The as-received NPs had spiked surface features, which offer substantially large high surface to volume ratio. The NP was formed through the agglomeration and assembly of P(VDF-TrFE) flakes formed during nucleation into the 3D spherical structures due to Ostwald ripening process. The NPs size and morphology can be controlled by tunning the rate of the reaction between the solvents used in the synthesis. The formation of the crystalline ferroelectric β phase of the as-grown NPs could be further improved through an annealing process. Piezoelectric force microcopy revealed a qualitative description of the converse piezoelectric structure-property relationship. Because of its strong piezoelectric property, the as-received NPs can effectively respond to external ultrasound stimuli and provide localized electric field. This self-generated piezoelectricity enables a self-powered electrostimulation that may be used to achieve many therapeutic purposes. Our studies further showed that these piezoelectric NPs may be an effective approach toward non-invasive cancer treatments through an irreversible electroporation (IRE) effect.

9:30 AM EL08.09.04
Wet Spun Core-Shell Fibers for Wearable Triboelectric Nanogenerators Doga Doganay, Melih O. Cicek, Onuralp Cakir, Onur Demircioglu and Husnu E. Unalan; Middle East Technical University, Turkey

The advancements in communication technologies and the cooperation of different disciplines such as the internet of things, artificial intelligence and data science have made a significant contribution to the development of wearable electronic devices. Rechargeable batteries and capacitors are currently used to power up these devices. However, the shortcomings of these power supplies limit the use of wearable electronics. First, they are heavy and bulky that reduce comfort. In addition, their capacity is limited. They require frequent charging, and they carry potential risks. Triboelectric nanogenerators (TENGs) have a significant potential to be used as a reliable, inexhaustible, sustainable, and economically feasible power source. In this study, core-shell TENG electrodes were fabricated via co-wet spinning process. The core of the TENG electrodes were consisted of thermoplastic polyurethane (TPU) matrix and carbon black (CB) and silver nanowire (Ag NW) additives. The core fibers were responsible to carry induced electrons resulting from contact electrification. The fabricated shell layer was bare TPU and acted as tribo-charged surface. The effect of TPU concentration within the doping solution for the shell on the output performance of the TENGs were investigated. The open circuit voltage, short circuit current, open circuit charges and maximum power output of the 1 cm long core shell fiber TENGs (PDMS/Al was the counter electrode) were recorded as 1V, 20 nA, 8 nC and 0.07 µW/cm, respectively. Moreover, the output performances of the core shell fibers were also quite stable up to 50 % strain. These results indicated that, wet spun core-shell fibers carry great potential for wearable TENGs.

9:45 AM EL08.09.05
Self-Powered Wireless Sensing Systems Enabled by Triboelectric-Discharge Effect Haoyu Wang[1] and Yunlong Zi[1,2]; [1]Chinese University of Hong Kong, China; [2]The Hong Kong University of Science and Technology (Guangzhou), China

With the rapid growth of the smart city, wireless sensors are highly preferred in plenty of application scenarios. However, traditional wireless sensing and transmission technology still requires multiple modules for sensing, signal modulation, transmission, and power, making the whole system bulky, rigid, and costly. The posed challenges, including but not limited to the distributed power supply and wireless signal transmission, limit the application scenarios of traditional sensing nodes. To address the challenges of real-time sensing, power supply, and wireless signal transmission in current wireless sensors, we proposed a paradigm shift wireless sensing solution based on the breakdown discharge–induced displacement current. With the working principle of triboelectrification, electrostatic induction, and breakdown discharge, the input mechanical trigger can directly convert to electromagnetic (EM) wave to achieve wireless signal transmission in this solution. Through that, we can combine the abovementioned functional modules in a single unit of self-powered wireless sensing e-sticker (SWISE), which is small (down to 9 mm × 9 mm), thin (down to 95 µm), light (down to 16 mg), intrinsically flexible, and fully self-powered without using batteries or cables, whose signal can be detected over 30 m away omnidirectionally. Furthermore, SWISEs have functions of multipoint motion sensing and gas detection in fully self-powered manner. On the basis of SWISE, through studies about EM wave characteristics and the equivalent circuit model, we put forward the signal modulation strategy of the SWISE wireless signal achieved through the parameters in the equivalent circuit model, such as resistance, capacitance, and inductance, where the experimental result matched the theory. Based on this signal modulation strategy, we couple commercial sensors of different mechanics with the EM wave generated by the triboelectric-discharge effect to realize a general self-powered wireless sensing solution for various physical signals, where the information of the sensors is coupled into the EM wave by SWISE and can be decoded by the receiver. Then, a self-powered wireless temperature and pressure sensing system is demonstrated, with an error rate down to 0.18%, and a multi-point sensing array is also realized for broad potential applications. To conclude, the triboelectric-discharge effect-enabled self-powered wireless sensing system proposes a self-powered wireless information transmission platform that is compatible with various commercial sensors with different physical signals detection abilities, which promises great potential for self-powered wireless sensing in the smart city and Internet of Things, such as robotic dynamic sensing, infrastructure monitoring, human-machine interface, etc.

10:00 AM BREAK

SESSION EL08.10: Triboelectric Devices
Session Chairs: Ying-Chih Lai and Rusen Yang

Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3008

10:30 AM EL08.10.01
Engineered Carbon Nanohybrids for Wearable Moist-Electric Generators Sang-Joon Park, Byeong-Cheol Kang and Tae-Jun Ha; Kwangwoon University, Korea (the Republic of)

Energy-harvesting electronics have been of great scientific and technological interests in the fields of self-powered systems utilized for powering various electronic applications [1]. Among energy harvesting technologies, nanogenerators such as triboelectric, piezoelectric, and pyroelectric nanogenerators have been widely investigated owing to their simple device configuration and power generation [2]. However, instantaneous alternating output current and low energy conversion efficiency generated by these types of nanogenerators limit their potential in self-powered electronics requiring sustainable direct current power [3]. In this presentation, we will demonstrate engineered carbon nanohybrids for high-performance moist-electric generators (MEGs) which enable to produce continuous and stable electricity for self-powered systems. The mechanism regarding effective collecting charges directly generated from atmospheric humidity is discussed by investigating the incorporation of engineered carbon nanohybrids. We will also demonstrate wearable MEGs exhibiting the improved electric characteristics of open-circuit voltage and short-circuit current under different relative humidity conditions and long-term operational stability against mechanical bending stress. We believe that this work can open-up a new route for emerging energy materials for self-powered nanogenerators.

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Acknowledgments
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10:45 AM EL08.10.03
Trifunctional Smart Finger Based on Triboelectric and Hygroelectric Hybridized Mechanism Xiaoting Ma, Jiaming Zhou, Jingyi Gao and Dong-Myeong Shin; The University of Hong Kong, China

Electronic skin (E-skin) mimicking the sensory functions of human skin holds huge application potential in fields such as robotics, prosthetics, healthcare, and human machine interface. However, most E-skin sensors are able to only detect one or two types of stimuli, which greatly limits their capabilities and further applications. Here, we present a trifunctional smart finger having the advantages of self-powering, simple structure, compacted size and multiple functionalities. The sensory unit of the smart finger was innovatively designed with an aluminum electrode, a gold electrode and a layer of single-ion conducting Nafion film which functions both as the triboelectric and hygroelectric layer. The instantaneous triboelectric signal can simulate the signal of fast adapting mechanoreceptors whereas the sustained hygroelectric signal can imitate the signal of slow adapting mechanoreceptors. Meanwhile, as the Nafion film is hygroscopic material, the triboelectric and hygroelectric signals can also reflect the humid level of the environment. By this triboelectric and hygroelectric hybridized mechanism, the smart finger is capable of simultaneously sensing the static pressure, dynamic forces and environmental relative humidity (RH). Assisted by machine learning data processing, the pressure, vibration frequency and RH of environment can be identified at an accuracy rate as high as 84.0%-100.0% by the smart finger. Furthermore, the sensing capability of the sensory units were well maintained even after being scaled into a 5×5 sensory array, proving the scalability and effectiveness of this hybridizing strategy. Such a versatile smart finger not only provides the fundamental insights into the hybridization of triboelectricity and hygroelectricity, but also a new paradigm of multiple functional sensors with extremely simple structure and excellent accuracy rate of perception for mimicking the human finger which has the highest density of sensory receptors in human skin.

11:00 AM EL08.10.04
Power Management of Triboelectric Nanogenerators for Self-Powered Electronics Applications Xiaoting Ma, Jiaming Zhou and Dong-Myeong Shin; University of Hong Kong, Hong Kong

In the era of the internet of things, wearable electronic technology can help citizens to avail advanced features and characteristics in different facets of their daily life. These wearable electronics are powered by current energy storage devices that need regular recharging, but the increasing demand for continuous operation is driving research into new power supplies that can deliver stable electricity. One major development has been a conceptual shift away from grid supply charging toward self-powering, in which the devices continuously operate without external power feeding. Triboelectric nanogenerators (TENGs) are emerging as a power supply for self-powered electronics due to their light weight, simple fabrication, diversity in material selection, and high energy conversion efficiency, but the power output of TENGs needs to be trimmed to power the electronics stably. There is a need for flexible power management for self-powered electronic applications, particularly for wearable devices. In this talk, I will address several strategies for power management of TENGs to achieve high-performing self-powered electronics, including voltage trimming, humidity insensitivity, and durability control.

SESSION EL08.11: Energy Conversion and Triboelectricity
Session Chairs: Miso Kim and Guylaine Poulin-Vittrant
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3008

1:45 PM EL08.11.02
Machine Learning Enabled Triboelectric Textile Sensing System for Object Recognition Shujia Xu[1,1] and Wenzhuo Wu[1,1,2]; [1]Purdue University, United States; [2]Regenstrief Center for Healthcare Engineering, United States

The human tactile sensation can perceive the properties of diverse objects when grasping objects. The development of smart artificial tactile sensory systems with the dexterity of human grasp remains a challenge. The self-powered triboelectric tactile sensor is attractive to be applied for grasp tactile sensing due to its simple construction, and ubiquitous triboelectric effect in daily life. The integration of machine learning techniques can reveal hidden information from tactile signals and enable intelligent sensing applications. Here, we develop a machine-learning enabled smart glove system based on triboelectric tactile sensors for object recognition, which could "feel" the properties (e.g., surface) of objects. TENG sensors are integrated into the glove to perceive information about various objects. The smart glove system equipped with self-powered triboelectric sensors while endowing dexterous hand manipulation of objects is promising for various emerging applications in human-machine interface, mixed-reality, robotics, etc.

2:00 PM EL08.11.04
***In Situ* Quantitative Study of Nanoscale Contact Electrification Between Identical Materials** Ruizhe Yang and Jun Liu; University at Buffalo, The State University of New York, United States

Contact electrification (CE or triboelectrification) is a well-known phenomenon in which charge transfer occurs between two distinct materials. In previous studies, the CE between insulators, semiconductors and metals has been widely discussed, while CE involving two identical materials has drawn increasing attention due to their implication for industries such as pharmaceutical powder processing, optics manufacturing and etc. It is generally accepted that the triboelectric effect depends on the transfer of electron ions and/or charged molecular fragments. A common idea is that the differences in work function of two contacting materials drive charge transfer, the Volt-Helmholtz hypothesis. However, this fails to explain many experimental observations, such as charging that occurs when two pieces of the same material are rubbed against each other. Although work function difference is important, it is not the only cause of triboelectricity. Here, we design and demonstrate the in-situ triboelectric characterization between two identical material based on a combination of contact-mode atomic force microscopy (AFM), Kelvin Probe Force microscopy (KPFM) and conductive AFM (CAFM). By analyzing force-dependent surface charging (charge density), *I-V* characterization (effective energy barrier height) and etc., the results indicate that flexoelectric effect may be involved in triboelectrification, where a coupling of strain gradients during asperity contacts, polarization and local band bending.

2:15 PM BREAK

3:15 PM EL08.11.05
Output Performance of the Triboelectric Nanogenerator with Carboxymethylated Cellulose Nanofiber and Perfluoroalkoxy Alkane Films Deepika Thakur[1], Soonmin Seo[2] and Jinho Hyun[1]; [1]Seoul National University, Korea (the Republic of); [2]Gachon University, Korea (the Republic of)

The carboxymethylated cellulose nanofiber (CM-CNF) and perfluoroalkoxy alkane (PFA) films were used for the fabrication of triboelectric nanogenerator (TENG). The fabrication of CM-CNF/PFA TENG was simply done by origami based folding technique. After drying the CM-CNF suspension at room temperature, the thin film with desirable dimension was obtained for the fabrication of TENG. The fabricated TENG device consisted of 5-layer folded structure, and could be stretched, compressed and released based on the contact-separation mode while operation. The carboxymethylation reaction time and the degree of substitution had the effect on triboelectric charge generation of CM-CNF film. Also, mechanical strength of CM-CNF film was dependent on the carboxymethylation degree. The output performance of TENG with CM-CNF film having different carboxymethylation content was analyzed systematically. The direct influence of functionalized CNF through carboxymethylation was first time explored for the triboelectric charge generations in this work.

3:30 PM EL08.11.06
Output Performance Enhancement of Perovskite Composite Triboelectric Nanogenerator by Light Modulated Surface Charge Density Minje Kim, Sol Lee, Viet Anh Cao, Pangun Park and Junghyo Nah; Chungnam National University, Korea (the Republic of)

Triboelectric nanogenerators (TENGs) have gained attention due to their ability to generate relatively high output power by excavating various vibrating resources that exist in our environment. To date, various efforts, such as surface patterning, chemical functionalization, and dielectric permittivity modulation have been made to improve output performance of the TENGs. However, the output performance of TENG has still been limited due to relatively low current density as the current induction relies only on the triboelectric frictional surfaces. Recently, methylammonium lead triiodide organometal halide ($MAPbI_3$) perovskite has been extensively investigated as light-emitting diodes and photodetectors due to its excellent light absorption capability. The irradiated light separates electrons and holes in $MAPbI_3$, accumulating the separated electrons and holes on the top and bottom surfaces. Therefore, by exploiting the light absorption property of perovskite layer as a friction layer, the surface charge density of the friction surface can be modulated by light irradiation. However, it is difficult to adopt as a triboelectric friction layer because it can easily deteriorate due to a physical impact applied to the perovskite layer in the friction contact separation mode.
In this work, we demonstrate the fabrication and performance of the TENG fabricated using ferroelectric $MAPbI_3$ and ferroelectric PVDF-TrFE polymer composite. By composite formation, the frictional surface charge density can be effectively modulated by light irradiation, to increase the output performance of TENG. In addition, degradation of the perovskite was effectively prevented since it is packaged inside PVDF matrix, guaranteeing a long-term stability. Besides, electrical polarization can also be applied to further increase surface charge density because the composite layer is composed of ferroelectric materials. The approach introduced here effectively enhances the surface charge density and thus output performance of TENGs.

3:45 PM EL08.11.07
Nanocomposite Materials for Eco-Friendly Tribo- and Piezoelectric Nanogenerators Bernd Wicklein[1,2] and Il-Kwon Oh[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Materials Science Institute of Madrid, Spain

Circularity and sustainability of energy devices are gaining importance in the face of growing global energy demand, which enlarges the electronics waste as well as increases the scarcity of critical energy materials. Triboelectric nanogenerators (TENG), which have a great potential in providing renewable energy, often lack sustainability themselves as the constituting materials are mostly petrol-based, fluorinated polymers and metals.[1,2] Therefore, revalorized biomass like lignocellulosics and agri-food residues are increasingly considered as triboactive components.[3] Similar concerns surround piezoelectric nanogenerators (PENG), where lead-free inorganic materials and natural polymers are sought as new sustainable components of PENGs.[4]
Here, we present preliminary results of eco-friendly nanogenerators based on different bionanocomposites. Biopolymers like cellulose, keratin, lignin, chitosan and alginate are investigated both as coating and matrix with different fillers such as nanocarbons and barium titanate (BTO) particles in order to tune the triboelectric and piezoelectric properties. In addition, the role of porosity is a further parameter under investigation both for the electrical output and complementary properties. Herein, carbon fiber assemblies and brushes are also explored as substrates for the construction of 3-dimensional triboactive elements. Finally, contact-separation and single-electrode nanogenerators are constructed and tested for different insulation and harvesting applications.

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4:00 PM EL08.11.08
Lignin-Based Bio-Triboelectric Films for Self-Powered Wearable Devices Robert Ccorahua[1,1], Yi Zheng[2] and Wenzhuo Wu[1,1,1]; [1]Purdue University, United States; [2]Kansas State University, United States

Lignin is a complex biopolymer that keeps the structural integrity of plants and represents ~ 40% (wt.%) of the plant biomass. It is also the second largest biopolymer on earth after cellulose. This naturally abundant material is a potentially renewable resource that is now part of transforming forest and agricultural feedstock towards a more sustainable resource management. However, a dominant aromatic structure hinders lignin's processability using non-organic solvents. Herein, we manufactured lignin films through blade-coating by implementing a new water-based environmentally friendly processing method without using organic or corrosive solvents. Lignin-based films were prepared by various blade-coating manufacturing parameters and the triboelectric performance was evaluated. The films manufactured by the optimal parameters were compared to pure biopolymer films, showing outstanding properties as a triboelectric material. Moreover, we assessed the performance of the films as self-powered wearable devices in human-machine interface applications. Our environmental-friendly processing method is expected to promote the broader application of lignin for wearable devices and other emerging technologies.

SESSION EL08.12: Poster Session: Nanogenerator and Piezotronics 2
Session Chairs: Xudong Wang and Rusen Yang
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL08.12.01
Humidity-Tolerant Moisture-Driven Energy Generator with Bi-Layer Aerogel/Hydrogel Asymmetrical Structure Kaiying Zhao, HoYeon Kim and Cheolmin Park; Yonsei Univeristy, Korea (the Republic of)

Free-standing and film-type moisture-driven energy generators (MEGs) that harness the preferential interaction of ionized moisture with hydrophilic materials are interesting owing to their wearability and portability without needing for a water container. However, most such MEGs work in limited humidity conditions where moisture is rapidly evaporated from the devices with a moisture gradient. Herein, we present a high-performance MEG with excellent humidity tolerance and sustainable power-production capability. The bilayer-based device comprises a negatively surface-charged, hydrophilic MXene ($Ti_3C_2T_x$) aerogel and polyacrylamide (PAM) ionic hydrogel. The preferential selection on the surface of the porous MXene aerogel of positive charges supplied from the salts, and water in the hydrogel is predicted by the first principle simulation, resulting in a high electric output in a wide relative humidity range: from 20% to 95%. Our MXene aerogel MEG produces a maximum open-circuit voltage, short-circuit current density, and power density of approximately 570 mV, 1160 μA cm^{-2}, and 24.8 μW cm^{-2}, respectively. Furthermore, by replacing the hydrogel with an organohydrogel of PAM that has excellent water retention and structural stability, a device with long-term electricity generation is realized, which has an output voltage lasting for more than 15 days in a broad temperature range (from –20 to 80 °C). Our MXene aerogel MEGs connected in series supply sufficient power for commercial electronic components in various outdoor environments. Moreover, a MXene aerogel MEG is mounted on the skin for recognizing finger bending and facial expression in the variation of its output current.

5:00 PM EL08.12.02
Effect of Various Ionic Liquids on the Performance of Triboelectric Nanogenerators Sujeong Gwak, Hyeonseo Joo and Ju-Hyuck Lee; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

In recent years, renewable and clean energy are attracting attention due to the increase in environmental problems caused by using limited traditional resources. Such renewable energy has excellent energy potential, but it also has a large amount of wasted energy, requiring developed technology to harvest energy sources effectively. Nanogenerators can be suitable, and different types of nanogenerators have been developed recently. A triboelectric nanogenerator (TENG) is one type of nanogenerator that makes electricity by converting mechanical energy into electrical energy. It is based on contact electrification and electrostatic induction effect by selecting two different suitable triboelectric materials and contacting each other.
All materials around us can have triboelectric properties; generally, they can represent them in the triboelectric series. When two materials with a significant difference in charge affinity on the triboelectric series are separated after contact with an external force, it shows a high output performance. From the material perspective, one of the most widely studied dielectric materials, the copolymer of (polyvinylidene fluoride) (PVDF) such as poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), has high dielectric constant and highly electronegative fluorine C-F bond which cause enormous charge accepting properties and. However, there is a limit to associating with only traditional triboelectric materials to improve the TENG output.
To advance the polymer charge accepting properties for increasing the lack of energy conversion efficiency, several materials were blended with polymer, but still, it has environmental and non-flexibility issues to use as an electrolyte. Therefore, ionic liquid (IL) has been reported for available materials with polymer electrolytes to cover up the disadvantages recently. It can enhance the TENG output of their high capacitance and mobility of ions in the polymer electrolyte layer. The specific capacitance of material can be defined as a dielectric constant which can significantly increase the charge density accumulation of materials surface while each material is physically contacted. Also, an electric double layer (EDL) is formed by the charge accumulation of mobile cations and anions when external forces are applied. It is also used as a plasticizer, making the polymer electrolyte flexible and boosting ionic conductivity by weakening the polymer chains to increase the mobility of ions. For this, varying each cation and anion type may affect the polymer electrolyte properties for enhancing the TENG output performance. Still, the effect of various types of IL in polymer electrolyte studies on improving TENG output performances is lacking; investigation of multiple varieties of IL on triboelectric properties is needed.

5:00 PM EL08.12.06
Distributive Role of Frictional-Heat on Sliding Contact Electrification—*In Operando* Measurement of Surface Charge and Temperature Variation Dong woo Lee, Daesol Kong, Young Joon Ko and Jong Hoon Jung; Inha University, Korea (the Republic of)

In-Operando technology can contribute to understanding the fundamental mechanisms and the mechanism of triboelectric charging through measurement of the relevant physical quantities during physical contact of two materials, which has not yet been clearly elucidated. For this goal, the correlation between frictional heat and triboelectric charge in metal-polymer triboelectric nanogenerators is reported by *in-operando* temperature measurements. Fluorine-doped tin oxide (FTO) metal slides under different contact pressures between polydimethylsiloxane (PDMS) polymers according to different degrees of cross-linking made by mixing ratios. Both triboelectric charge and temperature change increase and saturate with different time constants. Specifically, saturated triboelectric charge and temperature increase as contact pressure increases. In contrast, the saturated triboelectric charge increases, and the saturation temperature decreases with the mixing ratio increasing. X-ray photoelectron spectroscopy and thermogravimetry measurement showed that the chemical bonds rupture event during the triboelectrification and charged materials transferred from PDMS to FTO according to the mixing ratio and sliding time dependent triboelectric charge. This shows that frictional heat is distributed to bond failure and temperature change through the activation energy and friction coefficient of PDMS. Measurements of *in-operando* temperature changes provide important information on the specific coupling of triboelectric charging and detailed charge transfer processes during physical contact.

5:00 PM EL08.12.07
Stretchable and Transparent Plasticized PVC-Gel-Based Triboelectric Nanogenerators for Energy Harvesting Seung-Ju Oh[1], Insun Woo[1], Dong-Heon Han[1], Jae Uk Yoon[1], Hyun-su Park[1], Jin Woo Bae[1], Eun-Ho Sohn[2,3] and Jaewon Choi[4]; [1]Korea University of Technology and Education, Korea (the Republic of); [2]Korea Research Institute of Chemical Technology, Korea (the Republic of); [3]University of Science and Technology, Korea (the Republic of); [4]Jeongseok Chemical R&D Center, Korea (the Republic of)

Stretchable and Transparent triboelectric nanogenerators (STTENGs) for wearable electronics are in significant demand in the area of self-powered energy harvesting and storage devices. Here, a single-layer STTENG based on the plasticized polyvinyl chloride (PVC)-gel is proposed for mechanical energy harvesting. In particular, the plasticized PVC-gel plays a crucial role in both a dielectric and a conducting layer in the STTENG. The STTENG demonstrates high stretchability (~250%), high transparency (~91%), and great dielectric property (190 times than intrinsic PVC). Moreover, the plasticized PVC-gel-based STTENG shows more negative triboelectric property rather than the unplasticized PVC-based triboelectric nanogenerator. The output performance of the STTENG reaches 24.7 V and 0.83 µA, which is 20 times much higher output performance compared to the unplasticized PVC-based triboelectric nanogenerator. In addition, the STTENG at 80% stretched states even shows stable output voltage and current without the performance degradation. Consequently, the STTENG can be potentially expected to be used in stretchable wearable electronics, electronics skins, soft robots, smart displays, etc.

5:00 PM EL08.12.08
Switchable Power Generation in Triboelectric Nanogenerator Enabled by Controlled Electrostatic Discharge Jiaming Zhou, Xiaoting Ma, Jingyi Gao and Dong-Myeong Shin; University of Hong Kong, Hong Kong

As the main energy supply for people's daily life, the energy created by nuclear and coal plays an important role in the history of human development. However, at the same time, they also hinder environmental protection and sustainable development. With the growing awareness of the energy crisis, renewable green energy has been proposed as a promising solution. Among all types of energy, water energy has attracted great interest due to its abundance and recyclability. Humans have developed very well-established methods to harvest large-scale hydropower from waterwheel irrigation in ancient times to the current hydroelectric power generation. For small-scale water such as droplets, triboelectric nanogenerators (TENGs) have emerged as one of the main approaches to convert these ambient mechanical energies into electrical energy. The application of TENGs in droplet energy harvesting has been extensively studied by researchers. However, conventional droplet-based TENGs utilize the periodic sliding of droplets from the friction surface to generate pulsed alternating current (AC), which cannot be directly used as a power source. A rectifier bridge or a power management circuit used to transfer AC into direct current (DC) will greatly reduce the portability of TENGs.
In nature, DC discharge usually occurs during lightning; when the electric charge in the cloud accumulates to a certain strength, it will form a circuit (ie, lightning) by breaking down the air. The lightning tends to require extremely large voltages (several thousand volts), but the required voltage drops dramatically during the breakdown at extremely small distances (only 327V at 7.5 microns). Herein, inspired by the phenomenon of lightning, a droplet-based direct current triboelectric nanogenerator (DDC-TENG) without any rectifier is designed. It utilizes the electrostatic potential generated between the water droplet and the triboelectric layer, and based on the dielectric breakdown mechanism, a small gap is formed between the triboelectric layer and the electrode through photolithography. When the water droplet hits the triboelectric layer, the large voltage generated from the triboelectric layer can break down the air in the gap. Using this mechanism, this sandwich structure single electrode mode DDC-TENG can generate a unidirectional voltage (over 3 V) and unidirectionally transferred charge (maximum 0.63nC) in the periodic motion of droplets. This new design provides a new way to harvest the micromechanical energy of water droplets and directly use them in devices. Moreover, the flexible DDC-TENG produced by using flexible ITO film can be attached to rough and uneven places, which greatly broadens the application area. And due to the increase in the size of the device, the maximum voltage can reach more than 10V, and the maximum current exceeds 160nA.

5:00 PM EL08.12.09
Umbrella-Shaped Wind TENG for Omnidirectional Energy Harvesting WooYoung Jang[1,2], Dokyung Kim[1] and Jaesam Sim[1]; [1]Korea Institute of Industrial Technology, Korea (the Republic of); [2]Chonnam National University, Korea (the Republic of)

Novelty / Progress Claim(s)
In this study, we have developed a 3D(three dimensional) stereoscopic structure-based triboelectric nanogenerator for low speed and omnidirectional wind harvesting. This harvester consists of three stereoscopic structures each independently suspended on a pole by a thread that one stereoscopic structure of polytetrafluoroethylene (PTFE) material is located between two stereoscopic structures using aluminum (Al) material. The thread allows the stereoscopic structures to move freely, resulting to induce high kinetic energy even at low wind speeds. The stereoscopic structure design makes it to harvest electrical energy in all wind directions when wind is applied. The developed harvester exhibited output voltage and current of 2.584 mV and 0.169 µA at low wind speed of 0.5 m/s, and it was confirmed that the output power was increased as the wind speed was strong from 0.5 m/s to 4.0 m/s.
Background / State of the Art
Wind-driven triboelectric nanogenerator (WTENG) is a renewable energy source. WTENG is largely divided into two categories classified as low and high wind speed. It is easy to harvest energy in a high-speed environment, but there are limitations to the application because the universal wind speed on the surface is range from 2.5 to 4.0 m/s [1]. In addition, since the wind is not flow in one direction, harvesting the energy at low wind speed in all directions is necessary for actual environments to [2].
Description of the New Method or System
The three stereoscopic structures are arranged vertically in overlapping. This design induces to amplify kinetic energy through a chain reaction when the stereoscopic structures move by the wind. Unlike flapping-based WTENG harvesting energy in most unidirectional and bi-directional directions, our WTENG using thread stereoscopic structure allows energy harvesting in all directions of 360 degrees. When the Al stereoscopic structure at the top moves to the middle stereoscopic structure of PTFE contacts by applied wind, the electron flows from the Al stereoscopic structure at the top to the Al stereoscopic structure at the bottom. After that, the top stereoscopic structure and middle stereoscopic structure are separated, and then the middle stereoscopic structure of PTFE contacts on the Al stereoscopic structure at the bottom sequentially. This motion allows that the electron moves in reverse direction to harvest energy.
Experimental Results
The generated kinetic energy according to the number of moving stereoscopic structures. First case is that only middle stereoscopic structure of PTFE

moves whereas two stereoscopic structures of Al material are fixed. Second case is the reverse condition of the first case, and in third case, all stereoscopic structures move freely. In three cases, output voltages are 4.368 V, 8.8 V and 12.626 V, respectively. The output voltage in case of all stereoscopic structures moving is 2.89 times higher than that of first case. This is because the larger the number of stereoscopic structures, the larger the area of received the wind, and the kinetic energy is amplified as those stereoscopic structures sequentially collide. It can be seen that electrical energy was successfully harvested at the wind speed from 0.5 m/s to 4.0 m/s. As a result of impedance matching, the output power and voltage have maximum at an external load of 60 MΩ. It is confirmed that the open circuit voltage and short circuit current are 25.66 V and 0.726 µA. As a result, the developed device was confirmed to be capable of harvesting wind energy range from 0.5 to 4.0 m/s in omnidirectional wind.

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5:00 PM EL08.12.10

2D MXene Embedded Sulfur-Rich-Polymer for High-Performance Triboelectric Negative Material Woongbi Cho[1], Hyeonhoo Lee[1], Sungsu Kim[2], Minbaek Lee[2], Tae Hee Han[1] and Jeong Jae Wie[1]; [1]Hanyang University, Korea (the Republic of); [2]Inha University, Korea (the Republic of)

Recently, we reported an inverse-vulcanized sulfur-rich polymer (SRP) as a new framework in a series of tribo-negative materials via direct F_2 gas treatment on surface and phase-separation of poly(pentafluoro styrene) (PPFS), in order to achieve high-performance and waste-based triboelectric nano-generator (TENG). However, utilization of fluorine materials can cause environmental pollution. In addition, further enhancement of power density is required from previous systems to stably operate devices or sensors with high durability. Herein, an emerging 2D-material, MXene ($Ti_3C_2T_x$) was introduced to SPR due to its plentiful negatively charged terminal groups (-F, -OH, -O, -Cl). We construct vertical contact separation mode TENG by assembling the SPR/MXene composites with a minute amount of MXene and aluminum as a counterpart. In case of a 4-inch wafer sized TENG, the power density of SRP/MXene composites-based TENG reached 3.89 W m^{-2} after corona discharging to the TENG. We believe that our inverse-vulcanized SRP/MXene composites can contribute to constructing waste-based and self-rechargeable devices driven by power generations of the TENG.

5:00 PM EL08.12.11

Triboelectric Generation in Harsh Environments—Temperature and Pressure Dependence Under Methane and Crude Oil Catia Rodrigues, Andre Pereira and Joao Ventura; University of Porto - Faculty of Sciences, Portugal

There is an increasingly need to monitor crucial safety and environmental parameters in extraction wells in order to prevent disasters. However, present solutions to feed sensors are inefficient, costly and risky. Furthermore, present energy harvesting technologies do not cope well with the extreme conditions encountered in oil and gas wells that operate at high temperatures, high pressures and involve a highly corrosive environment. The demonstration of new energy harvesting technologies able to operate in these extreme conditions would make a leap forward in their applicability. Triboelectric nanogenerators appearing just in 2012 are the most promising energy harvesting technology able to convert ambient mechanical energy into usefull electrical power [1-3]. Here, we demonstrated a triboelectric nanogenerator (TENG) able to generate electrical energy in harsh conditions similar to those found in extraction wells (pressures up to 830 bar and temperatures up to 120 C) in direct contact with methane and crude oil [4]. The electrical performance of the assembled device shows a slight increase with increasing pressure from 28 to 119 bar, in methane. However, the electrical outputs decreased strongly with increasing temperature from 25 up to 80 C. This clearly demonstrates that temperature is the most critical parameter for TENGs operating in harsh environments. Furthermore, energy harvesting experiments performed in crude oil reveal a decrease of the electric outputs with increasing crude temperature and pressure, but the assembled device continued to generate electrical energy up to pressures of 830 bar and temperatures of 120 C. This study clearly demonstrates the suitability of triboelectric devices to harvest energy in harsh environments opening a wide new range of possible applications.

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5:00 PM EL08.12.12

Self-Poled Flexible Piezoelectric Devices Kim Hwanmin[1], Do Hyeon Woo[1,2], Hyoung-Su Han[1], Chang Won Ahn[1], Jong Hoon Jung[3], Tae Heon Kim[1] and Ill Won Kim[1]; [1]University of Ulsan, Korea (the Republic of); [2]Quintess Co., Ltd., Korea (the Republic of); [3]Inha University, Korea (the Republic of)

Flexible piezoelectric thin films have been widely studied recently as biomedical devices, MEMS, nano devices, body wearables, and energy harvesters. The flexible piezoelectric element is manufactured through an etching and transport process. There is a risk of damage and deterioration of properties in the process. Therefore, to avoid damage and deterioration of the piezoelectric film during the etching, transport, and poling processes, a simple fabrication process for an excellent flexible piezoelectric device is highly desirable [1]. In this study, $Pb(Zr_{0.52,}Ti_{0.48})O_3$ (PZT) thin films were directly grown on flexible metal foil substrates to fabricate flexible piezoelectric thin film devices without etching and transfer processes, and the ferroelectric and piezoelectric properties were investigated. The fabricated flexible PZT (1mm)/$LaNiO_3$/Metal foil heterostructure piezoelectric device shows a piezoelectric coefficient (d_{33}) of 89 ± 11 pC/N without the poling process, which means as-grown PZT film has a specific polarization alignment without the poling process. The self-polarization phenomenon in the film occurs from the metal foil substrate because the thermal expansion coefficient (α) if metal foil is relatively larger than the PZT film ($\alpha_{\text{metal foil}} \sim 18 \times 10^{-6}\ K^{-1}$, $\alpha_{PZT} \sim 8.5 \times 10^{-6}\ K^{-1}$) [2,3]. Due to different thermal expansion coefficients, the PZT film receives compressive stress (-724 MPa) from the metal foil substrate during the film growth at a high temperature (650°C) and then reduces to room temperature. In the PZT film, a strain gradient occurs because the compressive stress of the lower portion of the PZT film (interface between the substrate and the PZT film) is stronger than that of the upper portion of the PZT film (the surface of the PZT film). The strain gradient in the PZT/LNO/metal foil film causes the PZT film to have a specific polarization value due to the flexoelectric effect without polarization treatment. In addition, using an energy harvesting tester, the utilization of PZT/LNO/metal foil film as a flexible piezoelectric device was investigated. Therefore, it is expected that the flexible piezoelectric thin film of PZT (1mm)/$LaNiO_3$/Metal foil can be easily used as a piezoelectric sensor and energy harvesting device without transport, etching, and poling processes.

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5:00 PM EL08.12.13
The Application of Polyvinylidene Fluoride-Based Piezoelectric Nanogenerator for Harsh Environment Dawoon Jin and Jong Hoon Jung; Inha Univercity, Korea (the Republic of)

Energy harvesting system has become one of the most critical issues for sustainable development. Among various energy resources, mechanical energy is abundant and ubiquitous. Many studies have demonstrated that the piezoelectric nanogenerator (PENG) effectively converts tiny mechanical vibrations to electricity. However, their performances are rarely investigated under harsh environmental conditions. So, their performances should be investigated under harsh environmental conditions to harvest energy at various conditions
In this study, a multilayered polyvinylidene fluoride (PVDF) film-based piezoelectric nanogenerator (ML-PENG) is demonstrated to generate stable power outputs at cryogenic temperatures and low pressures, even under UV irradiation. ML-PENG generates an open-circuit voltage of 1 V and a short-circuit current of 8 nA at -266 °C and 10^{-5} Torr. The output power is enough to operate several light-emitting diodes by harvesting biomechanical energy under simulated Martian conditions, such as -50 °C, CO_2-rich, and UV-irradiated environments.

5:00 PM EL08.12.14
Energy Harvesting of Two-Phase Gas/Liquid Flows Using Piezoelectric Materials Joao Ventura[1], Catia Rodrigues[1], Andre Pereira[1], Joao Magalhaes[2] and Jonas Schmidt[2]; [1]University of Porto - Faculty of Sciences, Portugal; [2]inanoEnergy, Portugal

In today's world, it is becoming increasingly important to use every kind of energy that is available around us due to the major environmental crisis we face. Thus, there is an emerging need to develop new technologies that harvest energy from all renewable sources that surround us. Different nanogenerators using different physics effects have emerged in the last years as solutions to harvest energy from the environment through a clean process [1-3]. In this work, we simulated and developed a piezoelectric membrane assembled inside a Venturi tube to harvest kinetic energy from different fluid flows. The energy generation of our piezoelectric membrane was enhanced through the dimensions optimization of the Venturi tube using finite element method simulations. Thus, the velocity variation inside the Venturi tube was improved by changing the minimum chocking point diameter (in the middle), the length of the tube and angles of the slopes leading to the center. In addition, it was also simulated the influence of obstacles integrated inside the Venturi tube with different shapes (rectangle-, ellipsoidal-, right-angled triangle-, teeth-shaped obstacles) in order to increases the fluid speed and consequently the turbulence. An increase of the fluid speed was achieved, with the highest value obtained when obstacles based on right-angled triangle shape were located in the chocking point of the Venturi tube, i.e. in the smallest diameter. Based on the simulated results, experimental tests using a piezoelectric PVDF (polyvinylidene fluoride) membrane inside a simple tube and enhanced 3D printed Venturi tubes were performed under air, nitrogen (N_2) and carbon dioxide (CO_2). The maximum generated voltage by the piezo-membrane increased from ~ 1.5 V to 3V when implemented inside the Venturi tube under an airflow of ~ 45 L/min. Finally, we demonstrated the possibility of storing the generated electrical power under various flows in air (at room temperature) and gas-liquid $N_{2,}$ and gas-liquid CO_2 (at low temperatures, down to -50 C). This work shows the potential of mechanical energy harvesting technologies to be implement inside refrigeration systems to feed sensors and monitor in real time.

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5:00 PM EL08.12.16
On the Curie Temperature Dependence of a Hybrid Thermomagnetic-Triboelectric Nanogenerator Rita Bugalhao, Catia Rodrigues and Joao Ventura; University of Porto - Faculty of Sciences, Portugal

Energy is increasingly one of the major and most important forces on our society, making its generation and harvesting a broadened studied topic. Due to this high demand for the distribution of electrical power, the interest in Energy Harvesting (EH), the concept of converting unused ambient energy from our surrounding environment into electrical energy, is increasing. Amongst the various available external sources, thermal energy is one of the most researched for the purpose of EH, not only because it is the most ubiquitous one, but also for being the form of energy that all the others are eventually turned into. Thermal EH relies on "free heat", so a beneficial alternative of a green energy source would be to capture this lost heat, convert it into electrical energy and use it to re-power devices.

Thus, our study focuses on researching a device that performs such conversion in the low-grade temperature range. Our setup is composed of an NdFeB permanent magnet on top of a hot source and a triboelectric nanogenerator (TENG) directly above a cold source. Between them is a thermomagnetic material (TMM) with a Curie temperature (Tc) near room temperature, where an oscillatory motion is forced through heating and cooling. When heated above T_c, the thermomagnetic material transitions from ferromagnetic to paramagnetic and falls on the TENG, generating an energy peak. Then, the thermomagnetic material is cooled below Tc, leading to a paramagnetic-ferromagnetic phase transition. When that occurs, the thermomagnetic material is once again attracted by the permanent magnet and lifts off the TENG, generating another energy peak. This cycle repeats as long as the TMM's temperature oscillates around Tc.

Here, we present a study on how the Curie temperature (ranging from 32.0 to 43.7 C) of the TMM influences the energy generation, optimum resistance and oscillation frequency of the proposed device, aiming for its optimization and potential assessment. We demonstrate that the operating frequency range of the hybrid thermomagnetic-triboelectric nanogenerator strongly depends on the Tc of the TMM, with optimum hot side temperatures (for which the frequency is maximum) being found between 40 C and 70 C with increasing Tc. The combination of a TMM with Tc = 39.9 C and a zigzag PTFE-Nylon TENG led to the best results, giving an open circuit voltage of 8 V, a short circuit current of 0.36 µA and a motion frequency of 66 mHz.

ACKNOWLEDGMENTS
This work is funded by FEDER funds through the COMPETE 2020 Programme and National Funds through FCT - Portuguese Foundation for Science and Technology under projects UID/NAN/50024/2019 and POCI-01-0145-FEDER-031575. The authors also acknowledge support from the International Consortium of Nanotechnologies (ICON) funded by Lloyd's Register Foundation.

SESSION EL08.13: Virtual Session: Triboelectric and Piezoelectric Nanogenerators
Session Chairs: Yong Qin and Yunlong Zi

Tuesday Afternoon, April 25, 2023
EL08-virtual

9:00 PM *EL08.13.01
The Physics of Contact-Electrification and the Theory of TENG Zhong Lin Wang[1,2]; [1]Georgia Institute of Technology, United States; [2]Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, China

Contact electrification (CE) (or usually called "triboelectrification") effect, the most fundamental effect for electricity, has been known for over 2600 years since ancient Greek time, but its scientific mechanism remains unclear. The study of triboelectrification is recently revived due to the invention of the triboelectric nanogenerators (TENGs) by using the coupling of triboelectrification and electrostatic induction effects. In this talk, we first present the physics mechanism of triboelectrification for general materials. Our model is extended to liquid-solid contact electrification, reviving the classical understanding about the formation of electric double layers. Secondly, the fundamental theory of the TENGs is explored based on a group of reformulated Maxwell equations. In the Maxwell's displacement current proposed in 1861, the term $e\P\boldsymbol{E}/\P t$ gives the birth of electromagnetic wave, which is the foundation of wireless communication, radar and later the information technology. Our study indicates that, owing to the presence of surface polarization charges present on the surfaces of the dielectric media in TENG, an additional term $\P\boldsymbol{P}_s/\P t$ that is due to non-electric field induced polarization should be added in the Maxwell's displacement current, which is the output electric current of the TENG. Therefore, our TENGs are the applications of Maxwell's displacement current in energy and sensors.

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9:30 PM *EL08.13.02
Strategies to Improve Efficiency and Durability of Triboelectric Nanogenerator Chenguo Hu; Chongqing University, China

Triboelectric nanogenerator is one of the most important technologies to solve distributed energy supply of wireless sensor networks where the wired electricity is not available. However, its low output efficiency and interface abrasion hinder its practical application. The main factors affecting the output charge density of TENG are poor interface contact, air breakdown effect and insufficient charge generation capacity. Mechanical wear and thermal loss of the interface are another challenge for the TENG, which limits its durability and practical application. In this paper, I will introduce the strategies adopted by our research group to improve the output performance of the TENG and reduce interface abrasion, including charge excitation, material modification and enhancement of contact efficiency, and intermittent contact mode, non-contact mode, static friction mode and liquid lubrication mode. The mechanism of charge transportation and the device design method of obtaining maximized output charge density are presented.

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10:00 PM EL08.13.03
Inkjet-Printing Self-Powered Triboelectric Sensor on Fiber Substrate for Wearable Healthcare and Human-Interactive Applications Chi Zhang, Lei Zhang and Dachao Li; Tianjin University, China

With the development of IoTs, big data, and artificial intelligence, various wearable electronics have been rapidly expanded, such as wearable smart watch/bracelet, biomedical applications, smart sportswear, and virtual reality. However, current wearable electronic devices inevitably require power sources and have to be charged or replaced frequently, which will limit the applications of wearable electronics. Recently, the textile TENG which integrates self-powered triboelectric sensors with daily clothes, brings a novel insight into wearable electronics and improves personal intelligence in the era of the IoTs. For example, Meng *et. al* developed a triboelectric textile sensing system for human pulse wave monitoring (***Matter***, 2020, 2, 794-804). Zhou *et. al* developed a machine-learning-assisted stretchable triboelectric strain sensor array for sign-to-speech translation (***Nature Electronics***, 2020, 3, 571–578). In this respect, 1D-shaped fiber TENGs have become a research hotspot due to the advantages of light weight, small size, good air permeability, compatibility with daily clothes, and adaptation to frequent mechanical deformations in daily life. Nevertheless, most current fiber-based TENGs are based on either a mixing or coating method to integrate an elastic fiber matrix with conductive electrodes, which always struggles to achieve the high-precision and customized fabrication of the triboelectric sensors on the small-diameter and large-curvature fiber surface.

In this work, we report an inkjet-printed fiber-based triboelectric strain sensor (IPFTS) for wearable applications. The helical-structure Ag ink was successfully inkjet-printed on the stretchable PU fiber surface with controllable thickness and turn number, and then encapsulated by Eco-Flex elastomer. The printable fiber diameter is as low as 500 μm with a large curvature of 4000 m^{-1}. Benefiting from the structural advantages, the SPFTS presents a large strain range (0-250%), excellent linear sensitivity (0.47), fast response (70 ms), and great mechanical stability (no decay was observed during the 40-minutes reciprocating 100% stretching-releasing process). Several system-level wearable health monitoring and human-interactive applications are demonstrated through our IPFTS, including heartbeat signal detection for arrhythmia screening, respiration signal detection for assessing sleep status, motion monitoring, and sign language gesture recognition. Benefiting from these features, the IPFTS shows huge application potential in wearable electronics, human-machine interfaces, and artificial intelligence.

10:15 PM EL08.13.04
Hybrid Smart Fiber with Spontaneous Self-Charging for Wearable Electronic Applications Yuljae Cho; Shanghai Jiao Tong University, China

Wearable electronics have been commercialized in recent years as exemplified by smart watches and smart glasses which provide great convenience for our daily lives with advanced functions. Attributed to recent development in long-life batteries, these devices can be frequently re-charged through an external power supply with long life expectancy. The dependence on the external energy source, however, has limited implementation of the wearable electronics for advanced applications where standalone wearables are highly required, such as wearable bio-medical devices.

In spite of its importance, a self-charging capability in wearable devices has been its early stage of development at present. It has been a challenging issue to directly add advanced functions to wearable devices built on bulk textile platform due to lack of controllability in the bulk form. In contrast, for wearables, a bottom-up approach starting from the building block fiber/yarn allows to engineer and functionalize each layer and component with high controllability. Therefore, building wearables from fibers/yarns provides a viable solution to introduce advanced functionality, particularly, the self-charging capability for advanced wearable electronics. However, another challenge arises due to an one-dimensional (1D) nature of the fiber which makes it incompatible with conventional layer preparation methods on two-dimensional (2D) forms, such as the bulk textile. Therefore, the key to further advance wearable electronics is on (1) direct control of the building block fiber/yarn, and (2) development of the scalable method applicable to the 1D platform.

In light of this, we have demonstrated a template-free scalable method which enables to control key device parameters at the building block fiber scale. Our bottom-up approach using high plasma energy demonstrated an effective direct control of building block fibers, leading to an enhanced spontaneous self-charging capability. Successful implementation of the spontaneous self-charging at the building block fiber scale proves that our new method developed is a promising route to tackle the current bottlenecks that the wearable electronics confront and through this advance the future self-powered wearable electronics.

10:30 PM EL08.13.05
Enhancing the Output Performance of Triboelectric Nanogenerators Through Rationally Utilizing the Temperature Change and Electric Field Change Juan Wen, Bolang Chen, Changxin Qi, Ruichao Zhang, Li Ang Zhang, Longfei Wang and Yong Qin; Lanzhou University, China

Triboelectric nanogenerator (TENG) has wide applications in implantable biomonitoring, man-machine interaction, internet of things and smart city, et al. Continuously enhancing its output performance is the main challenge in the development of TENG. In this present, firstly, we will talk how to utilize the high temperature originally harmful to the performance of TENG to increase the output performance by rational design [1]. Then, the inhomogeneous triboelectric charge distribution and its cancellation effect on driving the free electrons flowing in the external circuit is pointed out to result in the low output of the flutter-driven triboelectric nanogenerators, and the method of electrode segmentation and integration is developed to enhance the output performance [2]. After that, the electric field distribution inside and outside TENG is detailly analyzed, and the outside electric field change is utilized to enhance the output current density [3], and simultaneously enhance the output current and output voltage [4].

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SESSION EL08.14: Virtual Session: Piezoelectric Devices and Applications
Session Chairs: Yong Qin and Zhen Wen
Wednesday Morning, April 26, 2023
EL08-virtual

8:00 AM *EL08.14.01
Self-Powered Human-Machine Interacting Sensors Yanchao Mao; Zhengzhou University, China

Human-machine interface (HMI) sensor is a technology to transfer and exchange information between human and machine, which has aroused lots of attention recently. We developed a series of self-powered HMI sensors on the basis of triboelectric nanogenerator (TENG). An intelligent wireless respiratory monitoring and alert system was developed by using a TENG based self-powered HMI sensor to real-time alert apnea remotely by using a cell phone to send a warning massage. By utilizing the charges naturally carried on the human body and a TENG, a self-powered touch-free HMI screen sensor is developed for recognizing diverse gestures in a noncontact operating mode. A thermoregulating and self-powered E-skin based on liquid metal as a phase change material is developed. And this TENG based self-powered E-skin can dynamically thermoregulate according to the surrounding temperature through a phase change. A liquid metal electrode that we call a kirigami-structured LM paper (KLP) is developed. Upon integration with a TENG principle, the KLP can also operate as a self-powered E-skin to call a cellphone on the human skin. An intelligent noncontact gesture-recognition HMI system is presented through the integration of a triboelectric self-powered touchless sensor and deep learning technology. This self-powered HMI system is further applied to control a robot for collecting throat swabs in a noncontact mode.

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8:30 AM *EL08.14.02
Optimization of a Two-Stage Power Management Circuit for Triboelectric Nanogenerators Philippe Basset[1] and Dimitri Galayko[2]; [1]Univ Gustave Eiffel, France; [2]Sorbonne Université, France

Optimization of a two-stage power management circuit for triboelectric nanogenerators

Triboelectric nanogenerators generate high AC voltages that are often rectified using stable charge-pumps such as half-wave and full-wave diode bridges. For better understanding and to provide guidelines for designing a practical system using a TENG to power a sensor, we have developed a comprehensive general theory that determines the optimal electrical bias conditions for this class of rectifiers. Generic formulas have been derived for any stable charge-pump to determine key figures, such as the optimal bias voltage of the TENG, the maximum energy that can be converted, or the number of mechanical cycles to reach this maximum [1].

Through theoretical analysis of the QV-cycles of a given TENG combined with its rectifier, the missing constants of the generic formulas can be obtained. We have applied this approach to full-wave and half-wave diode bridges and their key figures have been calculated and validated experimentally. It is confirmed that half-wave rectifiers always have a higher saturated voltage, as well as a higher maximum energy per cycle, but at the cost of a longer start-up time. On the contrary, full-wave rectifiers perform better only when the output voltage is much lower than the internal triboelectric voltage of the TENG [2].

In order to provide an output voltage of a few volts suitable for most applications, these rectifiers can be followed by a DC-DC buck converter, in a so-called two-stage configuration [3]. Based on the developed theory, we have shown that the optimal activation of the buck switch is between 0.5 and 0.7 of the saturation voltage of the charge-pump, depending on the hysteresis of the switch, and that the charging time of the output capacitor is at least twice as fast with a half-wave rectifier than with a full-wave rectifier. The theoretical results were confirmed by simulations and experiments using a plasma switch.

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9:00 AM EL08.14.03
Enhancing the Current Density of a Piezoelectric Nanogenerator Using a Three-Dimensional Intercalation Electrode Long Gu; Xidian University, China

The low output current density of piezoelectric nanogenerators (PENGs) severely restricts their application for ambient mechanical energy harvest. This has been a key challenge in the development of PENG. Here, to conquer this, based on a piezoelectric material with a high piezoelectric coefficient (Sm-PMN-PT), a new design of PENG with a three-dimensional intercalation electrode (IENG) is proposed. By creating many boundary interfaces inside the piezoelectric material, the total amount of surface polarization charges increased, which contributes to an increased current density. The IENG can output a maximum peak short circuit current of 320 μA, and the corresponding current density of 290 μA/cm^2 is 1.93 and 1.61 times the record values of PENG and triboelectric nanogenerator (TENG), respectively. It can also charge a 1 μF capacitor from 0 V to 8 V in 21 cycles, and the equivalent surface charge density of 1690 μC/m2 is 1.35 times the record value of TENG.

9:15 AM EL08.14.04
Towards Smart Tactile Sensing by Cascade Connecting Piezoelectric Film and Field Effect Transistors Jinbo Pang[1], Chongyang Hou[1] and Hong Liu[1,2]; [1]University of Jinan, China; [2]Shandong University, China

The electronic skin based tactile sensors [1] has become an important platform to host multiple sensors for wearable electronics in the Internet of Thing era [2, 3]. The piezoelectric pressure sensor [4, 5] has featured advantages of high sensitivity, i.e., large output voltage from subtle deformation and small strain. However, the large output voltage may suppress its applications due to the requirement of high-voltage meters. Therefore, the transduction of voltage to current provides an efficient solution. The field-effect transistors have shown great charge carrier mobility and current on/off ratio based on graphene [6-8] and other 2D materials [9-11]. Here, we employ the field-effect transistor based on metal dichalcogenides to convert the piezoelectric voltage of pressure sensor to the drain current by connecting the sensor electrode to gate electrode. We have achieved the linear response versus the weight load ranging from

2 g to 60 g. The pressure gauge has shown great potentials for applications in wearable healthcare electronics.

Keywords: Tactile sensors, piezoelectric voltage, PVDF, TMDCs, field-effect transistors, gate voltage regulation, transconductance

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9:30 AM EL08.14.05
Probing the Local Piezoelectric Response of Semiconducting ZnO Nanowires by Piezoresponse Force Microscopy and Finite Element Modeling
Gustavo Ardila and Thomas Jalabert; Grenoble Alpes University, France

Zinc oxide (ZnO) nanowires (NWs) are excellent candidates for the fabrication of piezoelectric transducers such as energy harvesters, mechanical sensors and piezotronic devices thanks to its low-cost and environment friendly fabrication process. However, most of theoretical works considering semiconducting properties in ZnO could not account for its high piezoelectric response [1] since the electric potential decreases because of free electron screening [2]. A Surface Fermi Level Pinning (SFLP) mechanism has recently been proposed as an intrinsic property of ZnO NWs to solve this contradiction [3]. Nevertheless important electric parameters for the energy conversion efficiency such as the piezoelectric coefficient (e.g. d33) and the open circuit potential (Voc) have not yet been investigated using models coupling semiconducting and piezoelectric properties.

We used a new strategy improving piezoresponse force microscopy (PFM) measurements to map the piezoresponse amplitude on the top surface of vertically aligned ZnO NWs. Consistently with previous models [3], the piezoresponse amplitude is larger than on ZnO thin films. We observed that the piezoresponse is larger on NWs with small diameters and when the tip is on the edge of the NWs. We interpret our results by a modification of the depletion region inside the NW due to the influence of geometry on the free carriers' distribution. We performed a Finite Element Method simulation to quantitatively support our experimental results. This is the first model including the mechanical, piezoelectric and semiconducting properties of the material in the PFM configuration. We also used this model to investigate the piezoelectric response of Vertically Integrated NanoGenerators (VINGs). We found a saturation of the piezoresponse with the increase of the NW length in VINGs made of thin NW depleted up to their core. This saturation was due to the incapacity of surface traps to maintain depletion along the whole NW beyond a critical height as a result of the electric potential shift induced by piezoelectric polarization. The critical height is strongly dependent on the surface trap density and on the crystal orientation and therefore on the type of mechanical load (compression/elongation). Finally, we showed that the influence of surface traps on the piezoelectric response of semiconductor based transducers was strongly dependent on the traps dynamics [4]. This emphasizes the strong influence of the working frequency on the piezoelectric performances of semiconductor based transducers.

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9:45 AM *EL08.15.02
Ferroelectric Integrated Self-Powered Photodetector and Optoelectronic Synapse Jianhua Hao[1,2]; [1]The Hong Kong Polytechnic University, Hong Kong; [2]The Hong Kong Polytechnic University Shenzhen Research Institute, China

It is known that a steady-state photovoltaic response can be generated along the ferroelectric polarization direction due to the strong inversion symmetry breaking. Such a unique mechanism endows ferroelectric photovoltaics with exceptional properties. It is noticeable that hybrid perovskite ferroelectrics produce a revival of interest in ferroelectric photovoltaics because of the robust ferroelectricity coexisting with superior semiconducting properties. In our recent work, the in-plane multiaxial ferroelectricity of hybrid perovskite ferroelectric was investigated. Systematic investigations, including electrical-poling-dependent photocurrent and ferroelectric polarization switching, are further carried out to reveal the photovoltaic behavior via a dynamic poling process. Electric-field-induced effects are responsible for the self-powered ability in the ferroelectric integrated photodetectors. On the other hand, the development of optoelectronic synapses can provide an important breakthrough toward creating a sophisticated and adaptable artificial visual system. We demonstrate multifunctional optoelectronic synaptic device based on ferroelectric α-In_2Se_3/GaSe heterojunctions to mimic the entire human visual system at the single device level. The results show that the ferroelectric integrated heterojunction device is capable of performing logic operations and recognizing images. The works are supported by the grants from the National Natural Science Foundation of China (No. 52233014) and Research Grants Council of Hong Kong (PolyU SRFS2122-5S02).

SESSION EL08.15: Virtual Session: Piezotronics and Tribotronics
Session Chairs: Long Gu and Yong Qin
Wednesday Afternoon, April 26, 2023
EL08-virtual

9:00 PM *EL08.15.01
High-Performance Triboelectric Nanogenerator and Tribophotonics Yunlong Zi[1,2,3]; [1]Hong Kong University of Science and Technology (Guangzhou), China; [2]The Hong Kong University of Science and Technology, Hong Kong; [3]Chinese University of Hong Kong, Hong Kong

As the development of the Internet of Things (IoT), trillions of widely-distributed devices are integrated for health monitoring, biomedical sensing, environmental protection, infrastructure monitoring, and security, which require power supplies. To provide a sustainable power solution, triboelectric nanogenerator (TENG) has been developed since 2012 for high-efficiency mechanical energy harvesting from the ambient environment. The PI's team has made significant contributions to fundamental studies about the triboelectric effect, discharge, and TENG output characteristics. and Multiple strategies to greatly enhance the output performance of TENG has been demonstrated, such as the high-pressure environment and the liquid-solid interface. On the other hand, the PI's team also proposed and developed the concept of tribophotonics: tribo-charge induced tuning or generation of photons toward self-powered wireless sensing, which can be achieved through tunable liquid lens, liquid crystal, optical switch, tribo-induced electroluminescence (TIEL), and discharge. These studies will drive the further development of TENG technology for broad applications in blue energy harvesting, the IoT, human-machine interface, health & infrastructure monitoring, wearable & implantable electronics, towards high-efficiency self-powered systems.

9:30 PM EL08.15.04
Bilateral Piezoelectric Charge Modulation——A Perspective of Piezo-Phototronic Effect in Multi-Layer Structured Optoelectronic Devices Wenbo Peng; Xi'an Jiaotong University, China

Piezo-phototronic effect utilizes the strain induced piezoelectric charges inside the piezoelectric semiconductors to modulate the local energy band diagram at the interface of junctions, thus controlling the photo-generated carriers' behaviors and the performance of optoelectronic devices. Since its invention in 2010, piezo-phototronic effect is vastly demonstrated in photodetectors, light-emitting diodes, and solar cells, where only one interface is modulated by piezoelectric charges. In 2018, we first propose to construct multi-layered structure for efficient utilization of piezoelectric charges with both polarities and obtain better performance optimization by piezo-phototronic effect, which we recently name as *Bilateral Piezoelectric Charge Modulation*. Here, we summarize the recent progresses of our researches on bilateral piezoelectric charge modulation, including both experimental results and analytical theories. An n-ZnO/p-Si/n-ZnO double heterojunction bipolar phototransistor is designed, and the regulation of bilateral piezoelectric charges on bipolar phototransistor's performances is studied from the perspectives of theoretical derivation and experimental research simultaneously. A theoretical model of n-ZnO/p-Si/n-ZnO double heterojunction bipolar phototransistor is established, and the influence of four polar combinations of piezoelectric charges induced by different strains formed at the interface of two heterojunctions on the characteristics of phototransistor is carefully studied. The theoretical calculation results show that, when positive piezoelectric charges are generated at both two interfaces, the regulation of strain on the phototransistor is a superposition of two positive effects, which can significantly improve the performances of phototransistor. Then an n-ZnO/p-Si/n-ZnO double heterojunction bipolar phototransistor is experimentally prepared. By rationally designing the device structure, positive piezoelectric charges could be simultaneously generated at the two heterojunction interfaces when an external compressive strain is applied. The saturation current of phototransistor is significantly improved, and the photoresponsivity is also improved to a certain extent by the applied compressive strain. To further optimize the performances, the effects of interdigitated electrode's size, substrate and ZnO layer on the strain regulation of device performance are carefully studied. The experimental results show that when the p-Si substrate is used, the size of interdigitated electrodes is chosen as channel width $W_0 = 80$ μm, the channel length $L = 5$ μm, and the number of electrodes $N = 14$, and the ZnO nanowires layer prepared by low temperature hydrothermal growth method is used as both emitter and collector, the strain induced bilateral piezoelectric charges regulation of the obtained bipolar phototransistor is the best. At a compressive strain of -1.37%, the photoresponsivity is enhanced from 0.96 A/W to 20 A/W with an increase of about 2000%, indicating the significant modulation of applied strain on the performances of heterojunction bipolar phototransistor.

SESSION EL08.16: Virtual Session: Flexible Nanogenerators
Session Chairs: Yanchao Mao and Yong Qin
Thursday Morning, April 27, 2023
EL08-virtual

8:00 AM *EL08.16.01
Liquid–Solid Interface-Based Triboelectric Tactile Sensor with Ultrahigh Sensitivity Zhen Wen; Soochow University, China

Traditional triboelectric tactile sensors based on solid–solid interface have illustrated promising application prospects through optimization approach. However, the poor sensitivity and reliability caused by hard contact-electrification still poses challenges for the practical applications. In this work, a liquid–solid interface ferrofluid-based triboelectric tactile sensor (FTTS) with ultrahigh sensitivity is proposed. Relying on the fluidity and magnetism of ferrofluid, the topography of microstructure can be flexibly adjusted by directly employing ferrofluid as triboelectric material and controlling the position of outward magnet. To date, an ultrahigh sensitivity of 21.48 kPa^{-1} for the triboelectric sensors can be achieved due to the high spike microstructure, low Young's modulus of ferrofluid and efficient solid–liquid interface contact-electrification. The detection limit of FTTS of 1.25 Pa with a wide detection range to 390 kPa was also obtained. In addition, the oleophobic property between ferrofluid and poly-tetra-fluoro-ethylene triboelectric layer can greatly reduce the wear and tear, resulting in the great improvement of stability. Finally, a strategy for personalized password lock with high security level has been demonstrated, illustrating a great perspective for practical application in smart home, artificial intelligence, Internet of things, etc.

8:30 AM EL08.16.04
Vortex-Assisted Assembly of Electrode Arrays onto Micro-Nano-Scale Piezoelectric Fibers Tong Li[1,2] and Zhang-Qi Feng[1]; [1]Nanjing University of Science and Technology, China; [2]City University of Hong Kong, Hong Kong

Electrostimulation, simulating endogenous bioelectricity, comes to the fore as a promising bioelectronic medicine in clinical practice and has been approved by the US Food and Drug Administration. Research in this field is largely driven by the use of micropipette electrodes, active transistor arrays and high-density multielectrode arrays. However, the inability to construct these electrode arrays on micro-nano-scale bioscaffold carriers remains a

roadblock toward practical applications. As a result, the existing precise electrostimulation theory and its studies are still primarily at the conceptual level and cannot be applied to biomaterial-based clinical trials.
In this work, we report the fabrication of electrode arrays on piezoelectric fibers by vortex-assisted assembly technique in large scale such that they can function well in vitro, and ex vitro, as well as in vivo. It shows extremely high spatial resolution of ~1.6 ± 0.2 μm, which is at least 5 times higher than reported conventionally. Electrodes assemble around piezoelectric fibers into D periodic banding-like arrays on native collagen fibers, which is conducive to the mechanical interlock with cells, so as to improve cell adhesion that is a key parameter for mechanical forces generated by cell activity. With this foundation, piezoelectric fibers are able to yield, in response to the cell-intrinsic force, a local electric potential favored by electroactive cells that varies in a stepwise gradient along the electrode arrays on piezoelectric fiber. This work offers a scalable solution for the construction of electrode arrays on micro-nano-scale bioscaffold carriers, paving the way for future bioelectronic therapies in clinical trials.

8:45 AM *EL08.16.07
Abstract Presented (ON-DEMAND ONLY) Piezoelectric Materials and Energy Harvesting Devices for Biological Applications Hamideh Khanbareh and Vlad Jarkov; University of Bath, United Kingdom

Aging, disease and injury can cause permanent tissue damage, particularly in the case of organs which have limited healing capabilities, such as the central nervous system (CNS) and cartilage. Electrical stimulation can enhance cell regeneration by altering the cellular response to stimulate repair. This has been shown on conductive materials, powered by batteries. However, once the batteries have exceeded their lifetime, they require surgical replacement, exposing patients to health risks. The challenge for the long-term use of such devices is a reliable source that generates electricity from human-activity-induced thermal and vibrational energy.
Ferroelectric materials possess an inherent polarisation, thus surface charge that varies upon a change in pressure and temperature, through piezoelectricity and pyroelectricity, respectively. Therefore, they can interact with cells through electrical signals to stimulate repair. However, common ferroelectric materials such as lead zirconate titanate (PZT) and polyvinylidene-difluoride (PVDF) contain toxic or non-biodegradable components and are thus not favourable for implantation. In this work we show successful fabrication and characterisation of biocompatible ferroelectric polymer composites in the form of thin membranes and 3D porous scaffolds.
Thin ferroelectric membranes of Polydimethylsiloxane (PDMS)-potassium sodium lithium niobate (KNLN) have been prepared via in-situ poling-dielectrophoresis to obtain high piezoelectric sensitivity while maintaining flexibility [1]. A significant improvement in piezoelectric properties of quasi 1–3 composites is achieved by a combination of dielectrophoretic alignment of the ceramic particles and poling process. The degree of structuring as well as the functional properties of the in-situ structured and poled composites are enhanced significantly compared to those of the conventionally manufactured structured composites [1, 2].
3D porous scaffolds of cellulose, poly (lactic acid) (PLA) and chitosan KNLN have also been produced by freeze-casting technique; using the anisotropic solidification of a suspension to achieve aligned porosity for guiding cell outgrowth. Piezoelectric particles of KNLN of varying weight fractions (10, 20, 30 and 40%) have been integrated and poled using corona technique. The resultant composites show enhanced average pore size and interconnectivity as well as piezoelectricity ideal for soft tissue regeneration applications. This research is the first to report the fabrication and material characterisation of highly porous Cellulose-KNLN and PLA-chitosan-KNLN composites prepared by freeze casting. Morphological characterisation of the obtained microstructures has been performed and linked to the processing parameters and final properties. A poling study has also been performed to achieve piezoelectric properties. The highly interconnected aligned structures with ideal mean pore size have been obtained with PLA and chitosan freeze-cast scaffolds and enhanced with the incorporation of KNLN, up to 20wt% desirable for soft tissue applications.
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SYMPOSIUM

April 11 - April 28, 2023

Symposium Organizers
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* Invited Paper
\+ Distinguished Invited

SESSION EL09.01: Synthesis of 2D Optoelectronic Materials and Their Heterostructures I
Session Chair: Sudha Mokkapati
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3009

10:30 AM *EL09.01.01
Magnetic Properties of Quasi-2D Layered van der Waals Crystals Under External Stimuli Srinivasa Rao Singamaneni; The University of Texas at El Paso, United States

The research on (quasi) 2D magnetism propelled rapidly since the first experimental discovery of atomically thin magnets in 2017. Since the magnetic properties of bulk (quasi-2D) crystals serve as a basis for the understanding of magnetic phenomenon in reduced dimensions (true 2D limit), a profound knowledge and understanding of these compounds is evidently needed at quasi-2D level, especially considering that magnetic mono and bilayers of a wide range of 2D magnets have now become accessible. In this talk, I will present and discuss our recent findings1-7 in tuning the magnetic properties of quasi-2D layered van der Waals magnets by photoexcitation, proton irradiation, intercalation, and by the application of pressure. NRC, ACS PRF, NSF, and DOE supported this work.

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11:00 AM EL09.01.02
Direct Growth of Graphene on UVC-LEDs by a Plasma-Enhanced Low Temperature CVD Process Hehe Zhang, Umut Kaya, Johanna Meier, Wolfgang Mertin and Gerd Bacher; Werkstoffe der Elektrotechnik & CENIDE, Germany

Among others, drinking water supply, medical care and air pollution control are major and global challenges of our time. For this, an efficient disinfection, e.g., by using ultraviolet (UV) light is required. It is expected that UV light-emitting diodes (UV-LEDs) based on aluminum-gallium nitride ($Al_xGa_{1-x}N$) heterostructures will replace Hg-containing light sources in the near future as they are considered to be an ecologically and economically attractive alternative. However, the efficiencies of UV-LEDs in the technologically relevant UVC-regime are still limited. One reason is the poor conductivity of the p-$Al_xGa_{1-x}N$ layer that requires the integration of a transparent current spreading layer (TCSL) for LEDs in standard geometry. Due to the poor transparency in the UVC range, ITO as commonly used for visible LEDs is not suitable. The high electrical conductivity and the high transparency over the whole UV-VIS-spectrum make graphene a highly promising candidate for the TCSL [1]. However, up to now, graphene used as TCSL in UVC LEDs is not yet reported.
In this work, we present the successful direct growth of a graphene layer on top of the p-$Al_xGa_{1-x}N$ cladding layer in a UVC-LED. For the growth, we employ a direct current plasma-enhanced (PE)CVD process with a methane / nitrogen mixture at temperatures as low as 670°C, expanding our previous work on GaN [2]. Optimizing gas mixture ratio, growth temperature and growth time, we obtained graphene with Raman intensity ratios $I_D/I_G \approx 2.1$ and $I_{2D}/I_G \approx 1.3$, respectively. The optical transparency of the as-grown graphene layer exceeds 90% over the whole spectral range spanning from 270 nm to 800 nm and we achieved a sheet resistance of around 5 kΩ/sq. Our UVC-LED with graphene as a TCSL shows a diode-like I-V behavior with a current density of approximately 0.1 mA/cm^2 at 4 V and 0.23 mA/cm^2 at 5 V, respectively. The emission maximum of the LED is at a wavelength of 275 nm (5 V). A distinct current spreading effect is observed.
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11:15 AM EL09.01.03
Epitaxial Molybdenum Disulfide/Gallium Nitride Junctions—Low-Knee-Voltage Schottky-Diode Behavior at Optimized Interfaces Hae in Yang, Danial Coyle, Michelle Wurch, Prachi Yadav, Michael I. Valentin, Mahesh Neupane, Kortney Almeida and Ludwig Bartels; University of California, Riverside, United States

The existence of bandgaps in transition metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS_2) offers an attractive possibility of using these two-dimensional layered materials in various device applications. Gallium nitride (GaN), initially introduced into semiconductor technology as a wide-band-gap material able to provide blue light-emitting diodes, has found a number of additional applications for power conversion. MoS_2 and GaN are almost lattice matched at a mismatch of only ~0.8%, leading to an interest in the epitaxial relationship. Integration of MoS_2 with wide band gap GaN could provide an avenue toward high-performance devices. The interface for MoS2 on GaN plays an important role in determining the properties of heterojunctions.

Here, we demonstrate the optimization of the MoS_2/GaN interface and MoS_2 growth epitaxially on GaN. We use a high vacuum CVD growth technique. First, we clean the GaN substrate with a broad range of sputter fluence and anneal it with ammonia gas to generate well-defined surface termination. Next, we grow a controlled layer number of MoS_2 by exposing hot metallic molybdenum to H_2S gas at 650 °C. All process was performed without breaking the vacuum. We grow single-layer as well as 4-layer, which are monitored by colorimetric measurements of the reflection of the filaments from the sample, allowing us to end the deposition process at the desired number of integer layers.

We use low-energy electron diffraction (LEED) and DFT simulation to demonstrate epitaxial MoS_2 grown on GaN and interface quality. We observed 22 patterns resulting from a doubling of the periodicity, which attests to a clean and well-ordered termination of the GaN substrate. X-ray photoelectron spectroscopy (XPS) is used to evaluate the cleanliness of GaN and interpret transport measurements. Atomic force microscopy (AFM) was analyzed to characterize surfaces after MoS_2 growth. We fabricate MoS_2-GaN diode to test the impact of different interface preparation on electrical properties. We find a high-performance behavior achieved by optimizing in situ interface preparation: low turn-on voltage (~0.3 V) Schottky-diode behavior, on/off current ratio of ~10^5. This highlights the technological potential of devices and gives us a guideline for interface preparation for further research.

11:30 AM EL09.01.04
Aerosol-Jet Printed, High Performance MoS_2 Nanosheet Photodetectors Enabled by Megasonic Exfoliation Lidia Kuo[1], Vinod K. Sangwan[1], Sonal Rangnekar[1], Ting-Ching Chu[1], David Lam[1], Zhehao Zhu[1], Lee Richter[2], Ruipeng Li[3], Beata Szydlowska[1], Julia R. Downing[1], Benjamin Luijten[1], Lincoln J. Lauhon[1] and Mark C. Hersam[1]; [1]Northwestern University, United States; [2]National Institute of Standards and Technology, United States; [3]Brookhaven National Laboratory, United States

Printing solution-processed inks of 2D materials offers a scalable and cost-effective path towards mechanically flexible optoelectronics. In particular, aerosol jet printing (AJP) is a promising means to achieve all-printed circuits and systems, offering micrometer-scale resolution and broad ink processing capabilities. In this work, I will present aerosol-jet-printed, ultrahigh-responsivity photodetectors that consist of well-aligned, percolating networks of semiconducting MoS_2 nanosheets paired with printed graphene electrodes on flexible polyimide substrates. An MoS_2 ink containing high-aspect-ratio nanosheets with a large fraction of monolayers is obtained by electrochemical exfoliation, followed by megasonic atomization during AJP, which not only aerosolizes the inks but also further exfoliates the nanosheets during printing. The ink is also formulated with terpineol, a high-boiling-point solvent that is critical for achieving aligned nanosheets in uniform morphology. After printing, the devices undergo photonic annealing, which removes insulating residues from the film and yields quasi-ohmic contacts between MoS2 and graphene. The resultant photodetectors have responsivities exceeding 10^3 A W^{-1} in the visible range (515.6 nm), outperforming previously reported all-printed photodetectors by over three orders of magnitude. These photodetectors are also mechanically robust, withstanding over 1,000 bending cycles with negligible changes in device metrics. Overall, this work demonstrates that megasonic exfoliation coupled with modular design of AJP ink formulation not only preserves superlative optoelectronic properties of individual MoS_2 nanosheets, but also offers a scalable additive manufacturing scheme for mechanically flexible optoelectronics.

SESSION EL09.02: Synthesis of 2D Optoelectronic Materials and Their Heterostructures II
Session Chairs: Sonia Conesa-Boj and Thomas Kempa
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3009

1:45 PM *EL09.02.01
Selenides and Hybrid Halide Perovskites for Superconducting, Quantum and Optical Absorber Applications Anupama B. Kaul; University of North Texas, United States

The excitonic and multibody interactions in some semiconducting two-dimensional (2D) crystallites, their strain-dependent properties and pristine atomically flat interfaces, coupled with the ability to solution-process these materials, offer a rich playground to unveil fundamental physical mechanisms for exciting and innovative devices. Amongst these, the transition metal dichalcogenides (TMDCs), such as tungsten diselenide (WSe_2) and niobium diselenide ($NbSe_2$) are finding promise in nanoelectronics, optoelectronics, sensors and quantum photonics. On the other hand, halide perovskites in their 2D form exhibit equally intriguing optoelectronic properties for photo absorbers and solar cells. In this work, we have analysed the light-matter interactions in superconducting $NbSe_2$, semiconducting WSe_2 and 2D perovskites toward sensing devices enabled by quantum phenomena. Solution-processing of some of these 2D materials has provided a pathway to realize a rich plethora of flexible and bendable sensing devices which will also be discussed.

2:15 PM EL09.02.02
Wafer Scale High Responsive Active Matrix Image Sensor Enabled by Nanoparous MoS2 Intregated with IGZO Switching Transistor Anamika Sen, Arindam Bala and Sunkook Kim; Sungkyunkwan University, Korea (the Republic of)

The image sensors development with in-sensor switching capability is important to realize high performance optoelectronics. In view of this, an active pixel image sensor array based on nanoporous bilayer molybdenum disulfide (MoS_2), two-dimensional (2D) transition metal dichalcogenides (TMDCs) have demonstrated. The presented active pixel image sensor includes one switching transistor with indium–gallium–zinc-oxide (IGZO) as an active channel material and a photo-sensing transistor with nanoporous bilayer MoS_2-channel. The nanoporous structure is fabricated directly on MoS_2, grown on a 4-inch Si/SiO_2 wafer, utilizing block copolymer lithography. The nanoporous structure of the MoS_2 sensing transistor gives rise to generation of subgap states within bandgap, which promotes trap-assisted photogating effect. The nanoporous MoS_2 phototransistors exploit mechanism involving the photogating effect to achieve high responsivity of 5.2 10^4 A/W. Further, nanoporous MoS_2 phototransistors integrated with IGZO switching transistors are assessed with image mapping for blue (405 nm), green (532 nm) and red (638 nm) incident lights using nine sets of 4×4 active-matrix image sensor throughout the 4-inch wafer. Generally, confronted challenge on TMDCs-based active-matrix image sensors is the fabrication of an integrated circuit with elevated performance is resolved by boosting trap assisted photogating mechanism in MoS_2. Marginal deviation in electrical performance parameters of 144 devices presents reliability in non-transfer, nanostructured MoS_2 fabrication technique. Our high-performance active-pixel image sensor matrix delivers the state-of-art in a 2D material based on integrated circuitry and pixel image sensor applications.

2:30 PM EL09.02.04
Growth of 2D Tungsten Disulfide on Sapphire and SiO_2/Si Using Ammonium Paratungstate as a Precursor Yi Ting Chen; National Taiwan University of Science and Technology, Taiwan

2D transition metal dichalcogenides have attracted extensive attention in recent years due to their intriguing features including semiconducting properties, tunable mobility, and flexibility. The potential of these materials for future applications largely relies on the strategies to effectively control the growth parameters for achieving large size and layer tunable material growth. In this work, we have attempted to directly grow WS_2 triangular flakes on sapphire and SiO_2/Si substrates via chemical vapor deposition (CVD) by using ammonium paratungstate as a precursor. Monolayer to few-layer of WS_2 can be effectively grown by controlling growth conditions such as sulfur concentration, argon flow rate, and growth temperature. Then, the as-grown WS_2 is further confirmed by the Raman, photoluminescence (PL), and atomic force microscopy (AFM). In addition, the as-grown WS_2 has been transferred on top of the electrodes on SiO_2/Si to fabricate a field-effect transistor device. The device shows the p-type behavior of WS_2 with a field-effect mobility of 0.00949 cm^2/Vs at room temperature. The result demonstrated herein shows the potential of ammonium paratungstate as an effective alternative precursor in the growth of tungsten based 2D semiconducting materials.

2:45 PM EL09.02.05
Unraveling the Charge Transport Mechanisms in Covalently Interconnected Solution-Processed MoS_2 Electronic Devices Francesca Urban[1,2,3], Stefano Ippolito[4], Wenhao Zheng[5], Onofrio Mazzarisi[6], Cataldo Valentini[1], Adam Kelly[7,2,3], Sai Manoj Gali[8], Mischa Bonn[5], David Beljonne[8], Federico Corberi[9], Jonathan N. Coleman[7,2,3], Hai Wang[5] and Paolo Samorì[1]; [1]Institut de Science et d'Ingénierie Supramoléculaires, France; [2]AMBER, Ireland; [3]Trinity College Dublin, The University of Dublin, Ireland; [4]A.J. Drexel Nanomaterials Institute, United States; [5]Max Planck Institute for Polymer Research, Germany; [6]Max Planck Institute for Mathematics in the Sciences, Germany; [7]Centre for Research on Adaptive Nanostructures and Nanodevices, Ireland; [8]Université de Mons, Belgium; [9]Università degli Studi di Salerno, Italy

Solution-processed semiconducting transition metal dichalcogenides (TMDs) are a hot-topic research trend in printed (opto)-electronics.
Indeed, liquid phase exfoliation is an efficient strategy to convert bulk layered materials into thin nanosheets dispersed in a suitable solvent[1]. The obtained inks can be printed into thin films using several approaches, including ink-jet printing, screen printing, and spray coating[2], thereby promoting the advances of printed electronics where low-cost and large-area fabrication is as relevant as device performance.
However, the device performance is limited by structural defects resulting from the exfoliation process and poor inter-flake electronic connectivity within

the films. The formation of covalent interconnected networks of TMDs potentially represent an efficient strategy to simultaneously heal sulfur vacancies and bridge adjacent flakes, thereby generating percolation pathways for the charge transport, ultimately boosting the electrical performance[3].
Here, we unveil the charge transport mechanisms of printed devices based on covalent MoS_2 networks via multiscale analysis, by comparing the effects of aromatic vs. aliphatic dithiolated linkers. Temperature-dependent electrical measurements reveal hopping as the dominant transport mechanism and a novel analysis based on percolation theory attributes the superior performance of devices functionalized with π-conjugated molecules to the improved inter-flake electronic connectivity and formation of additional percolation paths. Our findings provide valuable guidelines for improving the charge transport properties in MoS_2 devices based on covalent networks.

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3:00 PM BREAK

3:45 PM EL09.02.07
Growth, Properties, and Applications of Hexagonal Boron Nitride Thin Films Abhijit Biswas[1], Qiyuan Ruan[1], Frank Lee[2], Chenxi Li[1], Sathvik A. Iyengar[1], Anand B. Puthirath[1], Xiang Zhang[1], Harikishan Kannan[1], Tia Gray[1], A G. Birdwell[3], Mahesh R. Neupane[3], Pankaj Shah[3], Ruzmetov Dmitry[3], Tony Ivanov[3], Robert Vajtai[1], Manoj Tripathi[2], Alan Dalton[2], Boris I. Yakobson[1] and Pulickel Ajayan[1]; [1]Rice University, United States; [2]University of Sussex, United Kingdom; [3]DEVCOM Army Research Laboratory, United States

Two-dimensional van der Waals (2D-vdW) layered hexagonal boron nitride (h-BN) has gained tremendous research interest over recent years due to its unique growth morphology and consequent fascinating properties, and application potentials in nano-optoelectronics. However, the high-quality domain growth of h-BN thin films directly on insulating substrates remains significantly challenging because of high-bonding anisotropicity and complex growth kinetics, thus hindering its usefulness in integrated nano-devices. We report the growth h-BN thin films directly on low-miscut atomically smooth insulating c-Al2O3 substrates by using the pulsed laser deposition (PLD) method, showing remarkable unidirectional triangular-shape domain growth as well as nanosheets-like surface morphology, depending on the growth temperature. Comprehensive chemical, spectroscopic, microscopic, optical, magnetic and tribological characterizations further demonstrates the excellent crystalline quality, numerous functional properties, and application potentials of films [1]. Our observations might pave the way for large-area direct growth of electronic-quality 2D h-BN thin films on insulating substrates for high-performance nano-optoelectronics, and would be beneficial for hetero engineering of 2D-vdW materials with emergent phenomena.

[1] A. Biswas *et al.*, arXiv:2208.09469; A. Biswas *et al.*, arXiv:2208.09468.

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4:00 PM EL09.02.08
Stacking 2D Chalcogenides with Atomic Layer Deposition Jun Yang, Fabian Krahl, Samik Mukherjee, Sebastian Lehmann and Kornelius Nielsch; Leibniz Institute for solid State and Materials Research, Germany

Chalcogenides, especially transition metal dichalcogenides (TDMC, but also some other chalcogenides like SnS_2 and Sb_2Se_3) can have a layered structure similar to graphene, but instead of being a semimetal they offer a wide variety from semiconducting to conducting materials that are interesting for efficient, fast and flexible (opto-)electronics. Their electronic behavior can be strongly influenced by the thickness of the material (e.g. how many sheets are stacked on top of each other).[1]
With atomic layer deposition (ALD) the layer stacking and individual layer thickness can be precisely controlled in the nm scale and several 2D materials have already been successfully deposited with ALD [2,3]. ALD is scalable and can coat uneven surfaces, which sets ALD apart from many other methods for the synthesis of 2D materials e.g.exfoliation. This makes the prospect of depositing functional thin films of 2D materials with ALD very tantalizing.
We utilize ALD to deposit superlattice stacks of 2D materials with "spacing" materials in between to examine their electrical properties. An example is our fabrication of a superlattice consisting of SnS_2 and Sb_2S_3 with ALD. I'll present our results on the properties of ALD deposited SnS_2/Sb_2S_3 superlattices and future prospects of inorganic-organic hybrid materials with 2D materials using Atomic and Molecular layer deposition (ALD/MLD).

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4:15 PM EL09.02.10
Transfer-Free *In Situ* Growth of Tunable Au-WSe$_2$ Junctions Sathvik A. Iyengar[1], Lucas M. Sassi[1], Xingfu Li[1], Yuefei Huang[1], Anand B. Puthirath[1], Tanguy Terlier[1], Ali Mojibpour[1], Anna Paula C. Teixeira[2], Palash Bharadwaj[1], Chandra Sekhar Tiwary[1], Robert Vajtai[1], Venkataraman Swaminathan[1], Saikat Talapatra[3], Boris I. Yakobson[1] and Pulickel Ajayan[1]; [1]Rice University, United States; [2]Universidad Federal de Minas Gerais, Brazil; [3]Southern Illinois University, United States

Two-dimensional transition metal dichalcogenides (TMDs) remain a topic of immense interest due to their wide range of promising properties including but not limited to the electrical, optical, and mechanical kinds. Specifically, given their low operational switching costs, they find many niche applications such as in neuromorphic computing and low subthreshold swing Field Effect Transistors (FETs). Challenges, however, lie in the process of crystal growth— and more specifically—channel/contact engineering for various device applications. To date, two major methods to engineer metal-TMD contacts have been proposed. 'Top contacts' involve fabricating metal electrodes directly on the surface of TMD flakes, and 'edge contacts' involve transferring TMD flakes onto pre-patterned metal electrodes, possibly followed by a functionalization step to ensure better contacts. In this work, through a holistic approach, we demonstrate kinetics-governed in-situ growth regimes (surface or edge growth from metal) of WSe_2, provide mechanistic understanding of these regimes, and fabricate an in-situ device with flawless source-to-drain channel contacts, demonstrating a 2D semiconductor transistor via a "transfer-free" method within the 450-600 ^{0}C, 2 h-time window for Back End Of Line (BEOL) integration. We leverage directional edge growth to fabricate contacts that exhibit robust thickness-dependent junction tunability. FET measurements reveal a low subthreshold swing of ~140 mV/decade, a mobility of 107 ± 38 $cm^2V^{-1}s^{-1}$, and robust ON/OFF ratios of $\sim 10^6$.

SESSION EL09.03: Synthesis of 2D Optoelectronic Materials and Their Heterostructures III
Session Chairs: Thomas Kempa and Sudha Mokkapati
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3009

8:30 AM EL09.03.01
Photon Upconversion in a 2D Inorganic–Organic Semiconductor Heterostructure Reynolds Dziobek-Garrett[1], Christian J. Imperiale[2], Mark W. Wilson[2] and Thomas Kempa[1]; [1]Johns Hopkins University, United States; [2]University of Toronto, Canada

Van der Waals heterostructures (vdWHs) comprised of stacked 2D crystal monolayers can be used to elicit emergent electronic and photonic phenomena. Moreover, energy transfer processes may be engineered via vdWHs by taking advantage of the atomically-abrupt, Å-scale, and topologically tailorable interfaces within them. Here, we prepare heterostructures comprised of 2D WSe_2 monolayers interfaced with DBP-doped rubrene, an organic semiconductor capable of triplet fusion. We fabricate these films over large areas entirely through vapor deposition methods, thereby demonstrating a pathway toward device-scale heterostructures. Time-resolved and steady-state photoluminescence measurements reveal both quenching of WSe_2 emission by rubrene and emission from the DBP species at 612 nm, for excitation at 730 nm, which is clear evidence of photon upconversion. Through an analysis of the decay dynamics in the heterostructure we conclude that excitation transfer from WSe_2 to the triplet state of rubrene proceeds on sub-nanosecond timescales. The dependence of the upconversion emission on excitation intensity is consistent with a triplet fusion mechanism, and we achieve maximum efficiency (linear regime) of the upconversion emission at threshold intensities as low as 110 mW/cm^2, which is comparable to the solar irradiance. This study highlights the potential for advanced optoelectronic applications employing vdWHs which leverage strongly-bound excitons in monolayer TMDs and organic semiconductors.

8:45 AM EL09.03.02
Hierarchical Structuring of Solution-Processed 2D Semiconductors for Wafer-Scale, Stretchable Electronics Dongjoon Rhee[1,2], Myeongjin Jung[2], Jihyun Kim[2], Okin Song[2], Jason Lynch[1], Boyun Han[2], Deep M. Jariwala[1] and Joohoon Kang[2]; [1]University of Pennsylvania, United States; [2]Sungkyunkwan University, Korea (the Republic of)

Two-dimensional (2D) semiconductors have gained significant attention for next-generation electronics that are light-weight, flexible, and stretchable. Achieving stretchability in 2D semiconductors while suppressing crack formation, however, is still difficult without introducing lithographically etched micropatterns, which significantly reduces active device areas. Furthermore, scalable synthesis of high-quality 2D materials in a cost-effective, high-throughput manner remains challenging. In this talk, I will present a solution-based hierarchical structuring strategy to create stretchable 2D semiconducting films that are continuous over wafer-scale areas. Electrochemically exfoliated MoS_2 nanosheets with large lateral sizes (~1 μm) are first assembled into a uniform film on a pre-strained thermoplastic substrate, followed by strain relief of the substrate to create nanoscale wrinkles. Subsequent strain relief cycles with the presence of soluble polymer films produce hierarchical wrinkles with multi-generational structures. Stretchable MoS_2 films are then realized by curing an elastomer directly on the wrinkled surface and dissolving the thermoplastic. Because the film was continuous over large areas, an array of two-terminal devices could be deterministically fabricated by simply depositing electrodes without alignment procedures. Three-generation hierarchical MoS_2 wrinkles are resistant to cracking up to 100% substrate stretching and achieve drastically enhanced photoresponsivity compared to the flat counterpart over the visible and NIR regimes, while the flat MoS_2 film is beneficial in creating strain sensors because of its strain-dependent electrical response.

9:00 AM EL09.03.03
Quasi-One-Dimensional Molybdenum Disulfide Nanoribbons Ganesh Ghimire[1], Rajesh Ulaganathan[1], Denys Miakota[1], Agnès Tempez[2], Marc Chaigneau[2] and Stela Canulescu[1]; [1]Technical University of Denmark, Denmark; [2]Horiba France SA, France

One-dimensional (1D) materials, such as nanowires, nanotubes, and nanorods, have been studied intensively recently due to their unusual structural characteristics and novel physical properties[1–3]. Similarly, 1D structures of transition metal dichalcogenides (TMDs), such as WS_2 nanorods, have been shown to exhibit striking functionalities compared to their two-dimensional (2D) counterparts, such as enhanced photovoltaic effect in bulk, in the absence of a p-n junction [1]. These findings can lead to many exciting opportunities for their utilization in optoelectronic devices, such as solar cells, photodetectors, laser diodes, and light-emitting diodes.

This paper will discuss a novel approach for synthesizing MoS_2 nanostructures with tunable dimensionality ranging from 2D to 1D. In our process, epitaxial precursors of transition metal oxides, i.e., ultra-thin films of MoO_x ($x<3$) grown by Pulsed Laser Deposition (PLD), serve as precursors [2,3]. We will show that the addition of halides during sulfurization leads to unidirectional growth into quasi-1D MoS_2 nanoribbons. The morphological and atomic resolution imaging studies reveal an anisotropic growth of epitaxial quasi-1D nanoribbons in either 2H or 3H stacking orientation. Tip-enhanced photoluminescence (TEPL) spectroscopy reveals a photoluminescence (PL) emission from the edge of the nanoribbons and no emission from the core of the quasi-1D structures. Moreover, we observe an edge-enhanced secondary harmonic generation (SHG) of the quasi-1D MoS_2 nanoribbons, which will be discussed in detail during the talk. Finally, we will report the first ultrasensitive photodetector based on a single 1D MoS_2 nanoribbon. The highly crystalline quasi-1D ribbon device exhibits a high photocurrent response under illumination and outstanding stability. Photocurrent measurements of single-ribbon photodetector made on SiO_2/Si substrate exhibit a photoresponsivity above 500 AW^{-1} at a wavelength of 532 nm, which exceeds that of graphene, MoS_2, or other nanoribbon-based devices. The experimental results show that single-crystalline quasi-1D MoS2 nanoribbons have immense potential for high-performance photodetector applications.

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9:15 AM BREAK

SESSION EL09.04: Structural Characterization of Layered Optoelectronic Materials
Session Chairs: Thomas Kempa and Sudha Mokkapati
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3009

10:00 AM *EL09.04.01
2D Quantum Materials and Devices at the Atomic Scale Adina Luican-Mayer; University of Ottawa, Canada

In this talk, I will focus on two topics: 1. Scanning tunnelling microscopy and spectroscopy experiments aimed at creating novel moiré structures by twisting 2D layers, including the demonstration of reversible local response of domain wall networks in ferroelectric interfaces of marginally twisted WS_2 bilayers and spectroscopic evidence of flat bands in antiparallel twisted WS_2 bilayers; 2. I will discuss our progress in realizing quantum-confined devices in WS_2 monolayers including demonstration of gate-defined quantum dots, charge detectors and 1D transport.

10:30 AM EL09.04.02
Interferometric 4D-STEM Imaging of Lattice Reconstruction in Transition Metal Dichalcogenide Moiré Bilayers Madeline Van Winkle, Isaac Craig and Kwabena Bediako; University of California, Berkeley, United States

Moiré superlattices, formed by vertically stacking van der Waals layers with a small rotational offset and/or lattice mismatch, are a powerful platform for modulating the physicochemical behavior of two-dimensional solids. Moiré architectures comprised of semiconducting transition metal dichalcogenides (TMDs) are of significant fundamental and technological interest because they exhibit distinctively tunable optoelectronic features, such as inter- and intralayer moiré excitons and trions, as well as relatively robust correlated electronic phases, including Wigner crystal and correlated insulating states. While the electronic band structures of moiré superlattices can be intentionally modified by changing the extent of crystallographic misalignment between constituent layers, intrinsic lattice reconstruction also plays an underlying yet significant role in controlling the emergent behavior in these systems. Reconstruction of the superlattice and the development of intralayer shear strain subsequently lead to reconstruction of the electronic band structure, affecting features such as the depth of the moiré potential, the 'flatness' of low-energy bands, and the real-space localization of charge carriers. Visualizing the structure and strain fields of TMD moiré materials is therefore paramount to understanding and controlling their (opto)electronic behavior. Although scanning probe and electron microscopy techniques have provided a qualitative picture of reconstruction in TMD moiré bilayers, understood in terms of the variation in interlayer stacking energy throughout the superlattice, the physical mechanisms by which reconstruction occurs and the distribution of reconstruction strain have thus far only been simulated. In this talk, I will demonstrate how interferometric four-dimensional scanning transmission electron microscopy can be used to quantitatively map the mechanical deformations through which reconstruction occurs and the corresponding strain distributions in small-angle twisted bilayer MoS_2 and WSe_2/MoS_2 heterobilayers with sub-nanometer resolution. This work sheds light on the distinct effects of twist angle, lattice constant mismatch, extrinsic heterostrain, and symmetry of the superlattice on the reconstruction process in TMD moirés and provides a framework for measuring mechanical deformations and strain in a wide array of moiré materials for direct correlative measurements between structure and emergent (opto)electronic phenomena.

10:45 AM EL09.04.03
Thickness-Dependent Interactions Between Helical Chains of 2D Tellurene Kunyan Zhang[1], Gang Wan[2], Shelly Kelly[3], Wenzhuo Wu[4] and Shengxi Huang[1]; [1]Rice University, United States; [2]Stanford University, United States; [3]Argonne National Laboratory, United States; [4]Purdue University, United States

Tellurene is the two-dimensional (2D) form of tellurium consisting of helical Te chains. The unique crystal structure of tellurene brings about remarkable properties, such as high hole mobility, excellent thermoelectricity, and anisotropic optical nonlinearity. 2D tellurene is predicted to have different phases because of the interaction between helical Te chains. However, it is not clear yet how the bonding of the helical chain changes due to interactions between chains, especially for Te with different thicknesses. In this work, we directly measured the bonding of Te within one helical chain and between different chains using x-ray absorption spectroscopy (XAS). We further demonstrated that the interaction between chains was strengthened when the thickness of tellurene decreased. This dependence on thickness is also consistent with the increased phonon frequency for smaller thicknesses. This work reveals the atomic bonding of 2D tellurene and paves the way for investigating the phase change of nanoscale elemental semiconductors.

SESSION EL09.05: Emerging 2D Optoelectronic Materials—Perovskites, Metal-Oxides, Hybrid HeterostructuresandModelling of 2D Materials and Heterostructures—New Discoveries and Predictions
Session Chair: Sonia Conesa-Boj
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3009

1:30 PM EL09.05.01
Light-Induced Halide Segregation in Mixed-Halide Ruddlesden-Popper Quasi-2D Perovskites Kunal Datta[1], Alessandro Caiazzo[1], Michael A. Hope[2], Junyu Li[1], Aditya Mishra[2], Manuel Cordova[2], Zehua Chen[1], Lyndon Emsley[2], Martijn M. Wienk[1] and Rene A. Janssen[1]; [1]Technische Universiteit Eindhoven, Netherlands; [2]Ecole Polytechnique Fédérale de Lausanne, Switzerland

Layered Ruddlesden-Popper perovskite phases have emerged as a promising class of optoelectronic materials due to their high defect tolerance, structural tunability between a variety of lower-dimensional phases, and compositional versatility on account of a growing library of spacer cations. However, the photostability of mixed-halide compositions, relevant for light harvesting as well as emission applications, has not yet been comprehensively explored in such materials compared to in three-dimensional (3D) analogs.

This work characterizes light-induced halide segregation in lower-dimensional Ruddlesden-Popper perovskites.[1] Using *in-situ* time- and temperature-dependent photoluminescence (PL) spectroscopy, the optoelectronic behaviour of such mixed-halide layers is tracked.[2] The observations are compared to compositional and structural data, generated using solid state nuclear magnetic resonance (ssNMR) spectroscopy, density functional theory (DFT), and grazing incidence wide angle X-ray scattering (GIWAXS) tools, and a correspondence between optoelectronic instability upon illumination and structural nature of the layer is established.

Phenethylammonium (PEA)-based Ruddlesden-Popper two-dimensional (2D) mixed-halide perovskite thin films ($n = 1$) are first characterized for their photostability and are found to be largely resilient to halide segregation over prolonged exposure to visible light. ssNMR measurements show that this resilience is likely due to the presence of nanoscale iodide-rich sites that limit ion migration pathways which typically drives halide segregation in 3D perovskites.

Quasi-2D perovskite layers are then developed using a co-solvent engineering approach.[3] By tuning the crystallization rate of different *n*-phases, structurally stratified films with lower-dimensional ($n = 1,2$) phases at the substrate interface and higher-dimensional (3D-like) phases at the air interface can be formed. Here, a quasi-2D phase ($n = 2$) is found to be vulnerable to halide segregation, as also observed in 3D-like phases, showing the commonly observed PL red-shift. However, while entropic remixing of halide ions in dark conditions occurs in 3D-like phases, with a blue-shift of the PL peak, the process is absent in the $n = 2$ phase at room temperature and only occurs at elevated temperatures to restore the mixed-phase. This is due to a higher activation barrier for ion migration in such quasi-2D phases.[4]

These observations show that iodide-bromide phase stability in mixed-halide quasi-2D perovskites is strongly related to the structural phase of the layer (n = 1, 2, 3, …). The prevailing view that lower-dimensional phases are inherently stable to ion migration is challenged by observations that clearly show the vulnerability of the $n = 2$ phase to halide segregation. The structural nature of the perovskite is also found to not only determine the tendency of halides to segregate, but also control the halide remixing behaviour in dark conditions.

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1:45 PM EL09.05.05
Crystallization Mechanism of Regular- and Reverse-Graded Quasi-2D Perovskites Alessandro Caiazzo, Kunal Datta, Martijn M. Wienk and Rene A. Janssen; TU Eindhoven, Netherlands

Quasi-2D perovskites have recently attracted great interest because of their structural tunability and enhanced stability compared to 3D perovskites. Quasi-2D films display a higher degree of complexity because multiple structural phases are formed during film crystallization. As a result, it is common to observe multidimensional films with both 2D and 3D phases forming a phase distribution gradient, where lower-dimensional phases locate at the bottom, and 3D at the top of the film. Recently, a few studies have found that it is possible to create a reverse-graded quasi-2D perovskite films, where 2D phases locate at the top and 3D ones at the bottom. Even though the crystallization mechanism of quasi-2D perovskites has been investigated before, no study has analyzed the crystallization differences between regular- and reverse-graded quasi-2D perovskites.

In our work, we have fabricated quasi-2D perovskite films using spacers with increasing alky chain length, going from butylammonium to dodecylammonium. First, we found that alkyl spacer length plays a major role in the phase distribution gradient. Short spacers form a conventional 2D-3D gradient, with 2D phases at the bottom, whereas long spacers reverse the gradient. Interested by this behavior, we analyzed the crystallization mechanism via in-situ absorption measurements and described how film formation changes with increasing alkyl spacer length. With the help of these findings, we designed a new fluorinated spacer and used a multispacer approach to tune quasi-2D perovskite film properties, displaying yet another facet of their degree of tunability.

2:00 PM BREAK

2:30 PM EL09.05.06
Spatial Control of Substitutional Dopants in Hexagonal Monolayer WS_2: The Effect of Edge Termination Ana Laura Elias[1], Tianyi Zhang[2], Mingzu Liu[3], Kazunori Fujisawa[4], Michael Lucking[5], Kory Beach[6], Fu Zhang[3], Maruda Shanmugasundaram[7], Andrey Krayev[7], William Murray[3], Yu Lei[8], Zhouhang Yu[3], David Sanchez[3], Zhiwen Liu[3], Humberto Terrones[5] and Mauricio Terrones[3]; [1]Binghamton University, United States; [2]Massachusetts Institute of Technology, United States; [3]The Pennsylvania State University, United States; [4]Shinshu University, Japan; [5]Rensselaer Polytechnic Institute, United States; [6]Lawrence Livermore National Laboratory, United States; [7]HORIBA Instruments Inc., United States; [8]Tsinghua Shenzhen International Graduate School, China

The ability of controlling density and spatial distribution of substitutional dopants in semiconductors is crucial for achieving desired physicochemical properties. Substitutional doping with adjustable doping levels has been previously demonstrated in two-dimensional (2D) transition metal dichalcogenides (TMDs); however, the micron spatial control of dopant distribution remains an open field. In this work, we demonstrate that edge termination is an important characteristic of 2D TMD monocrystals that affects the distribution of substitutional dopants. Particularly, in chemical vapor deposition (CVD)-grown monolayer WS_2, we find that a higher density of transition metal dopants is always incorporated in S-terminated domains when compared to W-terminated domains. Two representative examples demonstrate this sub-micron spatial distribution control, including hexagonal Fe- and V-doped WS_2 monolayers. Density functional theory (DFT) calculations are further performed, indicating that the edge-dependent dopant distribution is due to a strong binding of W atoms at W-zigzag edges, resulting in the formation of open sites at S-zigzag edges that enable preferential dopant incorporation. Based on our results, we envision that edge termination in crystalline TMD monolayers can be utilized as a novel and effective knob for engineering the spatial distribution of substitutional dopants, leading to in-plane hetero-/multi-junctions that could display fascinating electronic, optoelectronic, and magnetic properties.

2:45 PM EL09.05.07
Defect-Induced Band Structure Variations in Monolayer Vanadium Molybdenum Disulfide Alloy Yu-Ling Liu[1], Septia Kholimatussadiah[1,2,3],

Mohammad Qorbani[1,2], Kuei-Hsien Chen[1,3] and Li-Chyong Chen[1,2,2]; [1]Center for Condensed Matter Sciences (CCMS), National Taiwan University, Taiwan; [2]National Taiwan University, Taiwan; [3]Academia Sinica, Taiwan

The atomic defects have introduced a wide range of physical properties and potentially invoked many functionalities in two-dimensional transitional metal dichalcogenides. By an advanced polymer-assisted chemical vapor deposition, monolayer $Mo_{1-x}V_xS_2$ alloy was prepared with a high alloying level of up to x ~15%. We observed an apparent photoluminescence quenching and a lower energy absorption edge in the UV-visible spectrum. With a detailed observation of the atomic arrangement in the STEM-HAADF images, we found vanadium substitutional doping and other intrinsic defects, such as sulfur vacancies, antisites, adatoms, and dopant clusters. Using first-principle calculations, we calculated the formation energy of the observed defect types and the corresponding density of states and band structure. The simulation results show obvious bandgap shrinkage after vanadium incorporation and the gap states emerging from the dopant clusters and antisites. We demonstrate that the change in optical property can be attributed to the band structure variation induced by the multiple defect types in the alloy.

SESSION EL09.06: Poster Session
Session Chairs: Sonia Conesa Boj, Thomas Kempa and Sudha Mokkapati
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL09.06.02
First-Principles Calculations of Excitons Including Radiative Recombination and Polaritonic Effects— The Retarded Bethe-Salpeter Equation
Zachary N. Mauri, Christopher Ciccarino and Felipe H. da Jornada; Stanford University, United States

Recent research in 2D materials has revealed a host of phenomena only present in low-dimensional systems, such as the presence of strongly bound excitons due to the electronic confinement and weak dielectric screening. The electronic and optical properties in such systems have been largely captured with success through first-principles techniques based on interacting Green’s function formalisms, such as the ab initio GW and Bethe-Salpeter equation (BSE) approaches, respectively. However, these methods are typically derived assuming instantaneous many-electron interactions. Here, we describe a formalism to include retardation effects into the Bethe-Salpeter equation that is computationally efficient and gauge invariant. While previous efforts have focused on the effect of retardation effects in the direct (screened) electron-hole interactions, we find here that retardation effects in the (bare) exchange interactions are important in low dimensions. Our work predicts a renormalization of the exciton dispersion and a broadening of the exciton dispersion when retardation effects are included. More broadly, our approach can be applied to the study of polaritonic effects directly from standard interacting Green’s-function formalisms.

5:00 PM EL09.06.03
The Role Of Lead Precursors In Driving The Crystallization Of Two-Dimensional Lead Halide Perovskites Leo Sahaya Daphne Antony[1], Sjoerd v. Dongen[1], Gianluca Grimaldi[1], Simon Mathew[2], Arno v. Weijden[1], Lukas Helmbrecht[1], Bruno Ehrler[1], Willem L. Noorduin[1,2] and Esther Alarcon-Llado[1]; [1]AMOLF, Netherlands; [2]Van 't Hoff Institute for Molecular Sciences, Netherlands

Hybrid organic-inorganic perovskite semiconductors have triggered a paradigm shift in the field of photovoltaics. Low dimensional 2D hybrid organic-inorganic lead halide semiconductors have recently attracted major attention, owing to the emergence of new photo-physical properties compared to the 3D perovskites, including exciton-phonon coupling, edge state-based charge dissociation at grain boundaries and photon confinement. The ionic nature of these layered materials also makes them ideal candidates for solution processing into both thin films and nanostructured crystals. Studying the wide range of process parameters in different solution processing techniques like spin coating, and drop casting are important as they greatly influence the crystallization of 2D perovskites. However, this wide range of parameters promoting the crystallization of 2D perovskites is not as well understood as their 3D counterparts, where the inorganic precursor is typically overlooked.
In this work, we report on the role of different lead precursors in the crystallization process of 2D perovskite in drop-cast-based synthesis. In particular, we carefully examine the effect of the lead chemical state of the precursor on the crystallization pathway of BA_2PbI_4 (BAPI) perovskite by exposing lead iodide (PbI_2), lead carbonate ($PbCO_3$) and lead dioxide (PbO_2) agglomerate films to BAI: IPA solution in a dry atmosphere.
We combine in-situ optical microscopy, solution UV-VIS spectroscopy, and time-resolved high-performance liquid chromatography (HPLC) to reveal the different crystallization mechanistic and kinetics in the different lead precursor cases. We find that BAPI growth is fastest for the PbO_2 precursor followed by PbI_2, and the slowest being $PbCO_3$ (unless exposed to air). The fact that PbO_2 is the fastest is very surprising as it is the only precursor with a lead oxidation state (Pb^{4+}) that differs from that in the final product (Pb^{2+}). Optically the reaction appears similar in PbO_2 and PbI_2, but we find that in both cases solvated iodoplumbate complexes are released into the solution. As a result, not only the aggregate film partially converts to BAPI, but also high-quality BAPI crystals form in solution as either square (from PbO_2) or hexagonal (from PbI_2) shaped floating micro-plates. Photoluminescence and single crystal XRD analysis show that these micro-plates are of high crystalline quality, being mostly monocrystalline for the PbO_2 precursor. Careful time-resolved chemical examination of the solution with HPLC reveals the presence of different reaction intermediates in the three cases and therefore pinpoint competing crystallization pathways taking place during exposure, as well as indicates that the in-situ water evolution during the reduction of Pb^{4+} acts as a crystallization catalyst. This work thus provides key insights into inorganic precursors in the BAPI synthesis dynamics, that will contribute towards high-quality 2D perovskite films and microcrystals.

5:00 PM EL09.06.05
Photoinduced Interlayer Heat Transfer in Two-Dimensional TMDC Heterobilayers Visualized by Femtosecond Electron Diffraction Amalya C. Johnson[1], Johnathan Georgaras[1], Xiaozhe Shen[2], Aditya Sood[1], Helen Zeng[1], Ashley P. Saunders[1], Hyungjin Kim[1], Helen Yao[1], Tony F. Heinz[1], Felipe H. da Jornada[1], Aaron Lindenberg[1], Duan Luo[1,2] and Fang Liu[1]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States

When photoexcitation creates charge carriers in TMDC van der Waals heterostructures, phonons will be emitted through electron-phonon coupling during charge carrier scattering and relaxation. After that, further heat exchange and thermalization will occur between the layers. Using ultrafast electron diffraction, photoinduced phonon dynamics are directly revealed in MoS_2/WS_2 and $WSe_2/MoSe_2$ twisted heterobilayers. Upon photoexcitation, the initial charge carrier transfer and relaxation leads to ≤ 1 ps ultrafast lattice heating in each layer of the heterobilayer. Subsequently, we identified a distinct heat transfer channel between the two layers that appears on the order of 20 ps after photoexcitation. We further identified the dependence of this heat transfer rate on heterobilayer twist angles. This experimentally determined heat transfer rate was found to occur up to an order of magnitude faster than predicted in a fully thermalized model. This heat transfer is likely facilitated by the initial nonthermal phonon distribution from carrier scattering and relaxation. Quantitative determination of the ultrafast lattice dynamics across TMDC interfaces is an essential key in understanding the structure-property relationships of 2D heterobilayers. These findings will have direct applications in the design and fabrication of 2D material quantum devices in the future.

5:00 PM EL09.06.06
A Novel Benzotriazole-Based 2D Interlayer for Passivation of $FAPbI_3$ Solar Cells Alessandro Caiazzo[1], Arthur Maufort[2], Bas T. van Gorkom[1], Willemijn H. Remmerswaal[1], Jordi Ferrer Orri[3], Junyu Li[1], Junke Wang[1], Wouter Van Gompel[2], Caterina Ducati[3], Martijn M. Wienk[1], Samuel D. Stranks[3], Dirk Vanderzande[2] and Rene A. Janssen[1]; [1]TU Eindhoven, Netherlands; [2]Hasselt University, Belgium; [3]University of Cambridge, United Kingdom

Perovskite solar cells based on $FAPbI_3$ active layer have become the standard to make high efficiency solar cells, which recently reached values above 25%. In regular device configuration, the interface between perovskite and hole-transport layer (HTL) has been shown to be highly detrimental for voltage losses, thus requiring the use of a passivation layer to mitigate this phenomenon. A variety of passivation layers have been used in the literature, the majority of them being 2D interlayers formed from conventional spacers such as butylammonium and phenethylammonium iodide.

In our work, we synthesised a series of benzotriazole (BTa)-based ammonium salts, and we showed that this class of materials can form 2D perovskite films and single crystals. When using BTa-2D perovskites as passivation layer onto $FAPbI_3$, we obtained solar cells with efficiency of about 22%, an increase of ~2% compared to the reference. The enhancement of performance is mostly related to an increase of open-circuit voltage (V_{OC}), which brings the V_{OC} to 91% of the radiative limit. The passivation effect was studied via quasi-Fermi level splitting and SEM-cathodoluminescence analysis, finding that BTa passivates both the neat perovskite film and the interface with Spiro-OMeTAD, used as HTL. On a nanometer-level, we show that both grains and grain boundaries are more luminescent after passivation with BTa.

To better understand the formation of 3D/2D heterostructures, we employed a variety of characterization techniques, going from photoluminescence and x-ray diffraction to ultra-sensitive depth-profiling x-ray photoemission spectroscopy. Here, among the insights we obtained, we found that the 2D interlayer is in the order of ~10 nm, but that BTa molecules penetrate in the bulk up to ~50 nm. Furthermore, non-uniform and open 2D passivation layers are enough to improve V_{OC}, whereas closed and thicker films are very detrimental for device performance.

Overall, benzotriazole-2D perovskites are a new class of lower-dimensional perovskites that are efficient in passivating 3D perovskites and that could be used, in future works, as photo-absorber in quasi-2D perovskite solar cells.

5:00 PM EL09.06.07
First-Principles Study of the Doping-Dependent Exciton and Trion Linewidth in Monolayer $MoTe_2$ Supavit Pokawanvit[1], Aurelie Champagne[2], Jonah B. Haber[2,3], Diana Qiu[4], Jeffrey B. Neaton[2,3,5] and Felipe H. da Jornada[1]; [1]Stanford University, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]University of California, Berkeley, United States; [4]Yale University, United States; [5]Kavli Energy NanoScience Institute, United States

The linewidth of excitonic complexes provides direct insights into the nature of optical excitations in materials and their decay pathways. In doped semiconducting monolayers of transition metal dichalcogenides (TMDs), the linewidth associated with an exciton resonance is sensitive to extra charge carriers due to the nontrivial dielectric screening from the Fermi sea and the variety of states an exciton can scatter to, even in the weak-doping limit. Therefore, computational approaches and first-principles calculations can provide unique insights into the microscopic origin of such interactions and the nature of the associated scattering events. In this talk, we present results from first-principles calculations of Dyson-like equations associated with 3- and 4-body interacting particle problems (involving electrons and holes) to address this problem. We compare our results with perturbative calculations based on the scattering of excitons to Fermi-sea electron-hole pairs and assess the importance of many-body screening, band-filling effects, and the *ab initio* description of electron-hole coupling terms.

5:00 PM EL09.06.08
Mimicking IR Visionary System via 0D-2D Heterojunction of InAs QD/WSe_2 Artificial Synapse Hyeongtae Kim[1], Dong Park Lee[1], Nuri Oh[2] and Jun Hong Park[1]; [1]Gyeongsang National University, Korea (the Republic of); [2]Hanyang University, Korea (the Republic of)

Emulating visionary and learning/memory function of biological neural system to use 3-terminal transistor is an important technology for effectively controlled in a low power state. In this report, we developed an artificial visionary WSe_2 based 3 Terminal FET with QD to emulate of IR sensitive biological synaptic behavior.

Quantum dots (QDs) combined with 2D WSe_2 to mimicking visionary biological synapse and demonstrate neuromorphic functionalities of the human brain via van-der-Waals (vdW) heterostructure. Compared with existing WSe_2, QD/WSe_2 heterojunction FET induced better electrical characteristic and sensitivity under the illumination of visible light and infrared light.

For mimicking potentiation and depression characteristic of biological synaptic behavior,
Surface morphology and Contact potential of Wse2 and QD/WSe_2 were analysis by Atomic Force Microscope (AFM) and Kelvin probe force microscope (KPFM), respectively. The bonding structure of 0D-2D heterojunction is confirmed by Fourier-transform infrared spectroscopy (FT-IR) and Raman spectroscopy.

This 0D-2D heterojunction structure provide a new pathway to emulating IR sensitive visionary neural system to develop IR sensitive visionary neural system, and emerging materials junctions.

5:00 PM EL09.06.09
NeuroWeb—Atomically Thin, Non-Invasive Surface Electrode Array for Probing Neural Activity Young-Woo Pyo[1], Jung Min Lee[1], Yeon Jun Kim[1], Jin Hee Hong[1,2], Yonghyeon Jo[1,2], Wonsik Choi[1,2], Dingchang Lin[3] and Hong-Gyu Park[1,2,1]; [1]Korea University, Korea (the Republic of); [2]Institute for Basic Science, Korea (the Republic of); [3]Johns Hopkins University, Korea (the Republic of)

Electrophysiological recording technologies can provide valuable insights into the functioning of the central and peripheral nervous systems. Surface electrode arrays (SEAs) made of soft materials or implantable multi-electrode arrays (iMEAs) with high electrode density have been widely utilized as neural probes. However, neither of these probe types can simultaneously achieve non-invasiveness and robust neural signal detection(Salatino, J.W., et al. *Nat. Biomed. Eng.* **1** (2017), 862). Here, we present an atomically thin, non-invasive neural probe (the "NeuroWeb") consisting of hexagonal boron nitride and graphene, which leveraged the strengths of both SEAs and iMEAs. The NeuroWeb open lattice structure with a total thickness of 100 nm demonstrated high flexibility and strong adhesion, establishing a conformal and tight interface with the uneven mouse brain surface. Vertical stacking of additional layers showed the feasibility of multiplexing with high electrode densities. Furthermore, *in vivo* electrophysiological recordings and whiskers stimulation experiment revealed that NeuroWeb detected stable single-unit activity of neurons with high signal-to-noise ratios for one week, exhibiting high performance comparable to implantable probes. Specifically, in comparison with 1 mm-thick polymer-metal SEA, NeuroWeb showed significant increases in spike amplitude and number of detected neurons as well as exceptional transparency. Therefore, NeuroWeb can be expected to pave the way for understanding complex brain networks with optical and electrophysiological mapping of the brain.

5:00 PM EL09.06.11
High Thermal Conductivity and Ultra-Low-K Dielectric Constants in Two-Dimensional Polymers Ashutosh Giri; University of Rhode Island, United States

To limit electronic crosstalks in miniaturized microprocessors, low-dielectric-constant (low-k) materials are necessary to limit charge build-up and signal propagation delay. However, lowering the dielectric constant also comes with low thermal conductivities in materials, which complicates heat dissipation in high-power-density chips. Two-dimensional (2D) covalent organic frameworks (COFs) combine high surface-to-volume ratios, which lead to low dielectric permittivities, and periodic layered geometries, which result in high thermal conductivities. Here, we report the measurement of high-quality COF thin films with thermoreflectance spectroscopy to reveal that 2D COFs have high thermal conductivities (1 $W\ m^{-1}\ K^{-1}$) with ultra-low dielectric permittivities ($k = 1.6$). Our results pave way for highly oriented, layered 2D polymers are promising next-generation dielectric layers.
Through systematic atomistic simulations, we also demonstrate that these porous polymers possess tunable mechanical and thermal properties that arise from their singular layered architecture comprising strongly bonded light atoms and periodic laminar pores. For example, the negative Poisson's ratio arises from the weak van der Waals interactions between the two-dimensional layers along with the strong covalent bonds that act as hinges along the layers, which facilitate the twisting and swiveling motion of the phenyl rings relative to the tensile plane. The mechanical and thermal properties of two-dimensional covalent organic frameworks can be tailored through structural modularities such as control over the pore size and/or interlayer separation.

5:00 PM EL09.06.12
Wafer-Scale δ-Waveguides for Two-Dimensional Photonics Hanyu Hong, Myungjae Lee, Jaehyung Yu, Fauzia Mujid, Andrew Ye, Ce Liang and Jiwoong Park; The University of Chicago, United States

Waveguides with strong light-matter interactions have been key ingredients in modern photonic technologies that are designed to confine, direct, and modulate light waves on chip-scale optical circuitry. Recently, van der Waals (vdW) crystals emerged as novel materials that can further miniaturize waveguides to the atomically thin limit, whose operation can be enhanced by plasmonic and excitonic interactions, as demonstrated using graphene and transition metal dichalcogenides. However, efficient large-scale generation and control of photonic modes guided by vdW materials, which is crucial for technological and scientific applications, remains as an unmet challenge. Here, we report three-atom-thick waveguides, named δ-waveguides, based on wafer-scale MoS_2 monolayers that can guide visible and near-infrared light over the millimeter-scale with a low loss of 0.5 dB/mm. They are extremely thin compared to the light wavelengths and the light-trapping mechanism is analogous to a δ-potential well in quantum mechanics. This results in the trapped waves that have a single-mode operation regardless of the wavelength, minimum additional waveguide-related dispersion, and phase propagation of a free beam propagating in the surrounding dielectric. We achieve as high as 30% in-coupling efficiency for the guided mode excitation using an edge-on incidence of a laser beam and produce discrete elements of δ-waveguides placed in a transparent polymer packaging. This enables key functionalities necessary for two-dimensional (2D) photonics, including focusing, interconnection, deflection, and intensity modulation. Our work provides a significant conceptual and technological leap toward developing atomically thin integrated photonic circuitry, where dissimilar photonic components with advanced plasmonic and excitonic properties can be integrated under a single platform.

5:00 PM EL09.06.13
Textured Growth of Oxide Materials via Chemical Solution Deposition – A Case Study for Electro-Optical Thin Films Klaartje De Buysser, Ewout Picavet, Hannes Rijckaert, Laura Van Bossele, Arend Mandelings, Isabel Van Driessche, Dries Van Thourhout and Jeroen Beeckman; Ghent University, Belgium

Shifting for randomly oriented polycrystalline films towards highly oriented thin films has been a subject of many studies. Often this goes hand in hand with vacuum techniques or expensive single crystal substrates. In this presentation, wet chemical solution deposition is used to deposit highly crystalline and orientated thin films. Several strategies are covered such as seed layer deposition, self-templating method and an interlayer deposition. A case study covering electro-optical thin films such as $Pb(Zr, Ti)O_3$, $BaTiO_3$, Nb-based materials and $BiFeO_3$ multiferroic is shown. This study highlights the importance of the chemistry of the precursor solutions, wetting behaviour, deposition method and thermal treatment

5:00 PM EL09.06.15
Optoelectronic Properties of Stacked CVD-grown MoS_2 Monolayers Towards High-Performance 2D Material-Based Photovoltaics Muhammad Aamir Abbas[1], Timothy Ismael[1], Noah Hill[2], Claire Luthy[1] and Matthew D. Escarra[1]; [1]Tulane, United States; [2]The College of Wooster, United States

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) MX_2 such as MoS_2, WSe_2, and $NbSe_2$, etc. show strong light-matter interaction which results in very high absorptance and photogeneration. Due to these excellent optoelectronic properties, TMDCs are being used for various applications e.g., transistors, memory devices, photovoltaics etc. In particular, TMDCs are promising as candidates for flexible and ultra-light photovoltaics. A single MoS_2 monolayer has a thickness of 0.65 nm and can absorb up to 10% of light at wavelengths in the visible and IR spectrum. Apart from high absorption, monolayer MoS_2 has a direct bandgap of 1.85 eV.
Due to the quantum nature of 2D MoS_2, the monolayer-like optoelectronic properties cannot be achieved from films synthesized with multiple layers. To maintain monolayer-like properties for multi-layer films, our strategy is to stack individual MoS_2 monolayers. These monolayers are synthesized on a sapphire substrate using chemical vapor deposition (CVD) with S and MoO_3 precursors carried by Ar gas at 750^oC. After achieving high-quality uniform monolayer MoS_2 films, optoelectronic properties were measured. The absorption spectra of a monolayer MoS_2 shows three peaks A, B, and C at 652 nm, 616 nm, and 431 nm respectively with a C peak absorption of 17.5 %. The absorption spectra were then compared with the computed absorption of the monolayer MoS_2 using measured n and k and the transfer matrix method (TMM). The relative error between model and experiment is <5%. Raman scattering for the monolayer shows E^1_{2G} and A_{1G} peaks at 383.5cm^{-1} and 405 cm^{-1} respectively. The normalized PL intensity of as-grown monolayer MoS_2 shows the peak at 670 nm.
A surface-energy-assisted transfer technique was then used for the stacking of individual monolayers from CVD-grown films. The obtained C-peak of absorption spectra for bi-layer, 3-layers, and 4-layers of stacked MoS_2 is 31%, 41%, and 49% respectively which is in accordance with the computed results using TMM. Raman scattering for bi-layer, 3-layers, and 4-layers of stacked MoS_2 shows peaks at 383.5cm^{-1} and 405 cm^{-1} like the monolayer scattering, as opposed to the well-known Raman peak shift in multi-layer MoS_2. Meanwhile the PL of the stacked films show a peak at 670 nm but with reduced intensity.
Schottky PV contacts were then fabricated using Ti and Pt on a SiO_2/Si substrate as an asymmetric work function interlocking-finger type device onto which the MoS_2 monolayer film is transferred. A band offset of -0.9 eV arises between the Fermi levels of Ti and MoS_2 at their interface while an offset of 0.41 eV arises at the Pt-MoS_2 interface. Efficiency of 0.000018% for a monolayer has been achieved in preliminary devices, with short-circuit current density (J_{sc}) of 0.0006 mA/cm^2 under 1 sun AM1.5D illumination. With much improved electronic transport, we project one monolayer to achieve J_{sc} as

high as 1.49 mA/cm^2 in AM0 conditions, based on measured photon absorption. By taking advantage of our demonstrated ability to stack layers while maintaining monolayer-like optical properties, using TMM we project that with 120 layers, the J_{sc} can be improved to 11 mA/cm^2 for a 2D MoS_2-based PV device.

Currently, we are focused on conserving the PL of the stacked monolayers to maintain high electronic quality in these 2D material stacks. For that purpose, we are optimizing the transfer process by applying different dry transfer techniques e.g., stamping methods, thermal release transfer (TRT), as well as improved wet transfer techniques. In addition to that, we are also working to measure the carrier concentration and mobility for monolayer and stacked monolayer structures using the Van der Pauw method. The results of this stacked monolayer 2D film analysis will be implemented in our COMSOL Multiphysics model of multiple monolayer Schottky 2D PV. The monolayer films will then be stacked on the fabricated Schottky PV devices to enhance their efficiency.

5:00 PM EL09.06.16

Infrared Nanospectroscopy of Photoluminescent Defects Ryan Kowalski[1], David Curie[1], Richard Haglund[1], Zhigang Wu[2] and Joshua D. Caldwell[1]; [1]Vanderbilt University, United States; [2]NASA Ames Research Center, United States

Quantum information sciences is advancing current technology in several fields by providing secure communications channels, impracticably difficult encryption codes, unprecedented sensing resolution, and uniquely massive computational power. However, realizing such technologies has been inhibited by an underdeveloped infrastructure. Currently, the most successful attempts are from major industrial companies investing largely in superconducting Josephson junction platforms for quantum computing. However, these examples cannot exist outside of cryogenic laboratory conditions, limiting their functionality. Other platforms employ trapped ions under ultra-high vacuum, or semiconductor quantum dots that also must exist at unrealistic temperatures for device usage. An alternative platform that is developing as an excellent candidate for quantum technologies are solid-state point defect single-photon emitters (SPEs). SPEs are optically-active point defects in semiconductor materials that alter the local electronic orbital and emit photons with sub-Poissonian statistics, a purely quantum characteristic.

Point defect SPEs are inherently tied to the crystal lattice of the host material, and therefore interact with the vibrational waves, phonons, that naturally exist throughout the medium. The consequences of these interactions can lead to poor radiative efficiencies, spectral diffusion, and quantum decoherence, a massive detriment to all quantum technology platforms. By studying the interactions between color center electrons and the adjacent lattice, we begin to understand the primary factors that degrade the performance of SPEs. Photoluminescence (PL) spectroscopy is the primary tool for studying SPEs and reveals the energy transitions of the local defect electrons. However, the spatial resolution of PL spectroscopy is restricted by wave interference of the emitted light, which is in the range of hundreds of nanometers compared to the atomic-sized defects. Furthermore, the majority of PL emission is centered around the zero-phonon line (ZPL) energy, while phonon-assisted PL only exists in some SPEs. We employ a novel technique using infrared nano-optic probes to examine SPEs on a much smaller length scale (< 20 nm) and extract more direct information about the local vibrational properties.

As a result of its layered two-dimensional structure, hexagonal boron nitride (hBN) is subject to hemispherical nanobubbles that form in between its layers. These nanobubbles are formed by trapping surface adsorbents between exfoliated layers of hBN crystals, other methods include low-energy ion irradiation. We identify bright, visible-wavelength PL located in nanobubble regions of exfoliated hBN. Examining the bright regions with infrared scattering-type scanning near-field optical microscopy (s-SNOM), we identify a curved morphology with a height of tens of nanometers. Across this feature, nanoscale Fourier transform infrared (nano-FTIR) spectra display a spectral red-shift of the transverse optic (TO) phonon, which has been previously reported and attributed to a strain effect. This evidence suggests strain is a key component to activating SPEs in hBN.

We examine other SPE materials, specifically V_{Si}'s in silicon carbide (4H-SiC). Through focused ion beam irradiation and subsequent annealing of 4H-SiC, we deterministically create V_{Si} defects, a spin-active SPE, at defined spatial intervals (25, 50, 100, 2000 nm). Examining the irradiated regions with nano-FTIR, we identify a blue-shift of the phonon resonance with respect to the non-irradiated regions. This has not been reported previously and the mechanism is still unknown.

Infrared nano-optic probes will reveal direct, nanoscale information about the electron-phonon interactions in SPEs, and therefore accelerate the knowledge and development of quantum technologies.

5:00 PM EL09.06.17

The Self-oriented $La_2O_2CO_3$ Layer: An Integration Tool For Textured Thin Films On Silicon Based Platforms Ewout Picavet, Hannes Rijckaert, Laura Van Bossele, Jeroen Beeckman, Dries Van Thourhout and Klaartje De Buysser; Ghent University, Belgium

A crucial role in the miniaturization of electronic and photonic components is the integration of ferroelectric thin films on silicon (Si) based platforms. As the properties of the thin films depend strongly on the quality and crystallographic orientation of the thin films, direct integration on photonic or electronic Si based chips is not straightforward, resulting in slow, complex and expensive integration processes which limits scalability. To bridge this gap there is a need for a scalable method to integrate highly textured ferroelectric thin films on Si based integrated circuits. We have developed a method that facilitates fast integration via a wet chemical solution deposition (CSD) route. Therefore, the use of an ultrathin (5 – 15 nm) self-oriented $La_2O_2CO_3$ thin film which acts as seed layer to obtain textured ferroelectric thin films was found crucial. In this research, the focus is on the thin film deposition via ink-jet printing, crystallographic phase determination and the self-oriented behavior. Furthermore, this $La_2O_2CO_3$ thin film has a low lattice mismatch with common ferroelectric materials, which makes the CSD deposited thin film an ideal candidate to build-up silicon based active integrated nanophotonic or nanoelectronic devices such as phase modulators, resonators, capacitors, … This research can pave the way towards the integration of ferroelectric thin films in the world of Si based platforms.

5:00 PM EL09.06.18

Molecular Beam Epitaxy of Rare Earth Telluride Thin Films—Crystal Growth and Physical Properties Adrian Llanos and Joseph Falson; Caltech, United States

The Rare Earth Tellurides (R-Te_x where x = 2, 2.5, 3 and R is a member of the lanthanide group) are a family of quasi two dimensional crystals which host a variety of low temperature phases including magnetic, charge-ordered and superconducting (under pressure) ground states. The crystal structure consists of corrugated R-Te insulating layers interspersed with conducting Te square-planar layers. Each additional Te in the chemical formula corresponds to an additional Te layer in the unit cell. Confinement of conduction electrons to these planes implies a strong 2D character reminiscent of the well-known high-Tc cuprate superconductors. A particularly well-studied feature of this family of materials is the formation charge density waves and their concomitant superlattice modulations.

Thus far, only studies on bulk crystals of these materials have been performed. In this talk we will present the first demonstration of epitaxial, single crystal thin films of $DyTe_2$ (Space group: P4/nmm, a = 4.29A, c = 8.91A). We will first describe our novel method for preparing atomically-flat MgO surfaces using laser annealing. We will then proceed to discuss the unique aspects of the layer-by-layer growth as monitored by *in-situ* reflection high energy electron diffraction. Oscillations in the specular intensity demonstrate a layer-by-layer growth mode and by comparing with thickness measured *ex-situ* , we conclude that each oscillation corresponds to the growth of a single unit cell. By observing the phase relationship between the temporal oscillations of spots of different diffraction orders, we are able to distinguish between the growth of corrugated layers and square-net sheets. We will show how changes to the diffraction pattern resulting from differing processing parameters can be used to optimize the growth conditions.

We will then discuss additional characteristics of films grown under differing growth temperatures and elemental flux ratios. Reciprocal space mapping using high resolution x-ray diffraction reveals films with lattice constants relaxed from the value of the substrate. Film quality is further demonstrated with scanning transmission electron microscopy (STEM) where minimal misoriented domains are observed. STEM measurements also confirm that the film grows unit cell-by-unit cell. A sharp interface with the MgO substrate formed by a single Te sheet was observed.

Similar to the bulk case, a wide range of stoichiometries due to Te deficiency were found to form stable, single crystal, single phase films. Using x-ray photoelectron spectroscopy we were able to both estimate relative stoichiometries between films and analyze the impact of off-stoichimetry on the photoelectron spectrum of Te and Dy. Additionally, *in-situ* low energy electron diffraction has revealed a variety of surface reconstructions for differing degrees of Te deficiency, evidence for the existence of charge density waves in the crystal.

Using electrical transport, we observe semiconducting behavior with a power-law temperature dependence, in line with previous reports on bulk crystals. This behavior, which deviates from the ideal Arrhenius-like activated transport behavior is reminiscent of a doped, small-gap semiconductor. While the formation of charge density waves is expected to open a gap in the fermi surface, this temperature dependence of resistance instead suggests an ordered lattice of Te defects may be responsible for the insulating behavior.

We conclude the talk with the prospects for growing other crystals in this family and also highlight some of the challenges for growth of crystals with larger numbers of Te sheets.

5:00 PM EL09.06.19

Wavelength Dependence of Polarization-Resolved Second Harmonic Generation from Ferroelectric SnS Few Layers Redhwan A. Moqbel[1,2,3], Yih-Ren Chang[4], Zi-Yi Li[1,2], Sheng-Hsun Kung[1], Hao-Yu Cheng[1,2,3], Chi-Cheng Lee[5], Kosuke Nagashio[4] and Kung-Hsuan Lin[1]; [1]Institute of Physics Academia Sinica, Taiwan; [2]National Taiwan University, Taiwan; [3]Taiwan International Graduate Program, Taiwan; [4]The University of Tokyo, Japan; [5]Tamkang University, Taiwan

Two-dimensional (2D) multiferroic materials, which contain two or more intrinsic ferroic orders hold great promise for different optoelectronic applications[1]. Recently, monolayer orthorhombic structures of group IV metal monochalcogenides (such as GeS, GeSe, SnS, and SnSe) have been predicted to be 2D multiferroic materials, which possess both in-plane ferroelectric and ferroelastic orders with low domain wall energy and low migration barrier[1]. However, it is still challenging to fabricate monolayer or few layer of group IV metal monochalcogenides either from exfoliation or vapor deposition methods [2]. For most bulk crystals, macroscopic ferroelectricity or multiferroic properties disappear because each layers are stacked in an antiferroelectric manner. In this work, we fabricated unique SnS few layer single crystal flakes in which the layers were stacked in an order to keep in-plane polarizations of each layer the same direction. This opens the gate to experimentally manipulate multiferroic phases in these ferroelectric SnS few layer flakes. For measuring the ferroic phases and crystal orientations, it could be conveniently achieved by a non-contact technique of optical second harmonic generation (SHG). We utilized SHG microscopy to measure the polarization-resolved SHG from numerous SnS flakes prepared by physical vapor deposition on mica substrates. The angular-resolved patterns dramatically changed under excitation wavelength between 800 and 1000 nm due to the frequency dependence on SHG susceptibilities. By using first-principles methods within the density functional theory, we calculated the frequency-dependent SHG susceptibilities in the AA-stacking SnS and AC-stacking SnS. The effect of layer dependence on the band structures and SHG susceptibilities was also theoretically investigated. The variation trend of calculated SHG polar patterns as a function of frequency agrees well with that of the experimental results.

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5:00 PM EL09.06.20

High-Resolution Microstructural Analyses of Polymeric Carbon Nitride Incorporated with Graphitic Carbon Shunsuke Mori[1], Niannian Wu[1,2], Nobuhiko Mitoma[1,2], Takuzo Aida[1,2] and Xiuzhen Yu[1]; [1]Riken Center for Emergent Matter Science, Japan; [2]The University of Tokyo, Japan

Graphitic carbon nitride (GCN) is a polymeric semiconductor having a layered structure. Owing to its desirable characteristics for solar water splitting, the GCN attracts much attention as a sustainable metal-free photocatalysis.[1,2] Among the polymorphs in GCN, heptazine-based structure aligned along the in-plane film direction is well-known as a stable one. Recently, research reports demonstrated that the GCN nanosheet incorporated with graphitic carbon can enhance the lifetime of photoexcited electrons due to its high electron-hole separation ability and increase the absorption under visible light.[2] Accordingly, such the C-incorporated GCN is expected to be applied for not only a high-efficiency photocatalysis but also the photovoltaic material promising to various next-generation optoelectronic devices. However, nanosheets are not appropriate for optoelectronics. We have succeeded in fabricating centimeter-scale GCN films that are applicable to optoelectronic devices.[3] The purpose of this study is to clarify the structural feature of the aforementioned polymer, which is still unclear.
Here we show microstructural analyses of C-GCN films using the high-resolution transmission electron microscopy (HREM) technique. Our HREM observations demonstrate the heptazine structure of GCN in the real-space, which is also confirmed by superstructural reflection in the corresponding Fast Fourier Transform (FFT) pattern. Both real-space images and corresponding FFT clearly show the super structure with a long period revealing the polymeric heptazine. Meanwhile, the primitive structure with hexagonal symmetry and a short period is observed and assigned to well-known graphitic carbon, which is clearly distinct from polymeric heptazine. The present study based on the HREM observations provides fundamental microstructural information of C-GCN film, that contributes to a practical design of polymer-based optoelectronic devices.

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SESSION EL09.07: Quantum Nanophotonics, Sensing, Flexible Devices and Non-Linear Properties of 2D Materials
Session Chair: Thomas Kempa
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3009

8:15 AM *EL09.07.01
Quantum Materials Optoelectronics Zeila Zanolli; Utrecht University, Netherlands

Controlling the properties of quantum materials via external stimuli is a key topic in modern condensed-matter physics. Due to its intrinsic quantum nature, light plays several roles: generating and controlling excited states, and forming hybrid quasiparticles with other excitations in solids. To unlock quantum advantage in electronic, photonic and energy technologies it is required to create new materials and manipulate their properties.

To reach this goal we develop theory and simulation techniques to fully describe the interaction between light (photons), bound electron-holes pairs (excitons) and lattice vibrations (phonons) without adjustable parameters in a quantum many-body framework [1]. Using this approach, we compute optical properties of 2D materials and heterostructures and predict how these properties can be controlled by defect engineering, strain, or twisting.

For instance, we find that vacancies in Transition Metal Dichalcogenides can univocally be identified by their absorption spectra and used as carriers of quantum information [2]. Further, we demonstrate the essential role played by exciton-phonon interaction in photoluminescence of negatively-charged boron vacancy in 2D hexagonal boron nitride [3]. We find intralayer and interlayer excitons in TMD heterostructures and use twisting to tune their absorption energy. Tunable materials are promising platforms for application in quantum information and quantum sensing.

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8:45 AM EL09.07.02
Uniaxial Strain Dependence on Optical Second Harmonic Generation from Indium Selenide Few-Layers Zi-Yi Li[1,2], Hao-Yu Cheng[1,2], Sheng-Hsun Kung[1], Hsuan-Chun Yao[1], Christy Roshini Paul Inbaraj[2], Raman Sankar[1], Min-Nan Ou[1], Yang-Fang Chen[2], Chi-Cheng Lee[3] and Kung-Hsuan Lin[1]; [1]Institute of Physics, Academia Sinica, Taiwan; [2]National Taiwan University, Taiwan; [3]Tamkang University, Taiwan

Since the Van der Waals materials can be mechanically exfoliated and transferred to any substrate including bendable polymeric or plastic substrates, studies of 2D materials also benefit the development of flexible devices. Indium selenide (InSe) is an emerging star of the Van der Waals semiconductors due to its superior properties such as ultrahigh mobility and large elastic deformability. It was also applied to bendable photodetectors with high performance and broad spectral response. For application of flexible devices, it is important to understand how strain affects the physical properties. Recently, optical second harmonic generation (SHG) techniques has been demonstrated to be a powerful tool for strain mapping. In addition to the intensity distribution of strain, the direction of the strain distribution can also be mapped by analyzing angle-resolved SHG patterns. For this application, it relies on fundamental understanding of strain effect on the SHG of InSe. In this work, we studied angle-resolved second harmonic generation pattern of InSe few-layers under uniaxial strain both experimentally and theoretically. We used the exfoliation method to fabricate InSe flakes on bendable and transparent substrate, and then measured the SHG images. We found the SHG intensity of InSe decreased while the compressive strain increased. By using first-principles electronic structure theory, we calculated how strain alters the susceptibilities and angle-resolved SHG pattern. The theoretical results agreed with experimental results qualitatively.

9:00 AM EL09.07.03
Controlling Single-Photon Emission with Ultrathin Transdimensional Plasmonic Films Igor Bondarev; North Carolina Central University, United States

The properties of a two-level quantum dipole emitter near an ultrathin transdimensional (TD) plasmonic film are studied theoretically [1]. TD quantum materials are atomically-thin films of precisely controlled thickness, films made of precisely controlled finite number of monolayers [2-5]. The model system studied mimics a solid-state single-photon source device. The spontaneous and stimulated emission intensity profiles are computed as functions of the excitation frequency and film thickness, followed by the analysis of the second-order photon correlations to explore the photon antibunching effect. It is shown that ultrathin TD films can greatly improve photon antibunching with thickness reduction, which allows one to control the quantum properties of light and make them more pronounced. The theory can be tested in experiments similar to those reported recently for epitaxial TiN films with thicknesses below 10 nm grown on MgO substrates and covered with an AlScN passivation layer [5], with nanodimond NV-centers as DEs deposited on the varied-thickness passivation layer. Knowledge of these features is advantageous for solid-state single-photon source device engineering and in general for the development of the new integrated quantum photonics material platform based on the ultrathin TD plasmonic films.

Acknowledgements: U.S. National Science Foundation Award No. DMR-1830874 (I.V.B.)

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9:15 AM EL09.07.04
Highly Sensitive and Selective Sensor Based on Surface Plasmon Resonance Structure with Graphene for the Detection of Sub-ppm 2,4-

dinitrophenol Sung Hwan Cho[1] and Ho Won Jang[1,2]; [1]Seoul National University, Korea (the Republic of); [2]Advanced Institute of Convergence Technology, Korea (the Republic of)

We demonstrate the enhancement of SPR sensor performance by graphene monolayer on the Au layer for detection of ppb-level 2,4-dinitrophenol dissolved in IPA solution. The thickness (50nm) of the Au layer was optimized through the Finite-Difference Time-Domain (FDTD) calculation, and this was confirmed through the reflectivity curve comparison through the actual SPR images to the IPA solution. The performance of the sensor is analyzed via SPR measurements, and the Au-graphene structure is characterized using field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), Raman spectroscopy, and transmission electron microscopy (TEM). The results from FESEM, AFM, and TEM confirmed the graphene monolayer transferred well on the Au thin film. We showed that the proposed structure has increased the shift in the SPR angle up to 550 resonance units (RU) within the range of 100 – 500 ppb due to the enhanced evanescent field at the sensing layer-analyte interface, and interaction between 2,4-dinitrophenol and monolayer graphene. We demonstrate that π- π interaction between 2,4-dinitrophenol and monolayer graphene plays a dominant role in the enhancement of the SPR response of 2,4-dinitrophenol onto graphene and it is calculated by density functional theory (DFT) calculation and verified through Raman spectrum analysis. As a result of DFT calculation, the 2,4-dinitrophenol was most stable when it existed parallel to graphene, and it was confirmed that the 2D/G ratio decreased and the peak position was shifted in the Raman spectrum in the state adsorbed with the 2,4-dinitrophenol. This sensor exhibits great linearity and repeatability in the ppb level concentration range. Measurement of various organic substances, as well as 2,4-dinitrophenol, was carried out, and selectivity to aromatic substances was confirmed. The results prove that our proposed Au-graphene SPR sensor demonstrated strong performance and reliability for aromatic ring organic compounds selective detection in IPA solution.

9:30 AM BREAK

10:00 AM EL09.07.05
Innovative MXenes Carrier Selective Contact for Sb_2Se_3 & CZTSe Hybrid Heterostructure Devices Axel Gon Medaille[1,2], Alex Jimenez Arguijo[1,2], Kunal Tiwari[1,2], Eloi R. Costals[2], Joaquim Puigdollers[2], Sergio Giraldo[2], Marcel Placidi[2], Zacharie Jehl Li-Kao[2] and Edgardo Saucedo Silva[2]; [1]IREC, Spain; [2]Universitat Politècnica de Catalunya, Spain

MXenes are a recently discovered family of inorganic 2D materials combining high conductivity, transparency in ultrathin layers, work function tunability via surface termination and ease of fabrication in large areas, which has found widespread possible applications in energy storage and conversion technologies. As carrier selective contacts become ubiquitous in state-of-the-art photovoltaic research, the use of MXene electrodes is a promising pathway to further improve thin film devices beyond the classic p-n junction architecture. Studies remain scarce and **a fundamental understanding of the absorber/MXene interface**, with a fine tuning of the 2D electrode, is of high interest for the community.
Through this work, we realize photovoltaic devices combining Ti_3C_2Tx as a charge (electron/hole) selective contact layer with Sb_2Se_3 and $Cu_2ZnSnSe_4$, two of the most promising emergent thin film PV absorbers. MXenes sheets are synthetized by selectively etching a Ti_3AlC_2 (MAX) phase using the minimum intensive layer delamination (MILD) method, forming in-situ HF allowing the selective removal of aluminum from the bulk MAX phase. Secondly, following centrifugation and washing processes, the obtained $Ti_3C_2T_x$ solution is deposited on FTO, Mo and ITO substrates with different MXenes concentrations and thicknesses by spray-coating at temperatures ranging from 100 °C up to 200 °C, which permits to obtain **an excellent reproducibility and homogeneity over areas up to 100 cm^2**. It is to our knowledge is the first time that spray-coating deposition of MXene is assessed for energy applications.
Subsequently, surface modifications with selenium Se are performed on the as-deposited $Ti_3C_2T_x$ to **modify the surface termination and consequently the material's work function**, allowing to finely tune the electrode and adapt it to the desired extraction energy level. Se deposition is carried out by thermal evaporation of the element followed by a reactive annealing phase in Se atmosphere. The resulting selenized MXene sheets are used as a substrate for the fabrication of Sb_2Se_3 and CZTSe hybrid heterostructures. An extensive Raman spectroscopy analysis reveals that following the selenization process, the **Se crystallographic structure deposited on the MXenes surface can be modified to be either an equilibrium between Se_8 rings and Se_μ chains or strictly Se_8 rings**. For the sake of comparison, other surface modifications involving organic compounds such as citric acid or perfluorinated ionomer (PFI) and UV-Ozone treatment are performed, with the similar objectives to tune the surface termination of as-deposited MXenes for selective carrier extraction. The devices are completed following the standard CdS/TCO front contact architecture for solar cells and are characterized using room temperature and temperature-dependent optoelectronic analyses methods, shedding light on the mechanisms involved in the photocarrier extraction at the absorber/MXenes interface.
Results of optoelectronic characterizations in the form of J-V, EQE and C-V for the devices will be presented to elaborate on the impact of MXenes concentrations and thickness on PV devices performance, and the **selenization of MXene is found to markedly improve the voltage, current, and conversion efficiency** of the resulting PV devices. Additionally, material characterizations by means of SEM, XRD, XPS and Raman spectroscopy are carried out to assess the physico-chemical properties of the as-deposited layers (both MXenes and absorber) along with the MXenes surface termination modifications. The results will be discussed in the frame of the state of the art and compared with reference devices fabricated on crystalline Silicon. Finally, improvement pathways will be proposed to further tailor the properties of MXenes film to the needs of thin film photovoltaic devices.

10:15 AM EL09.07.06
Multi-Scale Simulations of Supported Pt Nanoclusters on Single-Layer MoS_2 for Chemiresistive Wearable Biosensors Gabriele Boschetto[1], Stefania Carapezzi[1] and Aida Todri-Sanial[1,2]; [1]LIRMM, University of Montpellier, CNRS, France; [2]Technische Universiteit Eindhoven, Netherlands

The development of non-enzymatic sensors is a challenge which requires, on the one hand, careful design of the sensing materials with respect to the chosen analyte, and on the other hand, suitable device architectures. In this context, atomically-thin two-dimensional (2D) materials have attracted a great deal of interest given their desirable mechanical, electrical and optical properties. For instance, single-layer molybdenum disulfide (MoS_2) is an ultra-thin semiconductor which can be used to fabricate devices which go beyond the current state-of-the-art CMOS technology.
Aside from the device level, single-layer MoS2 as a material was also found to be suitable to be used as the sensing platform in FET sensors to detect small molecules (mainly gases) and small biomarkers such as glucose. However, the vast majority of MoS_2 FET sensors rely on an enzymatic sensing mechanism, which involves the functionalization of the 2D material with enzymes specific to the chosen analyte. Enzymatic sensors are generally prone to suffer of low stability with respect to temperature and pH.
In this work, we propose single-layer MoS_2 decorated with Pt nanoparticles as the non-enzymatic sensing platform for the detection of biomarkers (such as cortisol) in human samples. The aim is to assess the suitability of such a sensing platform for the development of wearable and portable cortisol sensors. We perform multi-scale computer simulations at the materials' level up to device scale. First, ab initio simulations within the framework of density functional theory (DFT) allowed us to gain insights into the interaction, at the atomic level, between the analyte (cortisol) and the sensing platform (MoS_2/Pt). Then, by carrying out technology computer-aided design (TCAD) simulations, we were able to consider a device architecture and investigate its performance as cortisol sensor. Following our multi-scale simulation strategy, we were able to propose a FET sensor, whose channel is made of Pt-decorated MoS2. The sensing mechanism relies on the chemiresistive response of the device to the adsorption of cortisol on the channel, which leads to a charge transfer from the analyte to the substrate and, consequently, to the measurable shift in the gate voltage threshold of the FET.
With our findings, we provided important insights and gave our contribution towards the development of highly sensitive non-enzymatic cortisol sensors

based on 2D materials.

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10:30 AM EL09.07.07
Ultra-Stable 2D Layered Perovskite Films for Flexible and Large area X- and Gamma-Ray Detectors Andrea Ciavatti[1,2], Matteo Verdi[1], Laura Basiricò[1], Daniela Cavalcoli[1] and Beatrice Fraboni[1]; [1]DIFA - University of Bologna, Italy; [2]INFN - Bologna, Italy

The recent impressive progress in the field of perovskites assessed their large potential for the development of direct detection of ionizing radiation, as they proven the ability to detect X-ray, coupled to unique properties such as solution-processability, cost-effective fabrication and scalability to large area systems. In particular, the development of light, portable and flexible devices would represent a breakthrough in the field of medical imaging, dosimetry, and public security. Indeed, perovskite film X-ray detectors based on polycrystalline morphologies exhibit excellent performances; however, they are limited by low bulk resistivity, high trap states density and significant ion migration effects leading to large dark current drift. Among the lead-halide perovskite, 2D layered hybrid perovskite have recently attracted increasing attention as active layer in UV-Vis photodetector [1]. These perovskites are represented by the general formula $(R\text{-}NH_3)_2A_{n-1}B_nX_{3n+1}$, where R is an alkyl or aryl group. Low-dimensional perovskites are characterized by a layered crystal structure in which corner-shared BX_6 octahedra sheets are intercalated between bilayers of $R\text{-}NH_3^+$ organic spacers. Their electronic structure is akin to a multiple quantum well where the inorganic layers constitute the wells and the organic spacers the barriers. Due to the high dielectric contrast between the organic and inorganic moieties, the charge carriers are strongly confined with large exciton binding energy, as well as highly anisotropic charge transport. The high resistivity, suppressed ion migration and superior ambient stability makes them an interesting alternative for radiation detection. We present a direct X-ray detector based on PEA_2PbBr_4 polycrystalline films directly deposited by single step spin-coating on a pixelated PET flexible substrate with prepatterned interdigitated metal contacts. The perovskite forms a polycrystalline film with average grain size of 33.5 ± 8.3 µm and thickness of 1.9 ± 0.8 µm. From Current-Voltage measurements the dark current was found to be extremely small (tens of 10^{-12} A at 10 V). The devices demonstrated excellent photocurrent under UV light (375 nm), with fast response of 147 ± 10 ns, an ON/OFF current ratio up to 10^4 and Responsivity up to 12 mA/W. Photocurrent spectrum show an energy gap located at 3.08 eV and a high excitonic peak about 0.06 eV below it. The detector showed a high sensitivity under 150kVp X-ray radiation with a top value of 806 µC Gy^{-1} cm^{-2} and limit of detection down to 42 nGy s^{-1}. The X-ray signal have been acquired under different bending conditions to assess the effect of the mechanical stress [2].
Additionally, the tested devices exhibit exceptionally stable response under constant irradiation and bias. Thus, to evaluate the aging effects and the radiation hardness we performed Photo-Induced Current Transient Spectroscopy (PICTS)[3] characterization and X-ray measurements after 30 days of shelf-storage and after 200 Gy of irradiation. The X-ray signal is constant after 200 Gy of radiation or ten minutes of continuous exposure. At the same time, photocurrent signal, sensitivity and µτ values are stable after 30 days. Interestingly, all the three levels individuated from PICTS spectra are identical after 30 days.
Finally, we implemented and tested devices working at low bias (<5 V), granting the possibility to be powered by a battery-operated, wearable readout electronics, with wireless data communication. We demonstrate how this sensing system can be exploit for the detection of high energy photons emitted by radioisotopes typically used in nuclear medicine (^{18}F, ^{99m}Tc and ^{177}Lu).
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SESSION EL09.08: Optoelectronic Characterization and Optical/Optoelectronic Properties of Layered Optoelectronic Materials and Their Heterostructures I

Session Chairs: Sonia Conesa Boj, Thomas Kempa and Sudha Mokkapati
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3009

10:45 AM *EL09.08.01
Exciton-Resonance Tuning for Atomically-Thin Metasurfaces Ludovica Guarneri[1], Qitong Li[2], Thomas Bauer[1], Jung-Hwan Song[2], Mark L. Brongersma[2] and Jorik Van de Groep[1]; [1]University of Amsterdam, Netherlands; [2]Stanford University, United States

Since the development of diffractive optical elements in the 1970s research has focused on replacing bulky optical elements such as lenses and grating by thin counterparts. Over the last decade, nanophotonic metasurfaces rapidly advanced the development of flat optical elements based on the realization that resonant optical antenna elements enable local phase control. Present applications of metasurface flat optical elements include lenses, polarization control, and beam steering.

Next-generation applications of flat optics such as light detection and ranging (LIDAR), dynamic holography, and computational imaging require dynamic control over optical functionalities, e.g. the focal position or efficiency of optical elements. However, most nanophotonic structures are static after design and fabrication. Current approaches for dynamic control like electrical gating exhibit limited tunability due to the finite electrorefraction and electroabsorption effects in metals and semiconductors.

Here, we demonstrate how exciton resonances in monolayer transition-metal dichalcogenides (TMDs) like WS_2 can function as a new type of tunable resonant light-matter interaction in nanophotonic metasurfaces. By directly patterning the monolayer material, the 2D material is turned into the antenna or metamaterial and incorporation of active materials into larger antenna structures will no longer be needed. Due to their sub-nm thickness, these materials are highly tunable through external control. In this presentation, I will present three applications of exciton-enhanced light scattering.

First, we demonstrate actively-tunable and atomically-thin optical lenses by carving them directly out of large-area monolayer WS_2. Using an electrochemical cell, we electrostatically control the carrier density in the monolayer WS_2 and thereby gain active control over the excitonic light scattering amplitude. Using confocal scanning microscopy, we characterize the focal shape and analyze the focal efficiency. We demonstrate dynamic electrical tuning of the focusing efficiency with a 33% modulation depth through manipulating of the excitonic material resonance properties as opposed to tuning of antenna resonances.

Second, we employ these atomically-thin lenses to directly study the influence of exciton decay and dephasing on the metasurface functionality and spectral line shape. To do this, we employ a helium cryostat to measure the efficiency spectrum as a function of temperature. At ambient conditions, the spectrum shows a strong asymmetric line shape revealing that the scattered light fields are directly governed by the monolayer susceptibility. For decreasing temperatures on the other hand, the exciton energy shows a blue-shift, non-radiative decay and dephasing are suppressed and the exciton becomes fully radiative. By comparing the resulting line shapes to an analytical model, we show that the efficiency of the metasurface lens directly scales with the excitonic oscillator strength and decay dynamics.

Third, we use reflection measurements of monolayer TMD on a quartz substrate to highlight that the interference of the substrate and TMD reflections can strongly influence the exciton line shape. By systematically controlling the substrate reflection with index-matching oils, we engineer the interference and thereby the line shape. We further show how basic, room-temperature reflection measurements allow investigation of the quantum mechanical exciton dynamics. By removing the substrate contribution with a properly chosen oil, we can extract the excitonic decay rates including the quantum mechanical dephasing rate.

The strong light-matter interaction and highly tunable nature of these exciton resonances opens an entirely new approach for the design of dynamic flat optics and metasurfaces with applications in free-space beam tapping, wavefront manipulation, and augmented/virtual reality.

11:15 AM EL09.08.02
Temperature Dependence of Excitonic Auger Recombination in Excitonic-Complex-Free Monolayer WS_2 by Considering the Auger Broadening Effect Donggyu Kim[1], Trang T. Tran[2], Jeongyong Kim[2] and Joon Ik Jang[1]; [1]Sogang University, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of)

Monolayer transition metal dichalcogenides (TMDs) have been extensively studied for their optoelectronic properties and application to sizable and flexible light-emitting devices. However, even at moderate exciton densities, their light emitting capability is severely limited by strong exciton-exciton annihilation (EEA) through nonradiative Auger recombination. Consequently, it is essential to understand the fundamental EEA dynamics to achieve a higher quantum yield. Numerous studies on EEA in TMDs, however, do not properly consider so-called Auger broadening, resulting in underestimated values for the Auger coefficient. Also, Auger coefficients measured at low temperatures were seriously affected by the presence of excitonic complex such as trions and biexcitons, yielding less confident results. In order to study EEA in an ideal excitonic system, we transferred monolayer WS_2 on a gold substrate with hBN encapsulation, in which excitons persist as the main species from room temperature to 3 K via suppression of the formation of excitonic complex by metal proximity. To account for the effect of Auger broadening, we numerically solved the rate equation for the precise estimation of the Auger coefficient as a function of temperature by considering the laser pulse width and by spatially averaging the inhomogeneous exciton density. The measured Auger coefficient is about 2.4 cm^2s^{-1} at room temperature, but it significantly drops down to 0.14 cm^2s^{-1} at 3 K. We found that the Auger coefficient A in monolayer WS_2 can be expressed as a function of temperature (T) in the form of $A = \alpha T + \beta$ where $\alpha = 0.00054\ cm^2s^{-1}K^{-1}$ and $\beta = 0.1371\ cm^2s^{-1}$, which is indeed consistent with a theoretical model predicted for direct and exchange processes, respectively. We believe that our results provide more profound understanding of the Auger processes in monolayer TMDs, which potentially provide a guide for enhancing the quantum yield of the TMD materials.

11:30 AM EL09.08.03
Nanothin $Bi_xO_ySe_z$-Enabled Modulation of Photoluminescent Properties of WSe_2 Bethany M. Hudak[1], Zachariah Hennighausen[1,2], Madeleine Phillips[1], Olaf van 't Erve[1] and Rhonda M. Stroud[1,3]; [1]U.S. Naval Research Laboratory, United States; [2]Massachusetts Institute of Technology, United States; [3]Arizona State University, United States

The bright photoluminescent (PL) properties of monolayer transition metal dichalcogenide (TMD) systems like WSe_2 and WS_2 make them appealing for applications such as next-generation optoelectronics and quantum information sciences. The PL originates from tightly bound exitons that are sensitive to changes in the surrounding dielectric environment. Here we show that by growing few-layer Bi_2Se_3 on WSe_2, the PL signal is quenched. Interestingly, the PL signal can be restored in discrete, sub-micrometer spots by exposing the Bi_2Se_3–WSe_2 heterostructure to a high-power laser (393 µW) in an oxygen-rich environment. The PL intensity can further be modulated through control of the laser power and oxygen partial pressure to achieve a continuum of PL values, demonstrating spatially selective tunability of the PL signal.
Raman spectroscopy and optical imaging indicate that the Bi_2Se_3 undergoes a structural phase change during the first laser-oxygen exposure. The laser-oxygen exposed spots were investigated using scanning transmission electron microscopy (STEM) and energy dispersive x-ray spectroscopy (EDS), which shows a 47% oxygen increase and 87% selenium decrease at those locations. Selected area electron diffraction (SAED) of the pristine Bi_2Se_3 and laser-exposed spots show a change in the crystal lattice constant. The SAED pattern of regions exposed to the laser-oxygen environment match well with the rhombohedral R3m Bi_2O_3 phase calculated from first-principles density functional theory (DFT). Bi_2O_3 is a good candidate for solid oxide fuel cells (SOFC) and oxygen separation membranes. Bi_2O_3 exists with a number of different polymorphs, and the properties vary dramatically with the different crystal phases. For instance, the monoclinic α-Bi_2O_3 is stable at room temperature, but it has poor oxygen ion conduction, while the rhombohedral phase offers more competitive oxygen ion transport. However, this phase is difficult to stabilize, resulting in few experimental studies without heavy dopant concentrations. To the best of our knowledge, we have synthesized for the first time a few-layer, nanothin phase of R3m Bi_2O_3 at room temperature and without high dopant concentrations. STEM-EDS measures a small amount of Se remaining, and thus we refer to this phase as $Bi_xO_ySe_z$.
The $Bi_xO_ySe_z$ phase allows for oxygen transport into the interlayer region of the $Bi_xO_ySe_z$–WSe_2 heterostructure, thus decoupling the two layers and restoring the WSe_2 PL signal. The PL intensity modulation is a result of intercalating and deintercalating oxygen between the two materials. The PL intensity cycles with partial pressure of oxygen during laser exposure, suggesting that the PL changes are dependent on an oxygen interaction that doesn't structurally alter the heterostructure, which is consistent with oxygen intercalating and deintercalating between the layers. Using Fick's 2nd Law of Diffusion, we measure oxygen diffusion through the $Bi_xO_ySe_z$ to be 2.61e-18 m^2/s under laser exposure at room temperature, several orders of magnitude above other room-temperature oxygen transporters. Other Bi_2O_3 phases have demonstrated faster oxygen diffusion but require temperatures of 500 °C or greater.
We have demonstrated the fabrication of nanothin $Bi_xO_ySe_z$, closely resembling the rare rhombohedral phase of Bi_2O_3. In addition to the ability to modulate the PL signal of WSe_2, nanothin $Bi_xO_ySe_z$ is a promising, unexplored room-temperature oxygen transporter that could advance low-temperature SOFC technology and syngas production.

11:45 AM EL09.08.04
Ultrafast Pump-Probe Microscopy Studies on Multilayer $MoSe_2$ Cullen P. Walsh, Jason Malizia, Sarah Sutton, John Papanikolas and James Cahoon;

UNC Chapel Hill, United States

As materials in electronics and photonics continue to shrink, nano- and micro-scale structures begin to have an outsized impact on the electronic properties. Studies have found that depending on the material, the structure, and the fabrication process, the energetics and carrier dynamics of a material can change in unexpected ways. Despite all this, structural features are often comingled in experiments, obscuring their individual effects. In order to overcome this, we use ultrafast pump-probe microscopy to isolate and study individual structural features in materials. This presentation will focus on the effects of thickness in the multilayer transition metal dichalcogenide $MoSe_2$ which shows promise in optoelectronic and photocatalytic device applications. Although $MoSe_2$ has been extensity studied in the monolayer, we still do not fully understand how changes in thickness and local structure change its electronic and optical properties. Using the diffraction limited spot size of our setup, we isolate the dynamics at the center of $MoSe_2$ nanoflakes and determine how the dominant carrier relaxation processes change going from 20- to 100-layers in thickness. We also observe and characterize non-linear modulations in the bandgap energy upon photoexcitation and how they change with time and carrier concentration. Finally, we observe a thickness-dependent internal etalon effect in the material which we analyze via a computational dielectric model. Using this comprehensive understanding of the thickness dependence of the carrier dynamics at the center of $MoSe_2$ flakes, we can in the future compare these results to the dynamics at the edges of flakes and around other internal structures (buckles/tears). Overall, by better understanding the impact these structural features have on the carrier dynamics and optical properties of these materials, our work allows for future structural optimization of these materials when used in new or improved optoelectronics and photocatalytic device architectures.

SESSION EL09.09: Optoelectronic Characterization and Optical/Optoelectronic Properties of Layered Optoelectronic Materials and Their Heterostructures II

Session Chairs: Sonia Conesa-Boj and Sudha Mokkapati
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3009

1:45 PM EL09.09.01
Confined Excitons at Monolayer Black Phosphorus Edges Souvik Biswas[1], Joeson Wong[1], Supavit Pokawanvit[2], Huairuo Zhang[3], Wei-Chang Yang[3], Hamidreza Akbari[1], Kenji Watanabe[4], Takashi Taniguchi[4], Albert Davydov[3], Felipe H. da Jornada[2] and Harry A. Atwater[1]; [1]California Institute of Technology, United States; [2]Stanford University, United States; [3]National Institute of Standards and Technology, United States; [4]National Institute for Materials Science, Japan

Atomically sharp or abrupt junctions provide a novel platform to study symmetry-broken physical phenomenon and modification of the local electronic structure at the interface – often resulting in localized or trapped state formation. We report emergence of quantum confined excitons in the emission spectrum in the edges of monolayer black phosphorus (BP). While the quasi-1D exciton in the interior of monolayer BP exhibits a single Lorentzian-like photoluminescence (~40 meV linewidth) at low temperatures (~5K), we observe additional red-shifted spectrally narrow (~1-5 meV) emission lines at the edges of monolayer BP flakes. We interpret the origin of such localized features to be due to a confining potential located at the physical edges of BP – supported by first principles GW-BSE calculations of BP nanoribbons. We observe the photoluminescence to be highly linearly polarized, with significant temperature and pump fluence dependence. Furthermore, we find that the emission is highly tunable with electrostatic doping and can be turned on and off, on demand – due to an interplay of doping and a linear perturbative Stark-effect. Our results help facilitate the understanding of fundamental optical excitations in monolayer BP under local structural modification and may enable further engineering of photoluminescence in BP nanostructures such as quantum dots or nanowires for bright, polarized, and reconfigurable light emitters.

2:00 PM EL09.09.03
Nanoscale Optical Characterizations of 2D Semiconductors via Near-field Photo-Induced Force Microscopy Jin Myung Kim[1,2], Peiwen J. Ma[1] and SungWoo Nam[1,2]; [1]University of California, Irvine, United States; [2]University of Illinois at Urbana-Champaign, United States

Atomically-thin van der Waals (vdW) semiconductors, such as transition metal dichalcogenides (TMDs), have garnered significant attentions as a platform for next-generation nano-optics and quantum optoelectronic devices. Strong light-matter interaction and reduced dielectric screening in low dimensionality allow excitons to govern optical responses of two-dimensional (2D) semiconductors. In particular, manipulating nanoscale energy landscape of 2D excitons plays a pivotal role in exciton funneling and confinement at localized energy trap. However, *in situ* and non-destructive characterizations of nanoscale optical properties persist as a challenge, particularly where optical responses are highly localized at nanoscale regions narrower than optical diffraction-limit. Here, we report nanoscale optical absorption properties of 2D TMDs via photo-induced force microscopy (PiFM). PiFM technique allows us to measure near-field tip-sample dipole interaction induced by coherent laser excitation. First, we employed polarization-controlled visible wavelength laser source to investigate the in-plane excitonic response of 2D vdW semiconductors. Aligning in-plane dipole moment of 2D TMDs with dipole in the metallic tip was achieved by controlling the polarization of incident illumination, which was critical for measuring light-induced dipole interactions. Second, we carried out PiFM mapping and spectroscopy of various monolayer TMDs. Strong resonance absorption peaks of A and B excitons were observed in fixed wavelength PiFM map as well as PiFM spectra with continuous wavelength sweep. Lastly, we analyzed nanoscale strain modulation in wrinkled and buckle delaminated 2D semiconductors. Strain-induced energy shift of A exciton was observed in PiFM hyperspectral line scanning across sub-micron buckle structure, while conventional photoluminescence (PL) scanning was not able to resolve energy shift due to limited spatial resolution. Spatial resolution of the PiFM hyperspectral mapping was revealed to be < 17 nm, indicating its capability of nanoscale optical characterization. These results suggest new opportunities for advanced nano-characterization for nanoscale optical properties of 2D semiconductors beyond optical diffraction limit.

2:15 PM BREAK

3:15 PM EL09.09.04
Proximity-Induced Moiré Exciton in a Transition Metal Dichalcogenide Monolayer Sudipta Kundu and Felipe H. da Jornada; Stanford University, United States

Moiré patterns in two-dimensional materials, formed due to a lattice mismatch or a relative rotation between the layers, have gained research interest as a platform to study exotic electronic and excitonic phases. The moiré potential responsible for the emergent phenomena is induced by the atomic reconstructions and the variation of interlayer interaction upon creating a moiré pattern. Using first-principles calculations, we explore a noninvasive way to induce a spatially varying moiré potential in the target monolayer transition metal dichalcogenide (TMD) by placing it on another multilayer material with domains of alternative electric polarization, for example, a parallel-stacked bilayer hexagonal boron nitride with a small interlayer twist. Our first-principles calculations reveal novel excitons with spatial localization and excited-state series that differ from those possible in regular stackings of twisted bilayer TMDs and suggest an experimental route for the engineering of tunable moiré potential post material synthesis.

3:30 PM EL09.09.06
Direct Probing of Excitons in Layered Moiré Superlattices Medha Dandu[1], Jordan A. Hachtel[2], Mit H. Naik[3,1], Patrick Hays[4], Sriram Sankar[4], Elyse Barré[1], Takashi Taniguchi[5], Kenji Watanabe[5], Steven Louie[3,1], Felipe H. da Jornada[6,7], Sefaattin (. Tongay[4], Peter Ercius[1], Archana Raja[1] and Sandhya Susarla[4]; [1]Lawrence Berkeley National Laboratory, United States; [2]Oak Ridge National Laboratory, United States; [3]University of California, Berkeley, United States; [4]Arizona State University, United States; [5]National Institute for Materials Science, Japan; [6]Stanford University, United States; [7]SLAC National Accelerator Laboratory, United States

Artificial superlattices [1] enable self-organized arrays of interacting quasiparticles on a long-range, offering routes for dynamic simulation of many-body physics and engineering quantum optoelectronic devices. Stacking of individual layered materials offers an unprecedented bottom-up approach to design artificial superlattices with tunable light-matter interactions. Such a stacking can yield nanoscale moiré superlattices [2] modulated by interlayer hybridization and atomic reconstruction, depending on the lattice mismatch and the twist angle across the constituent materials. So far, conventional optical spectroscopy techniques have revealed the moiré superlattice effects [2] only in an indirect manner due to their diffraction limits. Localized spectroscopy analysis is an absolute necessity to directly probe the nanoscale electronic and optical modulations across moiré superlattices in layered heterostructures. Monochromated-electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) is a versatile technique that can probe spectral information with sub-nanometer spatial resolution. In the context of atomically thin layered superlattices, EELS measurements can be directly correlated with the dielectric losses and attributed to excitonic resonances deduced from the optical absorption. In a recent work [3], in-plane structural reconstruction and the corresponding exciton localization were probed using the spatial and spectral resolution in cryogenic STEM-EELS, demonstrating the possibility of direct experimental correlation between the sub-nanometer moiré superlattice and the emergent excitonic transitions. However, the distinct spectral signatures of moiré excitons could not be directly probed due to limited energy resolution. In this work, we demonstrate both spatially and spectrally resolved features of individual intralayer moiré excitons from R-stacked WS_2/WSe_2. Using hyperspectral EELS from multiple regions across the sample, we deconvolute the contribution of oscillator strength of moiré excitons from different lattice sites. The unique advantages of high spatial and spectral resolution from the STEM-EELS technique could be extended to understand other layered superlattices where electrically tunable layer hybridization and moiré superlattice effects can be harnessed for tunable quantum emitters.

SESSION EL09.10: Poster Session
Session Chair: Sonia Conesa-Boj
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL09.10.01
Enhancement Visible Light Sensitivity of the PbS Quantum-Dot/Graphene Hybrid Photodetector Using Ag Meta-Pattern Substrate Yamujin Jang[1], Namyun Kim[1], Yao Zhang[1], Dongmok Whang[2] and Yi Jae Lee[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of)

Graphene is known to have excellent various characteristics such as electrical, mechanical, and optical properties. In particular, in terms of optical characteristics, graphene is transparent, has the advantage of light absorption in a wide range up to ultra-violet (UV) - infrared (IR), and has a constant light absorption rate of 2.3% at an electric wavelength. The reason why it could not be used as an optical application despite its wonderful optical characteristics is that the life-time of the optical carrier is very short at several ps, so it has a limitation in its use as an optical application. Accordingly, in order to overcome the optical limitations of graphene, hybrid structure with quantum-dot (QD) was produced to increase sensitivity and detection. This method dramatically increased the performance of the graphene-based photodetector (PD), but there are several problems. First, because organic QD is utilized, the effect of toxicity according to the components of QD cannot be avoided, and the absolute range is fixed. In addition, the second is the problem of the substrate. When light is irradiated, absorption and reflection occur simultaneously on the substrate, and the sensing characteristics of the photodetector are not maintained constant due to absorption into the substrates. Therefore, in this study, we utilized an Ag meta-surface (AMS), which can lead to maintaining the sensing characteristics of the QD-graphene-based photodetector and improving the sensing property. AMS produced a replica through nanoimprint lithography, used a method of depositing and detaching Ag on the replica, and could be ripped without damaging the AMS. After that, in order to manufacture a QD-graphene device, a flat layer is manufactured through spin coating of PVA (polyvinyl alcohol) on AMS. After that, patterned graphene is transferred on PVA/AMS, and electrodes are deposited using a shadow mask to manufacture devices. In addition, the PbS QD used in this study used commercially available PbS QD, and coating was coated using a widely known method. Before checking the characteristics of the manufactured PD, the effect of the PVA layer on the graphene layer was confirmed, and it was confirmed that the n-doping effect of PVA layer under the graphene through the Dirac point negative shift. In addition, when observing the change in the optical characteristics of graphene according to the presence or absence of AMS, it was observed that the current changes depending on the on/off of light, although the reactivity to light was not shown on the SiO2 substrate. Since it was confirmed that AMS can positively affect the optical characteristics of graphene, PbS QD was coated to improve the optical sensing characteristics of graphene-based PD. And a QD/graphene device was manufactured with SiO2 and AMS substrates to compare characteristics. Comparing the characteristics of PDs manufactured using the two substrates, it was confirmed that the current that changes in response to light at the IV curve was up to 3 times, and the current that changes at laser on/off was also 3 times higher than SiO2. In addition, it was confirmed that PD on the AMS substrate still showed similar current levels over time, but PD on SiO2 showed a characteristic that the current level gradually decreased. Therefore, we were able to present in this study that the use of AMS in PD or optical applications can improve optical properties. And the laser used in this study was a 532 nm wavelength laser. In conclusion, meta-surface and QD have the disadvantage that wavelength absorbed or reflected is fixed depending on the structure, size, and components, but on the contrary, it can be used in specific fields by increasing sensitivity to specific wavelengths, and it is expected that high-performance and high-sensitivity photodetector can be produced by combining them with graphene.

5:00 PM EL09.10.02
Monolayer TMDC Nanoribbon Exfoliation for Optical, Electronic, and Magnetic Characterization Ashley P. Saunders and Fang Liu; Stanford University, United States

Successful preparation of low dimensional materials is a prerequisite for exploring their physical properties experimentally and incorporating them in electronic and quantum devices. As a quasi-one-dimensional structure, monolayer nanoribbons have emerged as new candidates for

exotic quantum phenomena beyond those achieved in their bulk and monolayer counterparts. Atomically thin nanoribbons are expected to exhibit tunability in electronic, optoelectronic, and magnetic properties, depending on their width and edge structures. For example, nanoribbons of transition metal dichalcogenide (TMDC) will have potential properties including magnetism, topological phase transitions, and strong light matter interactions. Further discovery of new breakthrough properties for this intriguing material class depends on new sample preparation techniques with sufficient morphology control. We developed a top-down, scalable, and controllable exfoliation process to fabricate highly-aligned single-crystal two-dimensional nanoribbons directly from bulk crystals, with precise control of edge morphology and designed artificial structures. This strategy will enable a broad selection of single crystal TMDC monolayer nanoribbons, including MoS2, MoSe2, WS2, and WSe2 nanoribbons of various widths. This technique has allowed for experimental exploration of the optical, electrical, and magnetic properties of TMDC nanoribbons via photoluminescence spectroscopy, electrical transport measurements, and Magnetic Force Microscopy. 2D nanoribbons with artificially defined edge morphologies and widths will open up possibilities to realize novel quantum properties and to explore novel platforms for next-generation information processing, light processing, and quantum processing in the future.

5:00 PM EL09.10.03
A Molecuar Dynamics Investigation of Coherent Phonons in Layered Transition Metal Dichalcogenides Jesus A. Avendano Bolivar, Chaman M. Islam and Kevin Brenner; Southern Methodist University, United States

Coherent phonons (CPs) are the collective excitation of specific phonon modes in phase, which ultimately equilibrate into a distribution of thermal phonons (TPs). They are excited with laser absorption on timescales shorter than the phonon period (femtoseconds), and can be described as Raman-like scattering [1]. The device that is often formed around CPs is a resonator. When exciting CPs in a thin film, the interfaces can function as phononic mirrors, creating resonators that are central to many facets of optomechanics [2]. Furthermore, the frequency and quality factor (a measure of coherence) of these resonators determine the temperature at which their quantum ground state may be observed [3]. Layered materials, like transition metal dichalcogenides (TMDs), provide unprecedented control over the interfaces and heterogeneities (layer steps or rotations) that may be applied to tune the resonator's performance. As such, it is important to establish the fundamental relationships between the atomic structure and the decohering or deenergizing of the resonator.

In this work, we present a molecular dynamics (MD) investigation of CPs in multilayer TMDs. MD allows us to capture a wide range of atomistic disorder, and overcome limitations that other (quantum mechanical) methods may have with interfaces or nonbonded interactions. We detail new findings related to three areas of CP resonators in multilayer MoS_2. First, we present details on the manipulation of resonators via the inclusion of layer steps, layer rotations, and dissimilar layers (heterostructures). We provide some of first atomistic details on layer steps within the same resonator producing two physical-coupled yet frequency-decoupled resonances [2]. Second, we present details on the role of substrates in decohering and deenergizing the resonator. This includes how the thermal boundary resistance limits temperature rise (and anharmonic scattering) as CPs decohere into TPs. Third, we present details on ultrafast acoustic effects (Lamb wave generations) that not only leak energy from the resonator, but may also provide a foundation generating coherent in-plane and on-chip quantum signals. This work was partially supported by the Office of Naval Research's Summer Faculty Program, and we gratefully acknowledge discussions with the Naval Research Laboratory [2].

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5:00 PM EL09.10.04
Biaxial Strain Engineering of Transition Metal Dichalcogenide Heterostructures Jennifer Toy[1], Healin Im[1,2], Mihir Marathe[1], Chen Chen[3], Sefaattin (. Tongay[4] and Zakaria Al Balushi[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]The Pennsylvania State University, United States; [4]Arizona State University, United States

Van der Waals (vdW) heterostructure stacking of TMD monolayers with other TMD monolayers or organic molecules such as Tetracene have type-II band alignment which encourages the formation of strongly bound interlayer excitons due to the reduction in dielectric screening and increase in coulombic interaction strength. Interlayer excitons have been shown to have increased lifetimes, large binding energies, and permanent dipole moments as opposed to intralayer excitons. These heterostructures are atomically thin in nature which suggests they may be sensitive to mechanical strain which may alter material qualities such as bandgap. While such heterostructures have undergone intense studies to better understand interlayer excitons, the effects of biaxial strain on these interlayer excitons are still unknown. Heterostructures of organic and inorganic materials are particularly interesting because they open a new class of scalable heterostructures which also have interfacial tunability for device applications. Here we have designed and built a versatile biaxial straining platform for in situ Raman and Photoluminescence measurements of strained films. A thin polymer substrate (PET) is indented symmetrically by the platform to induce biaxial tensile strain via the change in the curvature of the substrate. The system is calibrated by mapping the location of features on the PET substrate as a function of indenter displacement. In this work, we will investigate strain induced optoelectronic response through Raman and PL on biaxially strained organic-inorganic heterostructures made from CVD grown material and evaporated organic powders. From these observations, we may better understand the tunability of the interlayer exciton as a function of mechanical strain which may be useful for applications in enhancing properties like band gap and optical density in flexible optoelectronic devices such as light emitters, photodetectors and photovoltaic cells, enabling excitonic devices.

5:00 PM EL09.10.05
Correlation between Defect States and Electrical Properties of InSnZnO/InGaZnO Multi-layered Channel Thin-film Transistor Dong-Joon Yi, Hyunmin Hong, Min Jung Kim, Dong Yeob Shin, Kwangsik Jeong and Kwun-bum Chung; Dongguk University, Seoul, Korea, Korea (the Republic of)

Amorphous oxide semiconductors (AOSs) are promising materials that can replace some usage of conventional silicon-based semiconductors on account of their high optical transmittance, high electron mobility, high uniformity over large areas, and fabrication process under low temperatures. AOSs have been mainly used for display backplane thin-film transistors (TFTs) in the past, but recently their applications using optoelectronic properties are being actively studied. Since the optoelectronic properties of AOSs can be controlled by their chemical composition, AOS can be used for next-generation devices, such as photonic memory devices, solar devices and synaptic devices. AOS-based devices are mainly fabricated with amorphous indium-gallium-zinc-oxide(a-IGZO) because of its high stability and solid electron mobility. But with the advances in electronic device technology, materials with better electric performances, for example, high-mobility amorphous indium-tin-zinc-oxide (a-ITZO), are in demand. However, it is difficult to make versatile devices with a single material, for reasons such as the commonly known mobility-stability trade-off in AOSs. A well-designed multi-layered device is one of the alternatives to solve the problem. It can have several advantages derived from each single material without disadvantages.
By the way, AOSs have intrinsic defect states inside the energy band gap which can affect device properties of AOS TFTs such as mobility, threshold voltage, and stability. Defect states have been usually analyzed with conventional methods like spectroscopic ellipsometry (SE) and X-ray photoelectron spectroscopy (XPS). Because these are qualitative analyses, it is difficult to correlate the defects and electrical properties by conventional methods and alternatives are required. With photovoltaic current and non-linear (NL) optical properties of AOSs, we developed methods that can detect the defects precisely.

Here, we report multi-channel-layered AOS TFT which has multi advantages derived from each channel layer. The channel layer is structured with a high-stability a-IGZO and a high-mobility a-ITZO. Device performance has improved compared to each single-layered TFT. Defect states of the multi-layered semiconductor are analyzed quantitatively by NL optical response and photo-induced current transient spectroscopy (PICTS). By analyzing NL optical signals time-dependently, which came from non-symmetric junctions at the interfaces of the device, we can get information about interfacial defects. And we got precise energy levels and density of the defect states in multi-layered bulk AOSs using PICTS. Then building an electronic-structure model of semiconductors, we could reveal the relations between the defects and electron transport mechanism in semiconductors and also the reason why performances of multi-layered TFT were improved. Based on these results, we propose precise methods to analyze the defects in semiconductors, and also the structure-optimized multi-layered device with outstandingly high mobility and stability.

5:00 PM EL09.10.06
Fully Vacuum-Free and Solution-Processed Phosphorescence OLEDs Based by Using Lamination Process Yejin Kim, Hyuckjin Nam, Yu Seong Lee, Inwoo Lee, Sejung Park and Changhun Yun; Chonnam National University, Korea (the Republic of)

OLEDs already occupy a significant portion of the smartphone and TV markets. Furthermore, OLED is a potential solid-state lighting technology that may be used in complicated lighting designs like smart packaging because it can produce light with the uniform brightness across a wide area. However, the cost of OLED products is still a challenge for those low-cost applications. Around the world, research and development efforts have been made to develop OLED manufacturing processes using solution process and printing process to avoid the pricey high vacuum deposition process. However, although organic semiconductor thin films can be prepared at ambient pressure, the expensive vacuum deposition approach is still required to form a top electrode of an OLED.
In order to dramatically reduce the cost of OLEDs, this study created a manufacturing technique that allows for the formation of a top electrode using a vacuum-free lamination process. A hybrid electrode consisting of the stack of a conductive polymer and a silver nanowire was developed to increase conductivity and transparency. And Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) with a high work function was used as a hole injection layer. For application to highly efficient OLED lighting and displays, it was essential to use phosphorescent dopant as an emissive layer with more than 50 cd/A of luminous efficiency. Therefore, the host material for phosphorescent OLEDs was prepared by combining the polymer host material (Poly(9-vinylcarbazole), PVK) and small molecular hole-/electron- transporting materials, to ensure that the charge balance was properly matched in the light emitting layer. In particular, a study was conducted to optimize the vacuum-free thermal lamination process to enhance the electrical and physical bonding characteristics between the hybrid top electrode and the underlying emissive layer. The glass transition temperature (Tg) of the polymer host material was the key factor in the hot-pressing process. In consideration of the process temperature of the laminator and the Tg of PVK, the rubbery characteristics could be approached by pre-heating the organic layer, which helps the electrical contact between the hybrid electrode and the organic light emitting layer. Through the careful optimization of the process conditions in vacuum-free lamination, a high-efficiency phosphorescent OLED devices with comparable performance with that from the vacuum deposition were developed.

5:00 PM EL09.10.07
Enabling Interface-Dependent Energy Transfer in PbI_2/SnS mixed-dimensional van der Waals Heterostructures Through Contact Geometry Sumin Ji and Neachul Shin; Inha University, Korea (the Republic of)

Heterostructures composed of van der Waals (vdW) layered semiconductor materials have attracted attention due to their anisotropic optoelectronic properties. By leveraging the structural anisotropy of 2D lattice, a new heterostructure configuration in which the vdW layer edges faced with the surface of other layers could provide additional control of exciton/charge transfer at the heterojunction, unlike conventional vertically-stacked or laterally-connected vdW heterostructure geometries. In this sense, the ability to integrate multi-dimensional vdW layered structures with various stacking orientations is of critical importance.
In this study, we report mixed-dimensional heterostructures based on the vdW multilayer semiconductor materials – 1D lead iodide (PbI_2) nanowires and 2D tin sulfide (SnS) flakes and demonstrate that the exciton energy transfer at the heterointerface is dependent on the contact geometry. By employing vapor-liquid-solid (VLS) growth using Pb catalysts, two different types of PbI_2 nanowires oriented in [001] and [010] directions were obtained, where their sidewall facets ({100} and {001} planes, respectively) form distinct contact interfaces with the {001} plane of SnS flakes after dry transfer. Structural characterizations in conjunction with optical analyses, including photo- and cathodoluminescence, revealed that the excitonic excitation in PbI_2 nanowire could be transferred to SnS through its sidewall edges at the heterointerface, which induces luminescence from SnS of which the bandgap is indirect. The vdW contact geometry-dependent energy transfer resulted in a substantial increase in excitonic emission of SnS domains from the heterointerfaces of PbI_2{100}/SnS{001} relative to those of PbI_2{001}/SnS{001}. Furthermore, we confirm that the transferred energy travels along the SnS domain edges efficiently via guided mode. Our results demonstrate a new toolbox for controlling the excitonic emission in vdW layered heterostructures for optoelectronic and nanophotonic applications.

5:00 PM EL09.10.08
Large-Area, High-Specific-Power Photovoltaics from CVD-Grown Monolayer MoS_2 Timothy Ismael[1], Muhammad Aamir Abbas[1], Kazi M. Islam[1], George B. Ingrish[1], Carlos M. Gutierrez[2], Meghan E. Bush[3], Jeremiah S. McNatt[3], Anthony J. Hoffman[3] and Matthew D. Escarra[1]; [1]Tulane University, United States; [2]University of Notre Dame, United States; [3]NASA Glenn Research Center, United States

The future of thin film photovoltaics (PV) requires the continued development of ultrathin materials, including two-dimensional (2D) semiconducting materials like transition metal dichalcogenides (TMDCs). 2D TMDC's exhibit high absorption at sub-nanometer thickness due to their unique properties, which makes them ideal for ultralight, flexible optoelectronics. Their light harvesting capabilities are especially suitable for applications where high-specific-power ultralight components are needed, e.g., in space. In this work, we present an interdigitated asymmetric contact Schottky PV device of 25 mm^2 monolayer MoS_2 suitable for space deployment.
To fabricate the 2D PV device, large-area monolayer MoS_2 film with area > 1 cm^2 is grown using a low cost and scalable chemical vapor deposition (CVD) process, with MoO_3 and sulfur as the precursors. Film uniformity is achieved through quasi-epitaxial growth on an atomically smooth C-plane sapphire substrate. MoS_2 of 1.88 eV bandgap is confirmed using photoluminescence spectroscopy, AFM scans show 0.65 nm film thickness, and Raman spectroscopy spatial mapping confirms 85% monolayer coverage. High quality MoS_2 is confirmed by an external quantum efficiency (EQE) of 25% at 620 nm laser illumination and a carrier mobility of 3.3 cm^2/V.s. Lateral transport, Schottky-junction PV with asymmetric workfunction interdigitated Ti and Pt contacts and monolayer MoS_2 are fabricated, exhibiting 2.2 kW/kg specific power under the standard one-sun AM1.5D spectrum. Hole collector work function (Φ_h) reduction due to Fermi level pinning and sub-nanometer absorber thickness partly account for low power conversion efficiency of 0.0005% in these devices.
This Schottky junction 2D PV device is modeled with COMSOL Multiphysics using measured MoS_2 optoelectronic properties to guide metal contact selection and device design. Improved V_{OC} is obtained by increasing Φ_h, while the J_{SC} is improved by increasing the mobility of the MoS_2 active layer. Model projections show that for a device with Φ_e as 4.33 eV and Φ_h as 5.65 eV, a carrier mobility of 10 $cm^2V^{-1}s^{-1}$ and 1 µs carrier lifetime, 69.9 kW/kg at only 0.02% efficiency is attainable with a 0.65 nm thick MoS_2 monolayer. Ongoing efforts to increase cell performance through enhanced electronic transport and stacking monolayers will lead to higher efficiency ultralight cell arrays, ideal for spacecraft such as a 6U CubeSat.

2D material properties and device performance is significantly affected by defects, such as grain boundaries, due to their atomically thin nature. These defects in CVD synthesized MoS_2 can lead to mid-gap states that lead to undesirable carrier recombination. Large-area mapping of the structural, optical, and electronic properties of the films can lead to the improvement of device design and performance. On-going efforts to understand and improve device performance is being carried out through correlative spatial mapping using imaging, Raman spectroscopy, transmittance, photoluminescence (PL), and photocurrent (PC) spectroscopy. Each mapping technique individually yields insight on the growth uniformity and morphology and their correlations show their influence on the PV device performance.
Further efforts are underway to fabricate these devices on flexible, few-micron thick polyimide substrates. This work includes radiation exposure and testing to confirm survivability of these devices in space. These devices may be packaged into ultralight foldable PV modules for stowed launch and in-space deployment. These ongoing efforts to demonstrate flexible ultra-light 2D PV modules for space missions will be discussed.

5:00 PM EL09.10.09
Growth of Ordered Hexagonal and Monoclinic Thin Layers of $MoTe_2$ on Sapphire and Their Characterisation Lenka Pribusová-Slušná[1], Tatiana Vojteková[1], Jana Hrdá[1], Karol Végso[2], Edmund Dobročka[1], Marian Precner[1], Michaela Sojková[1] and Martin Hulman[1]; [1]Institute of Electrical Engineering SAS, Slovakia; [2]Institute of Physics SAS, Slovakia

Molybdenum ditelluride (MoTe2) is a member of a family of transition metal dichalcogenide compounds. It might be attractive to some applications, including optoelectronics. It adopts three crystallographic structures - hexagonal, monoclinic and orthorhombic. The latter phase creates from the monoclinic one upon cooling bulk MoTe2 below 250 K. On the other hand, the transition temperature might be significantly reduced for MoTe2 layers only a few nanometres thick.
It is now clear that thin layers covering a large substrate area (~ cm^2) are crucial from an application point of view. Not only the size of the layer is essential, but also the crystallinity and arrangement of a thin layer on the substrate determine its (opto)electronic performance.
In our contribution, we address the growth of nanometre-thick MoTe2 layers with hexagonal and monoclinic structures. The layers were prepared by tellurization of predeposited Mo and MoO_3 thin films in a CVD chamber. Mo films 10 nm thick were DC magnetron sputtered on sapphire substrates and subsequently annealed in tellurium vapours at 680°C in the H2/Ar atmosphere and ambient pressure for getting the layers with the hexagonal structure. For the monoclinic phase, an additional step of oxidising the Mo film to MoO_3 at elevated temperature must be added before the tellurisation.
The layers' chemical nature and crystallographic phase were checked by Raman spectroscopy since the two phases exhibit different Raman peaks.
We performed GIWAXS (Grazing Incidence Wide-Angle X-rays scattering) measurements to examine the layer alignment on the substrate. All the samples were grown textured with atomic planes parallel to the substrate. We also completed angular-dependent GIWAXS measurements with samples rotating around the sample normal during the experiment. Intensity variations were recorded with a step of 1° for various diffraction spots of MoTe2 hexagonal and monoclinic lattices. The recognisable maxima in the angular dependence clearly indicate that MoTe2 layers exhibit a long-range order also in the *ab* plane parallel to the substrate. The layers tend to fit into the crystallographic directions of the sapphire substrate's trigonal lattice in an epitaxial manner.
The two phases have distinctly different optical spectra when the samples are about 10 nm thick. The reflectance of the monoclinic sample is almost featureless, with a broad maximum at around 400 nm. It decreases monotonically towards mid-infrared frequencies following approximately a power-law dependence. On the other hand, the reflectance spectrum of hexagonal $MoTe_2$ features several maxima, with a prominent one at about 1200 nm corresponding to an indirect transition in the electronic structure. These findings are complemented by temperature-dependent measurements of thin layers' resistivity. The latter increases with decreasing temperature for the hexagonal phase resembling a semiconductor-like behaviour. In contrast, the monoclinic sample's resistivity steadily decreases upon cooling, showing a metallic-like behaviour.

5:00 PM EL09.10.12
Exciton-Dominant Photoluminescence of MoS_2 by Functionalized Substrate Kyungmin Yang[1], Eunji Ji[2], June-Chul Shin[1], Youngbum Kim[3], Jin-Woo Park[2], Jeongyong Kim[3] and Gwan-Hyong Lee[1]; [1]Seoul National University, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of); [3]Sungkyunkwan University, Korea (the Republic of)

Transition metal dichalcogenides (TMDs) have been considered as promising candidates for transparent and flexible optoelectronic devices owing to their large exciton binding energy and strong light-matter interaction. However, monolayer (1L) TMDs exhibited different intensities and spectra of photoluminescence (PL), and the characteristics of their electronic devices also differed in each study. This has been explained in terms of various defects in TMDs, such as vacancies and grain boundaries, and surroundings, such as dielectric screening and charged impurities, which lead to non-radiative recombination of trions, low quantum yield (QY), and unexpected doping. However, it should be noted that the surface condition of the substrate is also a critical factor in determining the properties of TMDs sitting on the substrate. Here, we demonstrate that the optical and electrical properties of 1L MoS_2 are strongly influenced by the functionalized substrate. The PL of 1L MoS_2 placed on the oxygen plasma-treated SiO_2 substrate was highly p-doped owing to the functional groups of –OH on the SiO_2, resulting in a strong enhancement of PL by approximately 20 times. The PL QY of 1L MoS_2 on plasma-treated SiO_2 increased by one order of magnitude. Surprisingly, observed PL spectra shows the suppression of non-radiative recombination by trions, thus the exciton-dominant PL led to the prolong of lifetime in MoS_2 on plasma-treated substrate. The MoS_2 field-effect transistors fabricated on plasma-treated SiO_2 also exhibited a large hysteresis in the transfer curve owing to charge trapping of the functional groups. Our study demonstrates that the functional groups on the substrate strongly affect the characteristics of 1L MoS_2, which provides clues as to why MoS_2 exfoliated on various substrates always exhibited different properties in previous studies.

5:00 PM EL09.10.14
New Functionalized Mixed Si/Ge Nanosheets Amelie M. Mühlbach[1], Bernhard Rieger[1] and Jonathan Veinot[2]; [1]Technical University of Munich, Germany; [2]University of Alberta Edmonton, Canada

Nanosheets based on silicon or germanium exhibit special structural, electronic, and optical properties and are thus considered as promising materials for e.g. field-effect transistors[1], photovoltaic solar cells[2], photodetectors[3], or anode materials in lithium-ion batteries[4]. So-called germanane and silicane are hydrogenated analogues of graphene and are already well explored materials having direct band gaps. Surface functionalization of these nanosheets is known to influence their (opto)electronic properties, prevent the stacking of the nanosheets and in case of silicane avoid the oxidation of the material.[5]
As silicane and germanane are already well known materials, it is of interest to investigate mixed nanosheets consisting of germanium and silicon at the same time. Experimental studies showed that mixed Ge/Si nanosheets can be prepared like germanane and silicane by treatment of the Zintl phase $CaGe_xSi_{2-x}$ ($0 \le x \le 1$) with hydrochloric acid at low temperatures.[6] To the best of our knowledge, functionalization of mixed Ge/Si nanosheets with organic groups is not literature-known yet. We use hydrometalation reactions to functionalize mixed Ge/Si nanosheets with dodecyl groups. Alkylation has been accomplished. Detailed characterization, e.g. *via* FTIR, Raman, PL, DRA and TGA, and comparison of dodecyl-functionalized Si, Ge and Ge/Si nanosheets will show the influence of the functionalization as well as the Ge/Si ratio on the optical and electronic properties of the materials.

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5:00 PM EL09.10.15
Control Se Vacancy of 2D MoSe$_2$ Thin Films Deposited by Plasma Enhanced Atomic Layer Deposition Ji-Min Lee, Jeong-Hun Choi, Dong Geun Kim and Ji-Hoon Ahn; Hanyang University, Korea (the Republic of)

Two-dimensional (2D) transitional metal dichalcogenides (TMDs) have attracted intense interest because of their fascinating electrical, optical and mechanical properties such as high on/off ratio and high carrier mobility. Moreover, the bandgap of TMDs was tunable through control thickness of TMDs. Molybdenum diselenide (MoSe$_2$), one of the TMDs, has a unique property that the carrier type of MoSe$_2$ can be controlled through various post-treatments. N-type characteristics of the MoSe$_2$ field effect transistor (FET) were enhanced after oxygen plasma treatment. Whereas, when Se vacancies increase, MoSe$_2$ FET showed p-type characteristics. Based on these characteristics, there were studies that homo-junction PN diodes and homo-stack channel FET fabricated MoSe$_2$. Meanwhile, in most studies synthesis method of MoSe$_2$ was chemical vapor deposition (CVD) or mechanical exfoliation (ME). There are relatively few studies of MoSe$_2$ deposited atomic layer deposition (ALD). ALD based on the surface limited reaction which allows precise thickness control is a very useful deposition method for TMDs because of the layer-dependent optical properties of TMDs. Therefore, there is an increasing demand for control of carrier type and depositing TMDs with ALD.
In this study, we investigated Se vacancies control of MoSe$_2$ films deposited by plasma enhanced atomic layer deposition (PEALD) according to post-treatment and properties of MoSe$_2$ depending on Se vacancies in films. Pristine MoSe$_2$ film had many Se vacancies because of the low process temperature of ALD. To fill Se vacancies in MoSe$_2$ films, we performed selenization as a post-treatment. After selenization, some of the Se vacancies in MoSe$_2$ films were filled and it was confirmed by Raman spectroscopy. Compared to pristine MoSe$_2$ FET, MoSe$_2$ FET with selenization showed enhanced p-type characteristics and increased on/off ratio. The optical properties and chemical binding states of MoSe$_2$ films were analyzed using by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

5:00 PM EL09.10.17
Active Control of Plasmonic-Enhanced Interlayer Exciton Emission with Electrical Modulation Jiasen Zhu[1], Fuhuan Shen[1], Zefeng Chen[2] and Jianbin Xu[1]; [1]Chinese University of Hong Kong, Hong Kong; [2]Soochow University, China

Transition metal dichalcogenides (TMDs) are considered as one of the most promising materials due to their low-dimensionality and novel physical properties. More interestingly, Van der Waals (vdW) heterostructures formed by vertically stacking different materials offer even more optoelectrical properties, associated with the interlayer excitons (IEs) formed in different layers. Due to an offset in alignment of the monolayer band structures (type II heterostructures), the IEs in the heterostructure lie energetically below the excitons confined in each constituent monolayer, and typically exhibit longer carrier lifetime. Understanding and manipulation of the IEs in TMD vdW heterostructures hold great promise for the development of novel optoelectronic devices.
Due to the spatial separation of electrons and holes in different layers, the IEs carry an out-of-plane electric dipole moment, resulting in a significant decrease in the photoluminescence quantum efficiency, which hinders the further applications such as electroluminescence, nano lasers and exciton router, etc. Here, we realize the electrical control of plasmonic enhanced IEs emission in WS$_2$/InSe heterostructure. Around 6-time photoluminescence enhancement from IEs is achieved by sandwiching WS$_2$/InSe heterostructure into a gold mirror and plasmonic disk arrays. Moreover, the vertical electrical field is applied across the heterostructure to realize the active control of the resonance frequency of IEs, where more than 100 meV shift is observed for the IEs resonance. Stronger coupling can be achieved with plasmonic lattice by tuning the resonance frequency of the excitons with electrical modulation. We provide a novel method to control the excitonic processes in TMD heterostructures to build high performance optoelectronics devices.

5:00 PM EL09.10.18
Integration of Logic and Memory Functionalities Enabled by Asymmetric Dual-Gate Structure Yue Pang, Jianbin Xu and Yaoqiang Zhou; Chinese University of Hong Kong, Hong Kong

Conventional van Neumann computing architecture suffers from the massive time and energy waste due to theseparation of memory and processing units. Logic-in-memory architecture has emerged as an aggressive approach toimprove the computing efficiency, which demands for the higher integration of circuits. However, silicon-based system is facing the challenge of short channel effect, approaching to the limitation of Moore's law. Thus, two-dimensionallayered semiconductors are emerged as candidates for realizing down-scale semiconducting devices. Thanks to theiratom-scale thickness, the absence of dangling bonds and enhanced external field control, dual-gated FET is a practical configuration for more complicated applications. The top gate can be in sole control of the channel or utilized in reconfigurable modulation with a back gate. The top gate can also enhance the crucial parameters of transistors such as carrier mobility, on/off ratio and subthreshold swing value due to the capacitance coupling. Both independent and dependent gate control give rise to the probability in extending logic and memory functionalities of a single device unit.
In this work, we fabricate a two-dimensional field-effect transistor (FET) with an asymmetric dual-gated structure, where the top gate comprises the channel, which fulfils the logic and memory operations, typically in opposition to the common approach. The dual-gated FET(DGFET) is based on vertically stacked MoS$_2$−hBN−In$_2$Se$_3$ van der Waalsheterostructure. First, the DGFET can be functioned as a logic gate. The channel material MoS$_2$ with atomically thin body is sensitive to the electrostatic field, thus dual-surfaced channel and drain/source barriers are modulated by the top and back gates, respectively. The current level in the output presents a logic AND gate performance, giving rise toincrease the circuit density. Second, the DGFET can be operated as a non-volatile memory device. Our as-fabricateddevice exhibits a large memory window (up to 50 V), a high on/off ratio (≈ 10^5) and a long data retention (>80% data storage after 10 years). Also, the DGFET demonstrates the multibit storage state controlled by varying gate voltagepulses. The mechanism of the carrier trapping in the top gate is reported, the asymmetric gate design causes the capacitance coupling between top gate and bottom gate. The writing and erasing processes are original from the combination of capacitance coupling and charge tunneling. Besides, with photogate assisted, logic OR gate can be achieved in the DGFET due to the photo switchable property. The high value of photocurrent provides the feasibility to implement multilevel photo-erasing, and device shows 10 distinct states under different illumination powers and durations.

5:00 PM EL09.10.19
Revisiting the Burstein-Moss Shift, Bandgap Narrowing and Electron-Hole Effective Masses of Sputtered AZO and ITO Thin Films Erik A. Perez, Kevin Lizarraga, Luis A. Morán, Fabiola Bravo, Jorge Trevejo, Paul Llontop, Miguel Piñeiro and Andres Guerra; Pontificia Universidad Católica del Perú,

Peru

Transparent conductive oxides such as aluminum doped zinc oxide (AZO) and tin doped indium oxide (ITO) have been extensively studied for their use in new generation solar cells [1], gas sensors [2,3], luminescent materials [4], new electroluminescence device concepts [5,6], among others. The degenerated character, wide-bandgap, and the large charge carrier density in the conduction band induces the so-called Burstein-Moss shift, shifting the optical bandgap further into the ultraviolet [7,8]. In this context, recent advances in modeling the direct optical absorption edge considering Urbach tails and excitonic absorption bands, motivates a restudy and contrast of electron and hole effective masses determined by a combination of electrical and optical measurements.

In this work, we study sputtered AZO and ITO thin films with different charge carrier densities without compromising the material stoichiometry. For this, the layers are annealed after deposition at various temperatures in an argon atmosphere. We systematically investigated the variation of the optical bandgap as a function of the charge carrier density and estimate the electron and hole effective masses, as well as the intrinsic bandgap of these materials. The real and complex part of the dielectric function is obtained by ellipsometry measurements and analysis. We proceed to determine the plasma frequency and electron effective mass after each annealing step by means of the Drude and Sernelius [9] models for the free carrier contribution to the dielectric function, reflected in the infrared optical absorption. An increasing electron mass is observed for increasing charge carrier densities. This effect can be associated to a non-parabolic conduction band, which becomes evident due to the degenerated character of these materials. An analytical model that describes this nonparabolicity of the conduction band was used to determine the zero-density effective electron mass [10]. The optical bandgap of each sample is determined from fits of the dielectric function using new available models that consider the contribution of excitonic transitions by means of a band-fluctuations approach.

We perform a comprehensive review and test the available theoretical models that describe the Bandgap Renormalization effect as well as the Burstein-Moss Shift both impacting on the observed optical bandgap. The former is a result of many body interactions between electrons and impurities typically found in degenerated semiconductors leading to a bandgap narrowing, whereas the latter is a consequence of the conduction band occupation as the charge carrier density increases due to the population of low energy levels near the conduction band minimum, thus leading to a widening of the optical bandgap [7,8,11]. Finally, we estimate the hole effective mass and intrinsic bandgap of the studied materials by a simple fit of the optical bandgap as a function of the charge carrier density.

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5:00 PM EL09.10.20
Effect of O_2 Plasma Treatment on the Thickness Uniformity of Chemical Vapor Deposited MoS_2 Thin Films on SiO_2 Substrates Irang Lim and Woong Choi; School of Materials Science & Engineering, Kookmin University, Korea (the Republic of)

Molybdenum disulfide (MoS_2) is extensively investigated as a key element of next-generation thin-film transistors with high carrier mobility and low power consumption. However, for practical application, uniform growth of MoS_2 must be developed on large-area substrates, especially on SiO_2 substrates. Therefore, we investigated the effect of O_2 plasma treatment of SiO_2/p^{++}-Si substrates to enhance the thickness uniformity of chemical-vapor-deposited (CVD) MoS_2 thin films. Raman and atomic force microscopy measurements showed that O_2 plasma treatment of SiO_2 substrates improved the thickness uniformity of CVD MoS_2 thin films. Based on the higher surface reactivity after O_2 plasma treatment suggested by contact angle measurement and X-ray photoelectron spectroscopy analysis, we attribute the enhanced thickness uniformity to the uniform nucleation of CVD MoS_2 thin films. These results demonstrate the effectiveness of using O_2 plasma treatment in improving the thickness uniformity of CVD MoS_2 thin films on SiO_2 substrates, with potentially important implications of growing other two-dimensional semiconductor thin films.

5:00 PM EL09.10.21
Large-Area Spin Coating of 2D Layered Molybdenum Disulfide Ayush S. Gupta[1,1], Healin Im[1,2], Walker E. Browning[1,1], Sela K. Murphy[3], David J. Lewis[4] and Zakaria Al Balushi[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Pasadena City College, United States; [4]The University of Manchester, United Kingdom

Molybdenum disulfide, MoS_2, is a two-dimensional semiconductor with a direct band gap in the monolayer limit, and improved carrier mobility over silicon at nanometer-scale thicknesses. These properties make thin-film MoS_2 especially interesting for potential applications in optoelectronic devices, transistors, and flexible electronics, in addition to catalysis and energy storage. However, integrating MoS_2 into complementary-metal-oxide-semiconductor (CMOS) processes requires the development of a scalable deposition process occurring at temperatures no higher than 450°C. Two methods of producing MoS_2 are chemical vapor deposition (CVD) and mechanical exfoliation, but CVD generally requires a large thermal budget, while mechanical exfoliation is not a commercially scalable process. Instead, spin coating is a deposition technique than can rapidly produce consistent wafer-scale thin films. Here, we demonstrate the spin coating synthesis of uniform MoS_2 films of nanometer-scale thickness on silicon dioxide and sapphire substrates at CMOS-compatible temperatures. The rapid synthesis of large-area MoS_2 films via spin coating has not been demonstrated previously. We use a 0.25 M solution of a xanthate precursor chemical containing both molybdenum and sulfur in dimethylformamide (DMF), showing the feasibility of using a single-source precursor for producing a thin-film compound semiconductor. The spin coating procedure consists of an initial rotation step to form the film, followed by a low-temperature anneal via an integrated heater. We are able to anneal the entire substrate to produce a film of MoS_2, or use a laser to create specific patterns of MoS_2 on the substrate. We also verify that additional techniques such as solution ultrasonication and substrate pretreatment using ozone cause increased wetting of the precursor solution on the substrate surface, leading to improved film coverage and uniformity. Film characterization via Raman spectroscopy has verified the composition and crystallinity of the synthesized thin films. This work represents an important step towards the rapid, scalable synthesis of wafer-scale semiconductor thin films.

5:00 PM EL09.10.22
h-BN Gating Bipolar Junction Phototransistor Based on TMDs Material Doping Concentration Tunable by Gate Effect Sang-Hyeon Lee and Jong-Soo Lee; DGIST, Korea (the Republic of)

Bipolar transistors, also called bipolar junction transistors (BJTs), are one of the most important semiconductor devices. Widely used in high-speed circuits, analog circuits, and power supply applications. Semiconductor P-n junctions are used in electronic and optoelectronic devices. However, signal amplification is difficult in 2D material-based p–n structures. $MoS_2/WSe_2/MoS_2$ are cascaded to the h-BN gate (h-GBT). h-GBT can control the carrier concentration by exploiting structural specificity through selective electrostatic doping. We analyze the behavior of diodes and transistors by controlling the depletion region length as a function of gate bias. Visually identify changes in work function with KPFM and examine changes in the depletion region. The pinch-off phenomenon was observed with different effects on the gate bias depending on the contact area within the material. The diode characteristic indicates the negative gate bias, and the transistor characteristic indicates the positive gate voltage. Detectivity explores the dependence of optical properties on shot and flicker noise. The diode region decreased with increasing power from $3x10^{11}$ Jones at low optical power (0.3 $\mu W/cm^2$) to $9.7x10^{10}$ Jones at high optical power (8 $\mu W/cm^2$). On the other hand, the transistor region has constant detectivity ($9x10^{10}$ Jones) regardless of the optical power. The current gain is 4 in the diode region, and the transistor region is 20. This is because increasing the depletion length of base-WSe2 reduces the recombination rate.

5:00 PM EL09.10.25
Process Optimization to Fabricate Transparent, Highly Conductive Single-Wall Carbon Nanotube Film for Optoelectronic Applications Minji Bak and Woo-Jae Kim; Ewha Womans University, Korea (the Republic of)

For various optoelectronic applications, such as solar cells, displays and wearable sensors, carbon nanotube (CNT) film has been highlighted as an alternative to ITO due to its mechanical stability, electrical conductivity, and optical transparency. Among the many wet and dry methods for fabricating the CNT film, vacuum filtration is one of the simple techniques that doesn't need complicated equipment and can be readily scaled up. However, to obtain high-performance conductive film, the involved factors in the entire preparation and film fabrication process must be well coordinated. Numerous factors influence film performance, ranging from CNT synthesis to dispersion, purification, and filtering operation, and each factor are interrelated or dependent on the others. CNTs are one-dimensional materials, and therefore, the transport of electrons in the film is hindered or promoted depending on which CNTs are used and how the CNTs connected in the film, which ultimately affects the conductivity of the prepared CNT film. Those parameters can be subdivided; basic features of CNT walls including diameter, length and degree of damage on the wall, depending on the synthesis method; suspension pretreatment of CNTs including surfactant choice, dilution concentration, degree of dispersion and centrifugation, resulting in functionalization or additional defect of the wall; electronic configuration of CNT films including metallic, semiconducting properties of CNTs and their ratio, which can be controlled by various CNT separation methods; filtering conditions including filtering flow rate, loading volume and filter choice, resulting in CNT alignment and ordering of CNTs in film. In this study, we investigated these four major parameters: CNT synthesis method, suspension pretreatment, electronic configuration of CNT, and film filtering conditions, in the fabrication of CNT films using vacuum filtration. we revealed key factors in improving film’s conductivity: the diameter of individual CNT walls sufficient to form contact between each wall, low structural defect of CNTs and alignment of CNTs in film. Based on this, we produced highly conductive CNT film with locally aligned domains in which the structural defects of the CNTs in the loaded CNT suspension were effectively controlled, so that the electrical properties of the CNTs could be maximized.

5:00 PM EL09.10.29
Adsorption and Diffusion of B and N atoms on Ni (111) and O-incorporated Ni (111) Surfaces Hector Gomez, Yuan Li, Yanwei He, Tianchen Yang, Chengyun Shou, Roger Lake and Jianlin Liu; University of California, Riverside, United States

Two-dimensional (2D) hexagonal boron nitride (h-BN) has recently emerged as a superior inorganic material in nanoscale devices owing to its electrical, optoelectronic, and thermal properties. Nevertheless, the growth of high-quality films via epitaxy is challenging and, as a result, applications beyond the research lab are limited. However, altering the substrate properties can significantly influence the growth mechanisms to achieve high-quality films. Here, we investigate the influence of oxygen incorporation into Ni (111) surfaces and model the adsorption/diffusion energy barriers of B/N atoms utilizing density functional theory (DFT). Our results, in agreement with the experiment, demonstrate an increased activation energy in oxygen incorporated Ni (111) compared to the bare Ni (111) surface, which corroborates the observed inhibited growth of h-BN monolayer films.

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SESSION EL09.11: Optoelectronic Characterization and Optical/Optoelectronic Properties of Layered Optoelectronic Materials and Their Heterostructures III
Session Chair: Sonia Conesa-Boj
Friday Morning, April 14, 2023
Moscone West, Level 3, Room 3009

8:30 AM *EL09.11.01
Nonclassical Exciton Interactions in a 2D Semiconductor Xiao-Xiao Zhang; University of Florida, United States

The strong exciton binding in monolayer semiconductors of transition metal dichalcogenides gives rise to intriguing excitonic interactions that are unavailable in other semiconducting systems. The conventionally-studied bright excitons have short lifetimes below 10 ps at low temperatures, and the strong non-equilibrium limits the investigation of exciton-exciton interactions. In this talk, we will discuss the nonlinear excitonic response of long-lived dark excitons at low temperatures. With ultrafast laser excitation, exciton dynamics deviate from the classical scattering model. We will also talk about their unique magnetic field response and temperature dependence.

9:00 AM EL09.11.02
Ultrafast Carrier Dynamics and Layer-Dependent Carrier Recombination Rate in InSe Ting-Hsuan Wu[1,2], Hao-Yu Cheng[1,2,3], Wei-Chiao Lai[2], Raman Sankar[2], Chia-Seng Chang[1,2] and Kung-Hsuan Lin[2]; [1]National Taiwan University, Taiwan; [2]Academia Sinica, Taiwan; [3]Taiwan International Graduate Program, Academia Sinica, Taiwan

InSe layered semiconductors with high mobility have advantages over transition-metal dichalcogenides in certain device applications. Understanding carrier dynamics, especially around the bandgap, is important for fundamental scientific interest and for improving the performance of devices. Here, we investigated ultrafast carrier dynamics in exfoliated InSe by using time-resolved pump-probe spectroscopy. We found that a shrinkage of optical bandgap ~30 meV within 20 ps, attributed to the thermalization of hot carriers via the band-filling effect and bandgap renormalization. The understanding of hot carrier dynamics and photoinduced changes on the bandgap is important for optoelectronic devices such as hot carrier photovoltaics and photodetectors. In addition, we observed the carrier recombination rate increased when the thickness of InSe nanoflakes decreased, dominated by surface recombination. For the same flake, the recombination rate becomes larger after the freshly exfoliated InSe is oxidized in the air. Layer-dependent surface recombination velocities could be obtained by using a free carrier diffusion model. Since carrier recombination is associated with light emitting efficiency, photoconductivity, and carrier mobility of devices, our findings indicate the number of layers plays an important role in the device performance.

9:15 AM EL09.11.03
Resonance Energy Transfer from ML-WS_2 to a Near Infrared Organic Dye Sylke Blumstengel[1,2], Nicolas Zorn Morales[1,2], Nikolai Severin[1], Emil J. List-Kratochvil[1,2] and Stefan Kirstein[1]; [1]Humboldt-Universität zu Berlin, Germany; [2]IRIS Adlershof, Germany

Van der Waals hybrid structures consisting of 2D transition metal dichalcogenides (TMDC) and organic molecules hold the promise to benefit from synergy effects that can improve optoelectronic properties and provide new functions. In this contribution we discuss incoherent resonance energy transfer (RET) from monolayer (ML) WS_2 to a highly photostabile organic dye molecule that converts the TMDC luminescence to the near infrared spectral range and enhances the light output. The dye features a narrow-band absorption spectrum with negligible overlap with the ML-WS_2 absorption so that dye and TMDC can be individually optically addressed. Time correlated single photon counting reveals that about 70% of the excitons created initially in ML-WS_2 are transferred to the dye molecules. The transferred excitons produce photoluminescence (PL) of the dye molecule which is proven by PL excitation spectroscopy. Photoelectron spectroscopy shows furthermore that the hybrid interface is of type I so that quenching of the luminescence due to interfacial exciton dissociation is avoided. As a result, the total PL yield in hybrid sample is about ten times larger than that of pristine ML-WS_2 since the RET process competes favorable with non-radiative recombination in the TMDC. As a consequence, a large fraction of the excitons, which would undergo non-radiative recombination in ML-WS_2 are converted into radiative excitons of the dye molecule. Key hereby is the high PL quantum yield of the molecules. Due to the close proximity of donor and acceptor both Förster and Dexter transfer can contribute to RET so that not only bright but also dark states of the TMDC can be involved in the RET process. Due to the short interaction length (< 5 nm) and the negligible spectral overlap of the TMDC and dye absorption, the RET process can be used to read out locally the optical properties of TMDCs with an unrivaled spatial resolution. In respect to practical applications, our findings pave the way for electrically driven nanoscale light source based for example on a TMDC split gate field-effect transistor geometry with tunable light output.

9:30 AM BREAK

10:00 AM EL09.11.04
Imaging the Electron Charge Density in Monolayer MoS_2 at the Ångstrom Scale Joel Martis[1], Sandhya Susarla[2], Archith Rayabharam[3], Cong Su[4], Timothy Paule[4], Philipp M. Pelz[5], Cassandra Huff[1], Xintong Xu[1], Hao-Kun Li[1], Victoria Chen[1], Marc Jaikissoon[1], Eric Pop[1], Krishna Saraswat[1], Alex Zettl[4], Narayana R. Aluru[6], Ramamoorthy Ramesh[7], Peter Ercius[8] and Arun Majumdar[1]; [1]Stanford University, United States; [2]Arizona State University, United States; [3]University of Illinois at Urbana-Champaign, United States; [4]University of California, Berkeley, United States; [5]FAU Erlangen, Germany; [6]The University of Texas at Austin, United States; [7]Rice University, United States; [8]Lawrence Berkeley National Laboratory, United States

The distribution of electrons around atoms determines the emergent properties of matter. While techniques such as x-ray scattering provide atomic scale electron charge densities averaged over many unit cells and a large area, real space charge density imaging at the atomic scale is of great importance to understand the effects of perturbations such as defects, dopants, edges and grain boundaries.

Four Dimensional Scanning Transmission Electron Microscopy (4D STEM) center of mass (CoM) imaging is a real space imaging technique that has been shown to reveal atomic electric fields and charge densities[1,2]. In 4D STEM, at each probe position on the sample, the entire electron scattering (diffraction) pattern is acquired using a high speed camera[3,4,5,6]. The CoM of the diffraction pattern is then computed at each probe position to arrive at the electric field and charge density[2]. These electric fields and charge densities, however, represent the combined effect of the nucleus,core electrons and valence electrons, and separating them is non-trivial. Here we utilize simulataneously acquired 4D STEM CoM and annular dark field (ADF) images to derive the electron charge density in monolayer MoS2.

MoS2 is a 2D semiconductor of great interest because of its potential applications in optoelectronics and catalysis[7,8]. Using the ADF image, we derive the nuclear charge in MoS2 and subtract it from the net charge (derived from CoM imaging) to obtain the electron charge density. We show via DFT and STEM simulations that the electron probe shape significantly blurs the valence electron charge density, and most of the contrast in the image comes from the core electrons. We show that probe aberrations and incoherent effects contribute to the blurring induced by the probe. Our work highlights the importance of the probe shape in interpreting 4D STEM charge density images.

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10:15 AM EL09.11.05
Chemical and Optoelectronic Control of $Ti_3C_2T_x$ MXene via Covalently-Tethered Organic Monolayers Julia Martin[1], Erika Colin-Ulloa[1], Andrew Fitzgerald[1], Kateryna Kushnir[1], Rebecca R. Ramthun[1], Kiana Montazeri[2], Mary Hassig[2], Ken Ngo[3], Joshua R. Uzarski[3], Michel Barsoum[2], Lyubov V. Titova[1] and Ronald L. Grimm[1]; [1]Worcester Polytechnic Institute, United States; [2]Drexel University, United States; [3]U.S. Army Research Laboratory, United States

Two-dimensional MXenes have demonstrated promising results in catalysis, battery storage, electromagnetic shielding, and more, however, these materials tend to oxidize which has devastating impacts on overall performance. Passivation against oxidation as well as precise control over the chemical terminations and optoelectronic behavior is critical for scalable, widespread applications. Herein, we functionalized exfoliated MXene ($Ti_3C_2T_x$) surfaces with organosilanes to change local electron density based on the inclusion of electron-donating or electron-withdrawing groups. Ultraviolet photoelectron spectroscopy (UPS) quantified valence-band and Fermi energies for the resulting derivatized $Ti_3C_2T_x$ thin films. UPS reveals 1 eV shifts in band-edge positioning based on interfacial dipoles resulting from covalent organosilane attachment. Moreover, a combination of transient absorption (TA) and terahertz (THz) spectroscopy characterize the interplay between surface chemistry and the resulting changes in electronic structure and carrier dynamics. These results inform current research efforts which aim to exploit chemical and optoelectronic tunability via mixed organic monolayers with orthogonal reactivities at $Ti_3C_2T_x$ edges versus terraces. Candidate molecular organics to impart passivation against oxidatation, optoelectronic tunability, and chemical handles for tethering to polymers and other surfaces include silanes, catechols, and alkyl triphosphates as well as polyanionic salts. We discuss these results in the context of electromagnetic shielding, catalysis, chemical sensing, and energy applications

SESSION EL09.12: Light-Matter Interactions in Layered Optoelectronic Materials
Session Chairs: Thomas Kempa and Sudha Mokkapati
Friday Afternoon, April 14, 2023
Moscone West, Level 3, Room 3009

1:30 PM *EL09.12.01
Polaritonics and Nano-Photonics with van der Waals Materials Alexander Tartakovskii; University of Sheffield, United Kingdom

We present an overview of our work on nonlinear phenomena in trion-polarion system in strongly doped monolayer $MoSe_2$ exhibiting spin-selective strong light-matter coupling, and observation of nonlinear dipolar excitons and polaritons in bilayer MoS_2. We also report on a novel approach for controlling light-matter interaction using a nanophotonic platform utilizing an emerging class of layered van der Waals (vdW) crystals.

Strong coupling between light and the fundamental excitations of a two-dimensional electron gas (2DEG) is of foundational importance both to pure physics and to the understanding and development of future photonic nanotechnologies. Here we study the relationship between spin polarization of a 2DEG in a monolayer $MoSe_2$ and light–matter interaction in an optical microcavity. We find pronounced spin-susceptibility of the 2DEG to simultaneously enhance and suppress trion-polariton formation in opposite photon helicities. This results in a giant effective valley Zeeman splitting for trion-polaritons (g-factor of >20), exceeding the purely trionic g-factor by a factor of 5. We observe effective optical nonlinearity arising from the highly nonlinear behaviour of the valley-specific strong light–matter coupling regime, and allowing all-optical tuning of the polaritonic Zeeman splitting from 4 meV to 10 meV by using low-power cw laser depolarizing the electrons via formation of the trions.

In another experiment, we consider nonlinear interactions between excitons strongly coupled to light, which are key for accessing quantum many-body phenomena in polariton systems. Here, atomically-thin two-dimensional semiconductors provide an attractive platform for strong light-matter coupling owing to many controllable excitonic degrees of freedom. Among these, the recently emerged exciton hybridization opens access to unexplored excitonic species, with a promise of enhanced interactions. We employ hybridized interlayer excitons (hIX) in bilayer MoS_2 to achieve highly nonlinear excitonic and polaritonic effects. Such interlayer excitons possess an out-of-plane electric dipole as well as an unusually large oscillator strength allowing observation of dipolar polaritons(dipolaritons) in bilayers in optical microcavities. Compared to excitons and polaritons in MoS_2 monolayers, both hIX and dipolaritons exhibit about 8 times higher nonlinearity, which is further strongly enhanced when hIX and intralayer excitons, sharing the same valence band, are excited simultaneously. This gives rise to a highly nonlinear optical regime which we describe theoretically by introducing a concept of hole crowding.

In the last part, we study multilayer van der Waals structures in order to realize novel nanophotonic structures. We extract the dielectric response of 11 mechanically exfoliated thin-film (20-200 nm) van der Waals crystals, revealing high refractive indices up to n = 5, pronounced birefringence, sharp absorption resonances, and transparency windows from ultraviolet to near-infrared. We fabricate nanoantennas on SiO_2 and gold utilizing the compatibility of vdW thin films with a variety of substrates. We observe pronounced Mie resonances allowing observation of the strong exciton-photon coupling regime as well as previously unobserved high-quality-factor, hybrid Mie-plasmon modes on gold. We demonstrate further vdW-material-specific degrees of freedom in fabrication by realizing nanoantennas from stacked twisted crystalline thin-films, enabling control of nonlinear optical properties as well as post-fabrication nanostructure pick-up and transfer on another target substrate.

2:00 PM EL09.12.02
Self-Powered TMDC Photodetector with Ultra-High on-off Ratio Yannick Beckmann[1], Henrik Myja[1], Annika Grundmann[2], Julius Konietzka[1], Mohamed Abdelbaky[1], Amir Ghiami[2], Michael Heuken[3,2], Holger Kalisch[2], Andrei Vescan[2], Wolfgang Mertin[1], Tilmar Kuemmell[1] and Gerd Bacher[1]; [1]University of Duisburg-Essen, Germany; [2]RWTH Aachen University, Germany; [3]AIXTRON SE, Germany

Patent Pending

2:15 PM BREAK

2:45 PM EL09.12.04
Conversion of Classical Light Emission from a Nanoparticle-Strained WSe_2 Monolayer into Quantum Light Emission via Electron Beam Irradiation David Xu, Albert Vong, Dmitry Lebedev, Riddhi Ananth, Alexa Wong, Paul Brown, Mark C. Hersam, Chad Mirkin and Emily Weiss; Northwestern University, United States

Solid-state single photon emitters (SPEs) within atomically thin transition metal dichalcogenides (TMDs) have recently attracted interest as scalable quantum light sources for quantum photonic technologies. Among TMDs, WSe_2 monolayers (MLs) are promising for the deterministic fabrication and engineering of SPEs using local strain fields. The ability to reliably produce isolatable SPEs in WSe_2 is currently impeded by the presence of numerous spectrally overlapping states that occur at strained locations. Here we employ nanoparticle (NP) arrays with precisely defined positions and sizes to deterministically create strain fields in WSe_2 MLs, thus enabling the systematic investigation and control of SPE formation. Using this platform, electron beam irradiation at NP-strained locations transforms spectrally overlapped sub-bandgap emission states into isolatable, anti-bunched quantum emitters. The dependence of the emission spectra of WSe_2 MLs as a function of strain magnitude and exposure time to electron beam irradiation is quantified and provides insight into the mechanism for SPE production. Excitons selectively funnel through strongly coupled sub-bandgap states introduced by electron beam irradiation, which suppresses spectrally overlapping emission pathways and leads to measurable anti-bunched behavior. Our findings provide a strategy to generate isolatable SPEs in 2D materials with a well-defined energy range.

3:00 PM EL09.12.06
Site-Controlled Coupling Between Plasmonic Nanostructures and Strain-Localized Excitons in Nano-Indented WSe_2 Nicholas Proscia, Blake S. Simpkins, Samuel W. LaGasse, Dante J. O'Hara, Hsun Jen J. Chuang, Kathleen M. McCreary, Igor Vurgaftman, Berend Jonker and Paul D. Cunningham; U.S. Naval Research Laboratory, United States

Localized excitons can be deterministically created in 2D transition metal dichalcogenides (TMDs) via strain engineering, which modifies the local band structure. It has been shown that strain-localized excitons in TMDs give rise to site-controlled single photon emission, [1-3] which is of interest for quantum information and communications applications. This is of particular technological relevance given that TMDs are sensitive to environmental perturbations and can carry spin information through their valley occupancy. These discoveries have led to recent interest in coupling these strain localized quantum emitters to photonic structures,[4,5] to influence the emission properties and create on-chip-compatible platforms. Strong coupling to plasmonic nanostructures and cavities is a pathway to coherent control at room temperature.[6] However, all prior attempts to couple strain localized excitons in TMDs to plasmonic structures have remained in the weak coupling regime characterized by Purcell enhancement of quantum emission.[7,8]

Here we achieve site-controlled coupling between a localized surface plasmon resonance (LSPR) and the strain-localized excitons in WSe_2. We employ a nano-indentation technique using an atomic force microscope (AFM) to create on-demand spatially localized excitons that display quantum emission.[9] These nano-indentations are co-located above Au plasmonic discs that host LSPRs. The exciton-plasmon coupling is characterized by the familiar mode-splitting of the scattering spectra near the exciton wavelength, indicating fast energy exchange between the two systems. The LSPR wavelength is tuned via the plasmonic disc diameter in order to map the avoided crossing between the LSPR and localized exciton absorption resonance. The observed coupling strength approaches the strong coupling regime at room temperature. Our results establish this system as a potential platform for novel quantum light sources in which to study coherent control as well as nonlinear exciton-plasmon polariton behavior.

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3:15 PM EL09.12.07
Strain Tunable Optoelectronic Devices Based on Crumpled Graphene/Organic Semiconductor Heterostructures Zhichao Zhang[1] and SungWoo Nam[2,1]; [1]University of Illinois at Urbana-Champaign, United States; [2]University of California, Irvine, United States

The past few years have witnessed a rapid growth of graphene and organic semiconductor heterostructure in photodetecting applications. Stacking Graphene with organic semiconductor can result in a synergetic effect integrating the advantages of both materials, including high carrier mobility of graphene, efficient light absorption of organic semiconductors and potential capabilities to engineer organic semiconductor growth or interfacial charge transfer. Despite these substantial potentials, the effects of mechanical strains on the optoelectronic properties of the heterostructure remain unexplored. In this work, we introduced crumples into a heterostructure of graphene and a thin film of organic conjugated polymer (PDPP2T-TT-OD), investigating the effects of different strains (tensile/compressive) on their energy states as well as on the photoresponse. The crumples were formed by releasing pre-strains in an elastomeric substrate with heterostructure on top, and local tensile (compressive) strains were formed at the apex (valley) of the crumples. It was observed that the strains were capable of tuning the energy band structure of organic semiconductor as well as the work function of graphene, and the modulation facilitated charge carrier injections from organic layer to graphene. The modulation of energy states also contributed to a three-fold enhancement of photoresponsivity compared with flat control samples. This work provides a new perspective on strain engineering of graphene-organic semiconductor heterostructure and suggests new strategies in improving the performance of optoelectronic devices.

SESSION EL09.13: Virtual Session

Session Chairs: Thomas Kempa and Sudha Mokkapati
Thursday Morning, April 27, 2023
EL09-virtual

8:00 AM *EL09.13.01
Layered Hexagonal Metal Oxides Derived From the Metal-Gas Interface – Adding Oxides to 2D Toolkit Jian Zhen Ou and Bao Yue Zhang; RMIT Univ, Australia

Metal oxides – one of the most abundant substances in nature, are rarely found to be naturally layered crystal. Such intrinsic property hinders their potential to form into two-dimension (2D), since the cleavage of the weak, interlayer van der Waals bonds in layered bulk crystal serves as the benchmark to obtain the atomically thin high-quality 2D layers such as ZnO. 2D-like non-layered metal oxides are usually created *via* a space-confined-growth or soft-chemically exfoliation of unilamellar bulk crystal, in which external ionic groups are necessary for crystal stabilization. Here we present our recent discovery of a series of the layered metal oxides with a unique planar hexagonal phase which can be formed across a wide variety metallic element, including transition metals, post-transition metals, lanthanides and metalloids. These oxides can naturally grow on the metallic surfaces under a controlled oxidation environment without involving sophisticated equipment or other chemicals. Subsequently, the hexagonal 2D metal oxide monolayers can be exfoliated on a substrate in a mechanical manner with ease, similar to the way of obtaining graphene and other layered metal chalcogenides. We have showcased the hexagonal TiO_2 as a representative to reveal the distinct properties of such hexagon coordinated oxides apart from their bulk counterparts. The monolayered and few-layered hexagonal TiO_2 shows p-typed semiconductor behavior with the hole mobility up to 950 $cm^2V^{-1}s^{-1}$ at room temperature. This research findings can possibly expand the exploration of metal oxides in the 2D quantum regime and initiate numerous applications in the future.

8:30 AM *EL09.13.02

Interface Engineering with 2D Perovskites and 2D Carbon Based Systems—The Effects on the Device Efficiency and Stability Giulia Grancini; University of Pavia, Italy

Three-dimensional (3D)/low-dimensional (LD) perovskite solar cells (PSCs) offer an effective strategy to overcome the trade-off between perovskite solar cells device performance and stability. Improving the device longevity, while concomitantly simultaneously enhancing increasing the solar cell open circuit voltage and fill factor of the solar cell is the current challenge. Despite being one of the most popular and effective way processing techniques, whether the presence of this surface LDP layer would be - or not-represents the winning crucial path for the future of this technology remains elusive. In particular, atomic layer combined surface and bulk passivation using surface modifiers such as organic dopants, casts the doubts on the effective need for of having an homogeneous LDP cover capping layer. In this talk, I will discuss the interfacial passivation with different cations such as M-PEAI, M-PEABr, and M-PEACl, showing the role of the passivation and how different halides affect the device performance of the devices. In addition, I will discuss the use of low-dimensional carbon based systems - such as graphene monolayers- as additional interfacial modifiers on top of the 2D perovskites.. I will providing a comprehensive perspective on the benefits from of the passivation strategies, showing the effects on the interface processes such as charge transport[1,2].

Acknowledgements I acknowledge the “HY-NANO” project that has received funding from the European Research Council (ERC) Starting Grant 2018 under the European Union’s Horizon 2020 research and innovation programme (Grant agreement No. 802862).

Reference

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9:00 AM EL09.13.03
Electron-Phonon Coupling and Coherent Phonon in Thin Film $LaCoO_3$ on $SrTiO_3$ Wenjie Hao[1,2], Minghui Gu[1,3], Zhenyun Tian[1], Shaohua Fu[1], Meng Meng[1,3], Hong Zhang[2], Jiandong Guo[1,3] and Jimin Zhao[1,3,4]; [1]Institute of Physics, Chinese Academy of Sciences, China; [2]Sichuan University, China; [3]School of Physical Sciences, University of Chinese Academy of Sciences, China; [4]Songshan Lake Materials Laboratory, China

We employ ultrafast pump-probe spectroscopy to investigate the excited state photo-carrier dynamics in a tensile-strained thin film of $LaCoO_3$ on $SrTiO_3$ substrate. Through varying-fluence ultrafast relaxation dynamics, we obtain $\lambda\langle\Omega^3\rangle / \langle\Omega\rangle$ of $LaCoO_3/SrTiO_3$ to be $294.9 \pm 15.2\ ps^{-2}$ corresponding to a nominal electron phonon coupling constant value of $\lambda_{Eg} = 0.97 \pm 0.05$. Furthermore, a fluence-dependent coherent acoustic phonon with a central frequency of 45.21 GHz is ultrafastly generated and detected. We attribute its origin to the ultrafast light pulse induced transient thermal strain.

9:15 AM EL09.13.05
Optoelectronic Signatures of Positive and Negative Polarons in Two-Dimensional Lead Chloride Perovskites David R. Graupner and Dmitri Kilin; North Dakota State University, United States

Lead halide perovskites are of interest for light-emitting applications due to the tunability of their bandgap across the visible and near-infrared spectrum (IR) coupled with efficient photoluminescence quantum yields (PLQY). It is widely speculated that photoexcited electrons and holes spatially separate into large negative (electron) and positive (hole) polarons. Polarons are expected to be optically active, with the observed optoelectronic signatures expecting to show potential excited states within the polaronic potential well. From the polaron excited-state we predict that large polarons should be capable of spontaneous emission, photoluminescence, in the mid-IR to far-IR regime based on the concept of inverse occupations within the polaron potential well. Here we use density functional theory (DFT) based calculations using a two-dimensional Dion-Jacobson lead chloride perovskite atomistic model as a host material for either negative or positive polarons to examine the polaronic effects. Nonadiabatic couplings are computed to allow for dynamically coupling electronic and nuclear degrees of freedom allowing us to explore nonradiative relaxation of excited polaronic states. Radiative relaxation of excited polaronic states is found from Einstein coefficients for spontaneous emission. PLQY is used to determine the efficiency of polaron emission using rates of nonradiative recombination (k_{nr}) and radiative recombination (k_r) as $k_r/(k_r+ k_{nr})$.

9:20 AM EL09.13.06
Establishing Charge-Transfer Excitons in 2D Perovskite Heterostructures Jia Zhang; Linköping University, Sweden

Charge-transfer excitons (CTEs) immensely enrich the property-tuning capabilities of semiconducting materials. However, such concept has been remaining an unexplored topic within halide perovskite structures. Here, we report that CTEs can be effectively formed in heterostructured 2D perovskites prepared by mixing PEA_2PbI_4:PEA_2SnI_4, functioning as host and guest components. Remarkably, a broad emission can be demonstrated with quick formation of 3 ps but prolonged lifetime of about 5 µs. This broad PL presents the hypothesis of CTEs, verified by the exclusion of lattice distortion and doping effects through demonstrating double-layered PEA_2PbI_4/PEA_2SnI_4 heterostructure when shearing-away PEA_2SnI_4 film onto the surface of PEA_2PbI_4 film by using hand-finger pressing method. The below-bandgap photocurrent indicates that CTEs are vital states formed at PEA_2PbI_4:PEA_2SnI_4 interfaces in 2D perovskite heterostructures. Electroluminescence shows that CTEs can be directly formed with electrically injected carriers in perovskite LEDs. Clearly, the CTEs presents a new mechanism to advance the multifunctionalities in 2D perovskites.

9:35 AM EL09.13.08
Low-Temperature Synthesis of MoS2 by Plasma-Assisted CVD for Transparent Transistors Arindam Bala, Anamika Sen, Yongin Cho and Sunkook Kim; Sungkyunkwan University, Korea (the Republic of)

MoS_2-based transparent electronics can transform state-of-the-art display technology. The low-temperature synthesis of MoS_2 below the softening temperature of low-cost glasses is a crucial requirement. In this study, plasma-enhanced chemical vapor deposition is employed to synthesize large-area bilayer MoS_2 on an inexpensive microscopic glass (area $\approx 27\ cm^2$). A 7 × 7 array of top-gated thin film transistors (TFTs) with Al_2O_3 dielectric are fabricated. Additionally, the performance of TFTs is assessed under irradiation of visible light and estimated performance parameters, such as photoresponsivity, which is found to be $27\ A\ W^{-1}$ (at λ= 405 nm and an incident power density of $0.42\ mW\ cm^{-2}$). The stable and uniform photo-responsive behavior of transparent MoS_2 TFTs can facilitate the fabrication of transparent image sensors in the field of optoelectronics

SESSION EL09.14: On-Demand Presentation
Friday Morning, April 28, 2023
EL09-virtual

8:00 AM EL09.14.01
Electrically Gate-tunable Two-dimensional Schottky Diode Enabled by Asymmetric Semimetal Contacts Yaoqiang Zhou, Lei Tong, Yue Pang and Jianbin Xu; The Chinese University of Hong Kong, Hong Kong

Two-dimensional (2D) materials are envisaged to extend Moore's Law and ultimate the down-scaling transistor due to their ultra-thin bodies and dangling-bong-free surfaces. Compared to conventional silicon device, the 2D transistor also show a unique doping-free polarity control (p-type or n-type) which is achieved by contact engineering. These 2D transistors are regarded as the Schottky-barrier-field-effect transistor (SBFET) in which the selective carrier injection of holes or electrons is determined by the Schottky barrier formed at the metal/semiconductor (MS) interfaces. However, the SBFETs usually show intrinsic ambipolar behaviors which limit their applications in low-power consumption electronics due to the relatively low on/off ratio and high leakage current in the off state.
The optimization of contact materials of 2D SBFETs is the efficient approach to achieving the ambipolar to unipolar polarity conversion and suppressing off-state leakage current, but it is hindered by the Fermi level pinning (FLP) effect. Emerging 2D layered semimetals such as graphene and WTe_2 provide a state-of-the-art approach to building the van der Waals MS interface and optimizing the performance of 2D SBFET due to the immunity to FLP effect. Here, we report on a unipolarity-tunable WSe_2 SBFET with asymmetric semimetal WTe_2 and graphene contacts, in which the WTe_2 was synthesized by the one-step $MoTe_2$ epitaxial growth. By using the graphene/WTe_2 asymmetric contacts, the WSe_2 SBFET shows the arbitrary carrier polarity determined by the drain bias. The leakage currents of SBFET were effectively suppressed to below 10^{-13} A and showed the controllable I_{ds} on/off ratios with a maximum of 10^6. Benefiting from the immunity to the FLP effect, the n-type and p-type contact formed through applying positive and negative source-drain voltage V_{ds}: An electron Schottky barrier height $\Phi_{B\text{-}n}$= 90 meV and a hole Schottky barrier height $\Phi_{B\text{-}p}$= 140 meV was achieved when V_{ds} = 1V and V_{ds} = -1V, respectively. The SBFET can work as the gate-modulated Schottky rectifier showing the near-unity ideality factors of ~1.0, an ultralow reverse tunneling current of 10^{-15} A, and a high rectifying ratio of 3×10^6. Furthermore, with electrically gate-tuned band engineering, the asymmetric SBFET showed a reconfigurable photovoltaic performance in which the sign of the responsivity and external quantum efficiency be substantially tuned. This WTe_2/graphene contact strategy is generally applicable to other 2D materials such as WTe_2/MoS_2 gate-tunable n-type Schottky diode. This general modulating approach of carrier injection in 2D materials provides an alternative method to reduce the logic-circuit complexity and enhance the performance of the reconfigurable photodetector.

The work is in part supported by Research Grants Council of Hong Kong, particularly, via Grant Nos. AoE/P-701/20, 14206721, N_CUHK438/18, RGC Postdoctoral Fellowship, and CUHK Group Research Scheme.

SYMPOSIUM

April 12 - April 25, 2023

Symposium Organizers
C. Frisbie, University of Minnesota
Christian Nijhuis, University of Twente
Damien Thompson, University of Limerick
Herre van der Zant, TU Delft

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* Invited Paper
\+ Distinguished Invited

SESSION EL10.01: Neuromorphic Molecular Devices
Session Chairs: Christian Nijhuis and Yoeri van de Burgt
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3014

1:30 PM *EL10.01.01
Organic Neuromorphic Electronics for Sensory Coding and Biohybrid Systems Yoeri van de Burgt; Eindhoven University of Technology, Netherlands

Neuromorphic engineering is inspired by the efficiency of the brain and focusses on how to emulate and utilise its functionality in hardware. Organic electronic materials have the potential to operate at the interface with biology and offer promising solutions for the manipulation and the processing of biological signals with potential applications ranging from efficient artificial intelligence systems and bioinformatics to brain-computer-interfaces and smart robotics.

This talk describes state-of-the-art organic neuromorphic devices and provides an overview of the current challenges in the field and attempts to address them. I demonstrate two device concepts based on novel organic mixed-ionic electronic materials and show how we can use these devices in trainable biosensors and smart autonomous robotics.

Next to that, organic electronic materials have the potential to operate at the interface with biology. This can pave the way for novel architectures with bio-inspired features, offering promising solutions for the manipulation and the processing of biological signals and potential applications ranging from brain-computer-interfaces to bioinformatics and neurotransmitter-mediated adaptive sensing. I will highlight our recent efforts for such hybrid biological memory devices.

2:00 PM *EL10.01.02
Stable Universal Logic Gates Using a Single-Molecule Ran Liu[1,2], Enrique del Barco[1] and Christian A. Nijhuis[3]; [1]University of Central Florida, United States; [2]University of Georgia, United States; [3]University of Twente, Netherlands

Since the discrete orbitals of molecules can provide multiple distinguishable electrical states, controllable single-molecule devices stand as ideal candidates for ultra-simple circuit elements to perform high-density computations. However, the expansion of the energy levels of molecular orbitals (MOs) by the electrodes and the effect of the external potential on the absolute value of the energy levels make it difficult to build stable multifunctional devices based on the precise manipulation of MOs. Our recent study found that gated Au/S-$(CH_2)_3$-Fc-$(CH_2)_9$-S/Au (Fc=ferrocene) single-electron transistors (~2 nm) not only hold the advantage of controlling MOs via orthogonal bias (Vb) and gate (Vg) voltages, but also exhibit a unique electronic structure with two stable adjacent conductive MOs. With the $(CH_2)_n$ ($n >= 3$) chain effectively isolating the Fc from the gold electrodes, the MOs of the Fc moiety display narrow energy levels, allowing a clear current change as the energy level enters and leaves the bias window. Built upon the diamond-shaped Coulomb blockade response, a prototype single-electron logic calculator was proposed, implementing all universal 1- and 2-input logic gates within a single-molecule device. In addition, the asymmetry of the molecule leads translates into an asymmetric Coulomb blockade response, enabling switching the logic gate function by changing the bias direction.

2:30 PM *EL10.01.03
Mechanically Controlled Molecular Photoswitching Realized by Aggregation-Induced Emission Yuan Li; Tsinghua University, China

Molecular switches, which the electrical signal of conductance or voltage can be manipulated by external stimuli, have drawn great attentions recently, with photoswitches the most widely studied due to their theoretically ultrafast switching speed. While light provides a natural, addressable and tunable driving force, molecular photoswitches still suffer poor performance with low on/off ratio of electric current, poor reproducibility, or stochastic switching. One of the reasons is that all the photoswitches with on/off ratio more than 100 are based on the mechanism of molecular photoisomerization, which of the energy barrier is high and not able to provide reproducible fast switch theoretically. In this presentation, I will introduce our recent achievement of a fully reversible photoswitching in large-area self-assembled monolayers by aggregation-induced emission from bending flexible supporting electrodes to crowd the functional tetraphenylethylene molecules generating stable (>1000 reversible on/off cycles) switching with large ($3.8 \pm 0.1 \times 10^3$) on/off ratios with fast (140 ± 10 ms) switching time. The output electrical signal can be controlled by the wavelength of light, or the curvature of electrodes, or a combination of the two stimuli together. Structural characterization supported by spectroscopy and modelling shows mechanically controlled photoswitching relying on aggregation-induced emission with UV light enhancing the Coulomb interaction between the electrons and holes to decrease the energy gap between ground and excited states increasing the conductance through the junctions. Our work shows the possibility of precisely controlling the function of aggregation-induced emission to realize high-performance electronics with molecular level control via simple external mechanical force, which may also be interested by other fields where multi stimuli-responses (light/electric/mechanic) applied/required at micro/nano-region.

3:00 PM BREAK

SESSION EL10.02: Biomolecular Electronics I
Session Chairs: C. Frisbie, Christian Nijhuis, Damien Thompson and Herre van der Zant
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3014

3:30 PM EL10.02.01
Ferritin-Based Single-Electron Bio-Nano Devices Jacqueline A. Labra Muñoz[1,2], Arie de Reuver[1], Friso Koeleman[1], Martina Huber[2] and Herre S. van der Zant[1]; [1]Delft University of Technology, Netherlands; [2]Leiden University, Netherlands

In this work, we study, for the first time, the electrical response of single-ferritin particles at low temperatures. Our approach, based on wide (10 um) and small (8-25 nm) self-aligned-nano-gaps devices, facilitates the trapping of single ferritin particles. Below 100 K, the devices are stable enough to allow the acquisition of reproducible currents vs. voltage characteristics. A striking feature of single ferritin particles is that the data is in excellent agreement with the Coulomb blockade model, revealing single-electron tunneling as the main transport mechanism through them.
A ferritin single-electron device is, on one hand, a system for studying the electron transport phenomena in ferritin, and therefore it broadens the scarce present knowledge on single ferritin particles: as such single-electron devices could reveal information about ferritin that may be of importance in understanding its role in neurodegenerative diseases. On the other hand, it is a basic tool for future bio-based electronics, in particular, for the fabrication of protein-based single-electron transistors, due to the exceptional stability of the devices and reproducibility of the current vs. voltage characteristics.

3:45 PM EL10.02.02
Electrifying the Encapsulin—Charge Transport Studies across Protein Nanocages Saurabh Soni, Riccardo Zinelli, Jeroen J. Cornelissen, Sandra Michel-Souzy and Christian A. Nijhuis; University of Twente, Netherlands

Charge transport across biomolecules, such as proteins, DNA, and peptides, has been demonstrated to be efficient over long distances. This is called long-range tunnelling which is ubiquitous in nature in several biological systems. This phenomenon is very interesting for development of next generation bio-molecular electronic devices. However, it is unknown that under which conditions the long-range tunnelling regime can be accessed in the solid-state. Further, Encapsulin protein nanocages represent self-assembled compartments with adjustable number of monomers, and subsequently, the nanocompartment size. These nanocompartments can be used to load different types and amounts of cargoes with different properties. Recently, these nanocages have been shown as useful candidates for bioengineering in targeted drug delivery. However, the effect of these electronic properties has only been investigated for encapsulins in solution. Due to such tunable properties of Encapsulin nanocages, they present an interesting platform for biomolecular electronics.

In this project, we demonstrate a first investigation of self-assembled Encapsulin protein nanocages in the solid-state, either empty or containing different cargoes. We show that these encapsulin protein nanocages can be made stable in solution and on surface without any aggregation using dynamic light scattering, transmission electron microscopy, and atomic force microscopy. We investigated the electronic properties by measuring the current density over different voltage ranges using a conical top electrode of eutectic Gallium-Indium alloy. We determined that the encapsulated cargo has a significant effect on the electronic properties. Higher current densities and rectification ratios were measured in case of a redox active protein as a cargo, such as the ferritin-like protein, compared to a redox-neutral self-folding green fluorescent protein or without any cargo. This project presents a new platform for development of biomolecular electronic devices where the properties can be controlled via an active guest inside the protein host.

4:00 PM EL10.02.03
KPFM Visualization of the Schottky Barrier at the Interface Between Gold Nanoparticles and Silicon—Application to Biomolecular Electronics
Luis Lechaptois[1,2], Yoann Prado[1], Sierin Lim[2] and Olivier Pluchery[1]; [1]Sorbonne Université, France; [2]Nanyang TecUniversityhnological, Singapore

Schottky barrier appears when a metal and a semi-conductor (SC), with different work function, (metal one being larger) are in contact[1]. Determination of this Schottky barrier height (SBH) is well known for an ideal plan-plan interface[2]. However, when dealing with nanostructures, such as metallic nanoparticles in contact with a semiconducting surface, this barrier is hardly predictable because the nanoparticles are already significantly charged when their size is small, which profoundly modifies their apparent work function[3,4]. Moreover their work function also depends on their diameters[4,5]. Yet predicting the presence of a Schottky barrier and the Schottky barrier height (SBH) in case of nanoparticle has become an important topic (e.g. for hot electron in photocatalysis)[6-8]. Here, gold nanoparticles (AuNPs) of 50 nm are deposited on an APTES functionalized n-doped silicon substrate. The sample surface is probed by Kelvin Probe Force Microscopy (KPFM) which allows measuring the local work function through the contact potential difference (CPD) simultaneously with the topography. This technic allows to investigate the charge transfer effects at the nanoscale. SEM and Dark-Field Microscopy characterization are also performed. KPFM measurements reveals a surprising ring-shaped pattern around the nanoparticles. We discuss how this pattern correspond to a potential barrier of 30 mV with a SBH calculated at 300 mV. The value of the SBH is strongly reduced compared to an ideal plan-plan metal/SC junction (SBH = 930 mV). The reasons of this reduction are discussed and a qualitative model is proposed. Gold nanoparticles are objects studied since a long time and widely used in nanoelectronics devices. Our study using the KPFM can act as case study for other unknow metal nanoparticles once deposited on doped silicon. We use this approach for our study on ferritin. Ferritin is a biomaterial (protein) that is formed by the self-assembly of 24 monomers (amino-acid chains) in a 12 nm nanocage that contains an iron core (with up to 4800Fe). Ferritin nanocages have already been used in different electronics devices[9]. Here, ferritins are deposited on doped silicon and characterized by KPFM. Results show also ring-shaped potential around the nanocages.

References:
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4:15 PM EL10.02.04
Metal-Protein-Metal Junctions—Electron Transport and Mechanical Deformation Carlos Romero-Muñiz[1], Maria Ortega[2], José Guulherme Vilhena[2], Ismael D Diez Perez[3], Ruben Perez[2], Juan Carlos Cuevas[2] and Linda Angela Zotti[2]; [1]Universidad de Sevilla, Spain; [2]Universidad Autónoma de Madrid, Spain; [3]King\'s College London, United Kingdom

Proteins have proven to be promising candidates for molecular electronics, showing in some cases much higher conductance than one would naively expect from their size. In particular, the blue-copper azurin extracted from Pseudomonas aeruginosa has been the subject of many experimental studies. The exact nature of the transport mechanism, however, is still under debate. Here I will present our efforts towards gaining an insight into this issue from a theoretical perspective, analyzing both the electronic structure and the geometrical arrangement [1-6].

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SESSION EL10.03: Opto-Electronic Junctions
Session Chairs: Ivana Qianqi Lin and Herre van der Zant
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3014

8:30 AM *EL10.03.01
Electroluminescence from Tunnel Junctions Latha Venkataraman; Columbia University, United States

Light emission from tunnel junctions is a potential photon source for nanophotonic applications. Such tunnel junctions which function as nanoscale plasmonic structures have been primarily characterized through scattering studies, but electroluminescence offers an exciting alternative from a technological standpoint by removing the need for optical excitation. In this talk, I will present results from our recent work probing the nature of electroluminescence in tunnel junctions. I will show that the photons emitted from tunnel junctions can have energies exceeding the energy supplied to the electrons by the bias.[1] I will argue that multielectron processes provide the best framework for understanding overbias light emission in tunnel junctions. I will then present results from our simultaneous measurements of electroluminescence and conductance of Au tunnel junctions.[2] I will show that the plasmonic enhancement increases as the gap size is reduced showing that the efficiency of light emission is not quenched due to electronic tunneling across the junction.

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9:00 AM *EL10.03.02
High-Yield Large-Area Photoswitching Molecular Junctions Takhee Lee; Seoul National University, Korea (the Republic of)

To achieve the ultimate miniaturization of electronic devices, a wide range of studies in the field of molecular electronics has been carried out over the last decades. Important developments include utilization of functional molecules for realizing molecular wires, rectifiers, switches, transistors, and thermoelectric devices. Among such developments, the molecular switch is a promising building block because of its potential as a memory device. In particular, light is useful for switching devices because of its addressability and compatibility with solid-state device structures. Diarylethenes (DAEs) form a class of photochromes with two different conductance states, that is, a high conductance and a low-conductance state. DAEs can be converted between these two states by illumination with UV or visible light. This property makes them good candidates for photoswitching devices because of a large conductance difference between the two states and their response to light. I will present experimental results of photoswitching properties of DAE molecular junctions that were fabricated in a large-area and high-yield vertical metal-molecule-metal structure involving a conducting polymer, reduced graphene oxides, or graphene films as a top electrode [1]. And, I will also present a recent research result of photo-responsive molecular junctions activated by perovskite/graphene electrodes [2]. Specifically, in this study, an organohalide perovskite/graphene heterojunction was employed as a photoactive electrode that acted a source of photo-generated carriers collected as photocurrent in self-assembled monolayer molecular junctions.

References
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[2] Adv. Opt. Mater. 10, 2200049 (2022).

9:30 AM EL10.03.03
Intermolecular Charge Transfer Enhances the Performance of Molecular Rectifiers Ryan Sullivan[1], John T. Morningstar[1], Eduardo Castellanos-Trejo[1], Robert W. Bradford III[1], Yvonne J. Hofstetter[2], Yana Vaynzof[2], Mark Welker[1] and Oana D. Jurchescu[1]; [1]Wake Forest University, United States; [2]Technische Universität Dresden, Germany

Molecular diodes composed of self-assembled monolayers (SAMs) could yield cost-effective, versatile rectifiers that can complement the conventional silicon-based technologies with smaller, less expensive, and more versatile electronics. However, insufficient electrical performance has limited the use of this emerging technology. The efficiency in rectifying current, quantified as the rectification ratio, is dependent on factors like the molecular structure of the SAM, its density and degree of order, as well as coupling to the electrodes. In this work, we focused on molecular diodes consisting of SAMs assembled directly onto silicon, which, unlike metallic electrodes, has a very low natural roughness, and thus requires no additional processing. We co-assembled SAMs with strong electron donor and acceptor termini and found that the rectification strength increased by a factor of four compared to the neat SAMs, approaching rectification ratios of 10^4. This remarkable enhancement in rectification occurred in spite of a decrease in the order of the mixed SAMs, and is the result of the formation of a charge transfer state between the two molecules. Ultraviolet photoelectron spectroscopy (UPS) measurements confirmed a shift of 0.2 eV in the work function of the SAM, consistent with n-type doping. These results provide a novel method for controlling the electrical properties of molecular electronic devices through manipulating donor/acceptor interactions. Our molecules are obtained from a simple, robust, and high-yield synthetic procedure and may yield hybrid systems when integrated with more mature silicon technologies that are currently included in consumer electronics to expand their use toward novel functionalities governed by the molecular species grafted onto its surface. One example is that of a water sensor, which transduces the ambient moisture absorbed into the device through the porous electrode to an electrical signal. By monitoring these changes, we demonstrate clear and reproducible changes in the rectification ratio that are reversible upon multiple cycles. Their operation relies on the changes occurring in the electric field experienced by the molecular layer upon absorption of the polar water molecules, resulting in modifications in the height and shape of the tunnelling barrier.

9:45 AM EL10.03.04
Persistent and Versatile Self-Doping via Photoinduced Electron Transfer in One-Dimensional Charge-Transfer-Mediated J-Aggregates of Organic Semiconductors Lucile Chassat and Holger Frauenrath; École Polytechnique Fédérale de Lausanne (EPFL)), Switzerland

Easy-generation of stable charge carriers in organic semiconductors is a key challenge towards modern high-performance devices for electronics, photovoltaics, spintronics, sensing, and catalysis applications. In recent years, covalently tethering an appropriate dopant to a semiconductor of interest to achieve self-doping by charge transfer upon simple photoexcitation has emerged as a promising attractive strategy. In the case of self-n-doping, perylene bisimide (PBI) derivatives have garnered the most attention due to their high electron affinity and strong absorption in the visible range, as well as their good chemical robustness and excellent photostability. Several studies described the photogeneration of anions in amine or ammonium-functionalized PBIs. However, in these few examples, only charge lifetimes of tens of minutes, at best, were reported. Additionally, the role of the chromophores arrangement in this photo-n-doping process remains unclear, and a more thorough understanding is required to design efficient self-n-doped materials. Our laboratory has previously revealed the formation of unusually long-lived positive photo-charges in self-assembled nanowires from electron-rich semiconductor molecules substituted with chiral oligopeptide-polymer side chains. The doping was attributed to a photo-induced electron transfer to the lateral amide bond acting as an acceptor and it was demonstrated that the formation of well-defined helical, one-dimensional aggregates is one decisive prerequisite for its occurrence. Recently, we discovered that the same molecular architecture and self-assembly strategy can also lead to self-n-doping of supramolecular nanowires based on well-chosen electron-poor chromophores. Dicyanoperylene bisimide (CN2-PBI) along with tetrachloroperylene bisimide (Cl4-PBI) were substituted with oligopeptide-polymer side chains and their supramolecular aggregates were investigated by a combination of spectroscopies as well as atomic force microscopy and X-ray scattering. While Cl4-PBI aggregates show no photo-doping, illumination of the CN2-PBI nanowires leads to the formation of air-stable radical anions with extraordinarily long lifetimes on the order of hours that can accumulate to concentrations of up to 7 mol%. In addition, devices prepared from these aggregates exhibit macroscopic transport properties typical for a strongly doped electron conductor with a highly persistent photocurrent. The comparison of these two systems reveals that the formation of mixed Frenkel/Charge-Transfer excitons in the aggregates plays an essential role in the efficiency of the photo-n-doping. Moreover, this conclusion was further confirmed to be a universal condition by the study of two additional self-p-doping systems. These results prove that the macroscopic electronic properties are not only inherent to the employed molecular structure, there are an “emerging property” that is strongly affected by the intermolecular chromophore arrangement which thus needs to be carefully designed as well in self-doped organic electronic materials.

10:00 AM BREAK

SESSION EL10.04: Chiral Induced Effects
Session Chairs: Yonatan Dubi and C. Frisbie
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3014

10:30 AM *EL10.04.01
What Can We Learn from the Chiral Induced Spin Selectivity Effect on Electron Transfer? Ron Naaman; Weizmann Inst, Israel

The chiral induced spin selectivity (CISS) effect means that electron transport through chiral systems is spin dependent. The effect was found to exist not only on molecular scale but also in crystals when the scale of the spin transport exceeds microns. In addition, in many cases, the effect was found to increase with increasing temperatures. Recent studies on electron transfer (ET) through proteins established that the effect is indeed long range and with extremely high spin selectivity, reaching 100%.
Experimental results obtained on long range CISS effect will be presented and the dilemma they present will be discussed. Since the CISS effect involves also charge transfer, its mechanism must reflect the ET process. The observations obtained regarding the long range CISS effect, are not consistent with hopping or mechanism. A new insight on the ET mechanisms will be presented that is consistent with many experimental observations that could not explained by the “conventional” models.
It will be shown that within the modified scheme both the ET and the CISS effect can be explained in principle, although the real first principle calculations remain a major challenge.

11:00 AM *EL10.04.02
Spinterface Mechanism for the Chirality-Induced Spin Filtering - From Transport to Photoexcitation Yonatan Dubi; Ben-Gurion University, Israel

When electrons are injected through a chiral molecule, the resulting current may become spin polarized. This effect, known as the chirality-induced spin-selectivity (CISS) effect, has been suggested to emerge due to the interplay between spin–orbit interactions and the chirality within the molecule. However, such explanations require unrealistically large values for the molecular spin–orbit interaction without any physical justification. Put simply, to date, the physical origin of the CISS effect is unknown.
Here, we present the “spinterface mechanism” for the CISS effect, based on the interplay between spin–orbit interactions in the electrode, the chirality of the molecule (which induces a solenoid field), and spin-transfer torque at the molecule–electrode interface. The spinterface mechanism has already been shown to allow remarkable fit between theory and data for numerous experiment. We will provide new examples for such fits, further corroborating the mechanism. We will describe a set of experiments which can be used as a “smoking gun” for differentiating this mechanisms from other theoretical explanations. Finally, we will describe a spinterface mechanism for the CISS effect in photo-excited electrons scattered off a layer of chiral molecules.

SESSION EL10.05: Biomolecular Electronics II
Session Chairs: David Cahen and Diana Dulic
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3014

1:30 PM *EL10.05.01
Experiment and Hope—Evidence for Quantum Solid-State Electronic Conduction Across Proteins David Cahen; Weizmann Institute of Science, Israel

Electron Transport (ETp), *electronic* conduction, across ultra-thin protein films as active layer in a solid-state junction, can be surprisingly efficient. Length-normalized ETp efficiency can be similar to, or even exceed that of conjugated molecules; moreover, it can be temperature-independent down to at least 4K. If intra-protein transport dominates (contacts are not limiting; a challenge as proteins are poly-electrolytes), no significant transport barrier is measured, challenging the simplest explanation for this transport, hopping conduction.
Such results have, nowadays, the banner “quantum” all over them, as they seem consistent with quantum tunneling; one of the problems with such an explanation. While recently the first golden standard evidence, with alkyl-thiol molecule films, for such, interference, was reported, it is still lacking for proteins. In truth, coherent transport through proteins, non-periodic systems that are dynamic, even at low temperatures, is not at all obvious. Still there are some results that are
surprising in this context:
- the above-noted temperature independence, which we have now found for up to ~ 20 nm (multilayers of bacteriorhodopsin, bR)
- the inability to fit, small, short proteins (Azurin, Az) data to any reasonable hopping model
- the possibility to bring short proteins (Az, Cytochrome C) in and out of resonance by applied bias
- clear inelastic electron tunneling spectra for Az (and their absence for larger proteins).

Unraveling the transport mechanism is, apart from scientific curiosity, of interest, as understanding ETp may have relevance for ET (replace coupling to contacts by electron injection / extraction). I will discuss our recent experimental data and their analyses, and try to put them in perspective also with reports from other groups. The aim is to separate expectation and anticipation from experimental observables, to define the puzzle that we try to solve3, even if it starts to resemble the ‘duck test”.

* work done with **Mordechai Sheves and Israel Pecht**, students & PD fellows, all @theWeizmann Institute; further collaborations are with A Vilan, J Blumberger, G Vattay, E Papp, C Cuevas, L Zotti; M Tornow, +++
References: 1 C. Bostick et al. Rep. Prog. Phys (2018); 2 N. Amdursky et al., Adv. Mater. (2014); 3 D.Cahen, I.Pecht, M. Sheves, J. Phys.Chem. Lett.

(2021)

2:00 PM EL10.05.02
Large Cooperative and Dielectric Effects on the Tunneling Rates Across Molecular Tunnel Junctions Christian A. Nijhuis; University of Twente, Singapore

The measured tunneling rates are in molecular junctions are often large over surprisingly large distances.[1] In addition, often the temperature dependency (or lack thereof) is still poorly understood. We are investigating the mechanisms of charge transport across junctions of the form metal—molecules—metal where the molecules are present in the form of self-assembled monolayers (SAMs). I will give a brief summary of our effects to elucidate charge transport mechanisms in molecular tunneling junctions by measurements of dielectic constast coupled with temperature dependent measurements.[2] We find that charge transport increases with dielectric contstant, with increasing dielectric constant the tempersature dependency (or activation energy increases).[3] In mixed monolayers, we find a soft atom induces positive cooperative effect on electron transfer rates.[4,5] These studies as group highlight the complex interplay between several intertwined factors (molecular structure, molecular organization, dielectric properties and interfaces) in the mechanism of charge transport across molecular junctions.

References

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Li, Y.; Wang, D.; Peng, W.; Jiang, L.; Yu, X.; Thompson, D.; Nijhuis, C. A. *Nano Today* **2022**, *44*, 101497.

2:15 PM EL10.05.03
Long-Range Charge Transport Through Bacteriorhodopsin Multilayers Domenikos Chryssikos[1,2], Jerry A. Fereiro[1,3], Jonathan Rojas[1], Mordechai Sheves[4], David Cahen[4] and Marc Tornow[1,2]; [1]Technical University of Munich, Germany; [2]Fraunhofer Research Institution for Microsystems and Solid State Technologies, Germany; [3]Indian Institute of Science Education and Research Thiruvananthapuram, India; [4]Weizmann Institute of Science, Israel

Proteins are ubiquitous in the vital functions of the cell, many of which rely on charge transfer, such as respiration and photosynthesis. Recent research has revealed that certain proteins maintain their structure, as well as their conductive properties, even in the unnatural "dry" state (with only some structural water retained). [1, 2] As a result, researchers have strived to exploit the electronic properties of proteins in the context of hybrid solid-state devices, such as protein-inspired sensing, photovoltaics and memory devices. [3] To this end, understanding the nanoscopic charge transport mechanisms inside dry proteins is crucial. In this study, we focus on bacteriorhodopsin (bR), a proton pump in the purple membrane of *Halobacterium salinarum*. bR is a promising candidate for solid-state devices due to its thermal stability and photoactivity. [4] While the self-assembly and electrical characterization of bacteriorhodopsin-rich layers is well-established, [5] the controlled preparation of multilayers remains challenging for structural and electrostatic reasons. Here, we present a technique for the preparation of multilayers of octylthioglucoside-treated bR (OTG-bR) embedded in protein-lipid vesicles, on amino-terminated TiN substrates. The technique employs the cationic polymer polydiallyldimethylammonium (PDDA) as an electrostatic linker between the protein layers. Our analysis using atomic force microscopy (AFM) revealed the successful preparation of stacked films of OTG-bR, with heights 8.2, 13.0, and 16.2 nm for one, two, and three OTG-bR layers, respectively. X-ray photoelectron spectroscopy (XPS) verified the relatively high macroscopic surface coverage of approximately 90% for the triple layer. DC current-voltage measurements where performed in a vertical configuration using the TiN substrate as bottom, and eutectic gallium-indium or evaporated Ti/Au as top contacts. We observed an exponential attenuation of the current as a function of layer thickness, with attenuation coefficients of $0.7 - 1.0$ Å^{-1}. These values are somewhat smaller than previously reported [2, 6] and in addition, show a small yet intriguing increase with increasing voltage bias. Variable-temperature measurements revealed temperature independence below $T \approx 50$ K, and Arrhenius-like temperature dependence with activation energies of roughly 50 meV above this temperature. Considering the above findings, we propose a possible multistep charge transport mechanism, which would combine both, off-resonant and resonant charge carrier tunneling, as well as thermally activated hopping processes.

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2:30 PM BREAK

SESSION EL10.06: Light Matter Interactions in Molecular Junctions
Session Chairs: Jeremy Baumberg and Ivana Qianqi Lin
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3014

3:30 PM *EL10.06.01
Seeing Directly How Picocavity Adatoms Control Molecule-Metal Coupling Jeremy J. Baumberg; University of Cambridge, United Kingdom

Our ability to trap light into extreme nanoscale gaps between coinage metals using plasmonics has enabled routine vibrational measurements of molecular monolayers, even within active molecular electronics devices [1]. We recently showed that single metal atoms can be pulled out of the interface by light [2] (or electric fields), and that coordination bonds with individual molecules can be tracked in real time [3-6], or their redox state observed [7]. We discuss new observations for the thousand-fold enhanced optical forces in such nanogaps.
Such spectroscopy reveals a wealth of information: from how applying voltages can twist the conducting molecules in a gap [8], to how solvated charge is able to penetrate self-assembled monolayers [9]. The robust and precise self-assembly of the nanoparticle-on-mirror geometry is ideal for tunnelling photocurrent devices [10], and shows that asymmetry is created in the junction, likely by such picocavities. We also discuss the dynamics of the picocavity formation [11], and how this may be now controlled.

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4:00 PM *EL10.06.02
In-situ Spectro-Electrochemistry of Conductive Polymers Using Plasmonics to Reveal Doping Mechanisms Ivana Qianqi Lin[1,2], Jialong Peng[2], Tamás Földes[3], Hyeon-Ho Jeong[2], Yuling Xiong[2], Charalampos Pitsalidis[2], George G. Malliaras[2], Edina Rosta[3] and Jeremy J. Baumberg[2]; [1]University of Twente, Netherlands; [2]University of Cambridge, United Kingdom; [3]University College London, United Kingdom

Conducting polymers are a key component for wearable organic electronics due to their low-cost fabrication compared to silicon counterparts, and their mechanical flexibility compatible with foldable devices. The reversible doping/dedoping of conductive polymers is the basis of organic thin-film transistors, sensors, and displays.

Doping transfers electrons in/out (i.e., reduction/oxidation) of the neutral conductive polymers, creating negative/positive charge carriers. Two-electron transfers are involved in generating polarons or bipolarons. The former contains mono-radical ions, and the latter contains di-anions/cations. Although many techniques have been used to characterize the doping/redox process, conflicting conclusions often arise from the **difficulty in obtaining well-defined electrochemical response from the polymers**, and **it is unclear why short-lived polaron intermediates are sometimes observed but sometimes not.** Understanding of the doping/redox mechanism is thus scarce, limiting development of widespread polymer-based applications.

In this work [1], we present an in-situ spectro-electrochemical technique to address this challenge. Using nanoparticles encapsulated by thin shells of conductive polymers, their redox dynamics can be interrogated. By drop-casting the core-shell nanoparticles onto a gold substrate, an electrochromic nanoparticle-on-mirror (*e*NPoM [2,3]) geometry is formed giving well-defined electrochemical response, as well as actively-tuned scattering color through switching their refractive index. More importantly, the plasmonic hotspots formed in the *e*NPoM geometry confine light into nanocavities at the volume of < 100 nm^3, enabling vibrational Raman scattering enhancement of $>10^4$ and high signal-to-noise ratios. Surface-enhanced Raman spectroscopy (SERS), in combination with cyclic voltammetry, uncover structural fingerprints at the few-molecule level during redox transitions. Our data intriguingly show that the **doping mechanism varies with polymer conductivity: a disproportionation mechanism dominates in more conductive polymers, while sequential electron transfer prevails in less conductive polymers**. This technique thus allows in-situ study of the thin-film conductive polymer redox in real-time to reveal new features in the doping mechanism.

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4:30 PM *EL10.06.03
Combining Single-Molecule Raman with Molecular Conductance Measurements Josh Hihath; Arizona State University, United States

The ability to manipulate and characterize individual molecules with atomic-level precision is necessary to develop a thorough understanding of the intricacies of the effects of changes in molecular structure on a range of phenomena such as reaction mechanisms, catalysis, local effective temperatures, surface interactions, and charge transport. Along these lines, the field of molecular-scale electronics has evolved tremendously in recent years: from the initial experiments claiming single-molecule conductance measurements to the development of platforms that provide a detailed understanding of the charge transport properties of these systems. It has now become possible to probe the chemical, structural, mechanical, and electrical properties of single-molecule devices and explore unique functional paradigms for applications. However, continued advances in *in situ* characterization of a molecular junction are needed to provide detailed information about the molecular configuration and its impact on the charge transport, reactions, and device behavior. Single-molecule conductance and Raman spectroscopies each provide unique perspectives into the behavior of molecular systems and reactions at the single-molecule level. In this talk we will discuss the development and implementation of system designed to simultaneously obtain conductance information and Raman spectra from a molecular junction to provide direct structural and chemical information about a single-molecule junction.

This multi-dimensional information yields repeatable, self-consistent, verification of single-molecule resolution, and allows for detailed analysis of structural and configurational changes of the molecule *in situ*, and provides new opportunities for identifying molecular substituents, conformations, and the impact of these changes on the transport properties of the molecular systems. We will discuss the correlation between single-molecule binding events and changes in Raman spectra (intensity, modes, etc.) and conductance to explore the possibility of obtaining single-molecule spectra from the molecule bound between two electrodes. We will further explore the utility of this system for *in situ* characterization of single-molecule devices including electrically-active single-molecule switches, memory devices, and biomolecules.

SESSION EL10.07: Poster Session
Session Chairs: Christian Nijhuis and Damien Thompson
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL10.07.02
Beyond Fermi-Level Pinning: Control over Energy Level Alignment at Molecule-Electrode Interfaces via Proton-Coupled Electron Transfer Fuad Alami, Georgios Katsoukis and Christian A. Nijhuis; University of Twente, Netherlands

Intelligent design of energy level alignment for molecular electronics is crucial for developing complex charge transfer systems. The majority of approaches for energy level alignment pertain to chemical modification. However, molecule-electrode interactions can also present a means of modulating alignment within the junction via interactions such as push-back effects[1] and Fermi level pinning[2]. In addition, substrate-mediated interactions can induce structural, chemical, and electronic changes in self-assembled monolayers.[3] To the best of our knowledge, studies between the coupling of a proton-coupled electron transfer (PCET) system and substrate-mediated interactions have yet to be investigated. In these studies, we examine the influence of substrate choice on the well-known PCET demonstrated in hydroquinone redox reactions. By using 11-mercaptoundecylhydroquinoine (11-MHQ) tethered to platinum or gold, we can differentiate the substrate's influence on the charge transfer mechanism. We believe that the substrate's influence on the charge transfer mechanism induces a variance in the molecular dipole contribution to change in work function. To further understand this phenomena, we investigated whether the substrate influences the redox equilibrium by characterizing the monolayer by Fourier transform infrared spectroscopy (FTIR) and cyclic voltammetry (CV) and X-ray Photoelectron Spectroscopy (XPS). Furthermore, understanding the resulting energy alignment of the system was done through Ultraviolet Photoelectron Spectroscopy (UPS) and the manifestation of such influences on the electronic tunneling behaviors is demonstrated by forming a two-terminal junction composed of metal/11-MHQ/EGaIn (eutectic alloy of gallium and indium). These junctions demonstrated a reversal in rectification only dependent on electrode choice.

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5:00 PM EL10.07.03
Dynamic Molecular Switches Based on HATNA Derivatives for Application in Neuromorphic Computing Alessandro Borrini; University of Twente, Netherlands

Currently, about 5%–15% of the world's energy is spent in some form of data manipulation and this fraction is expected to rapidly increase. Between 20 and 30 MW are estimated for von Neumann type computers to emulate same level of complexity as our brains. Our brain works with 20 W.[1] Neuromorphic computing architecture focuses on building electronic neural processing systems that directly emulate real neurons and synapses. Currently, most approaches to neuromorphic computing rely on high energy consuming silicon materials.[2] An attractive energy efficient solution is given by molecular switches which can potentially simulate synaptic plasticity. However, up to now, molecular switches can only switch between fixed on and off states, hence showing a static rather than dynamic behaviour. The key factor to reproduce synaptic plasticity is coupling different processes each characterised with its own time constant, analogues of action potential coupled to slow diffusion of Ca^{2+} and neurotransmitters in synapses. 5,6,11,12,17,18-hexaazatrinaphthylene (HATNA) in a tunnelling junction is a promising candidate because it can couple a fast electron transfer to slow proton transfer.[3] Synthetic modification of HATNA with diphenylacetylene (DPA) moieties can potentially facilitate tunneling electron transfer rates in the junction while at the same time enhance packing density of molecules on the electrode.[4,5] In this poster we give an overview of the synthesis route to achieve the dynamic switch HATNA-DPA and initial monolayer composition studies.

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3. Nijhuis, C. *et al.* Dynamic Molecular Switches Drive Negative Memristance Emulating Synaptic Behaviour. (2022) doi:10.21203/RS.3.RS-1156230/V1.
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5:00 PM EL10.07.04
Mechanical Stabilization of Molecular Junctions by Interaction with Polar Media Yoni Langbeheim and Uri Peskin; Technion-Israel Institute of Technology, Israel

The build-up of energy density in nano-scale electronics via inelastic resonant electron transfer is detrimental to chemical bonds' stability and molecular structure's integrity. This effect may be harnessed for control of the electron (hole) current, but on the other hand, accumulation of excess vibrational heat may lead to bond rupture and breaking of the nano junction. Therefore, finding physical conditions at which these junctions can sustain high-voltage resonant transport is of prime importance for experimental application.
We predict that polar media interacting with the transient charging of the molecule may stabilize junctions under resonant transport. The Polaron-like coulomb interaction of polar media with the charged species is lowering the energetic range for discharging events. In highly-polar solvents, this effect tends to favor cooling transport processes over heating ones, stabilizing the overall charge transfer event. A second effect is brought up by the thermally-induced growth of the number of interacting solvent particle configurations. The widening band of emerging virtual states broadens the possibility windows for charge transfers from (or to) the electrode. This thermal broadening also tends to promote the cooling inelastic charge transfer pathways over the heating ones, overall inducing a temperature + polarity dependent transport-induced cooling effect. These findings are added on top of a temperature-dependent electrode cooling process known from previous studies.

5:00 PM EL10.07.05
Synthesis of Oligomers in Molecular Junctions Tal Klein and Oren Tal; Weizmann institute of science, Israel

We use the Ullmann reaction to successfully synthesize individual oligomers in molecular junctions at 4 Kelvin. Our motivation is twofold: first, finding a scheme based on a very general and widespread reaction for in-situ preparation of a single polymeric chain suspended between two electrodes for the study of charge, spin, and heat transport across such quanzi-1D systems. Second, a better understanding of chemical synthesis in very peculiar conditions. We will discuss the role of low-coordination substrates, electric fields, and unusual energy resources, as friction, on the reaction and the resulted single-oligomer junctions.

SESSION EL10.08: Modeling of Functional Devices

Session Chairs: Ryan Chiechi and Ayelet Vilan
Friday Morning, April 14, 2023
Moscone West, Level 3, Room 3014

8:30 AM *EL10.08.01
Distinguishing Tunneling from Hopping—Temperature, Length and Voltage Behavior Ayelet Vilan; Weizmann Institute of Science, Israel

A key question of molecular electronics is how far the charge transport is coherent, which is often coded to '*tunneling*' (coherent) vs. '*hopping*' (incoherent). Although coherent transport is associated with rich quantum mechanical phenomena, coherent electrons are "too-fast" to interact with the molecular medium and therefore yield a rather featureless voltage response. In contrast, incoherent transport involves molecular deformation and environment polarization, which leads to far richer current-voltage characteristics. Traditionally, the lack or existence of *temperature* dependence is taken as a prime criterion for *tunneling* or *hopping*, respectively. However, there are opposite cases of *temperature*-independent *hopping* (as in inverted Marcus regime) or *temperature*-dependent *tunneling* (by temperature broadening of DOS of the contacts). Overall, it undermines the reliability of *temperature* response for *tunneling / hopping* distinction. It is less known, that also the *voltage*-response differs considerably between the two mechanisms: off-resonance *tunneling* is characterized by mild, polynomial *voltage* dependence in contrast to *hopping*, which is characterized by a strong, exponential dependence on *voltage*. The third control-parameter, *length*, has somewhat 'opposite' effect: *tunneling* decays exponentially (strongly) with *length*, and *hopping* is only weakly *length*-dependent. Therefore, it is often argued that *hopping* is typical of long transport distance, exceeding ~4 nm. In contrast, we recently demonstrated transport by *hopping* across a minute distance of merely ~1 nm. Moreover, observing the combined interplay of the three parameters: *temperature*, *voltage* and *length*, reveals behavior that exceed simplistic models, suggesting that the real transport model is yet beyond our conceptualization. My talk will bring various examples of experimental transport traces and suggest possible analytical protocols to elucidate the *tunneling* - *hopping* dilemma.

9:00 AM *EL10.08.02
Molecules in Nano-Conduction-Junctions and Optical Cavities—Electron Transfer and Transmission, Polaritons, Vibrational Strong Coupling and Collective Response Abraham Nitzan[1,2]; [1]University of Pennsylvania, United States; [2]Tel Aviv University, Israel

Transport phenomena involving molecules confined within dielectric or metallic nanostructures involve coupling and energy conversion processes between charge carriers, phonons and photons. From both their scientific aspect and technological potential studies of such phenomena stand at the interface of two important fields: molecular electronics and molecular plasmonics. In this talk I will describe our work on such processes, focusing on phenomena that involve interaction with the radiation field, along several main issues: (a) Transport and spectroscopy in illuminated molecular junctions. (b) Molecular optical response when interacting with confined radiation fields (optical cavities). (c) Molecular electron transfer in optical cavities. (d) Cavity induced vibrational strong coupling and its implications on chemical reactivity.

9:30 AM *EL10.08.03
Theoretical Insight into the Electronic Properties of Switchable Molecular Junctions Jerome N. Cornil; University of Mons, Belgium

In this contribution, we will review some of our recent theoretical works focusing on the electronic properties of switchable molecular junctions. We will describe photoswitches sandwiched between gold or ferromagnetic electrodes in close connection with corresponding experimental data and will illustrate that the design of functional molecules can be strongly hampered by pinning and/or collective electrostatic effects in the junction; a new chemical design will be introduced to enhance the on/off ratio in diarylethene-based molecular junctions. Finally, we will report calculations of magnetoresistance for junctions in the field of molecular spintronics.

10:00 AM BREAK

SESSION EL10.09: Robust Functional Junctions

Session Chairs: Ryan Chiechi and C. Frisbie
Friday Morning, April 14, 2023
Moscone West, Level 3, Room 3014

10:30 AM *EL10.09.01
Robust Devices Comprising Self-Assembled Bilayers Ryan Chiechi[1,1], Xinkai Qiu[2] and Sumit Kumar[2]; [1]North Carolina State University, United States; [2]University of Cambridge, United Kingdom

In this talk, I will discuss our work on self-assembled ensembles of (bio)molecules that are sufficiently robust to function in arrays capable of memristor-like function, diode logic and binary information storage. When sandwiched between electrodes, these ensembles mitigate charge-transport primarily via non-resonant tunneling, presenting the opportunity to control the flow of charge across interfaces at the quantum level, through self-assembly and synthetic modification. We are developing a new type of self-assembled monolayer that enables the creation of robust molecular ensemble junctions that can be printed, integrated into devices and that are bench-stable for weeks. Using this approach to program the self-assembly of protein complexes that sustain coherent tunneling over distances of 10 nm, we have been able to create simple diode logic and memristor-like devices that read out stochastic information encoded in trains of droplets in microfluidic channels. By optimizing the self-assembly of photo-switches, we have demonstrated the ability to read, write, erase and rewrite binary-encoded. While rudimentary, these devices demonstrate the utility of molecular self-assembly in the fabrication of molecular-electronic circuits using soft materials.

11:00 AM *EL10.09.02
Single-Protein Electronics—Effect of Surface Mutagenesis and Multiheme Redox Cofactors Ismael D Diez Perez[1], Albert Cortijos Aragones[2], Eliseo Ruiz[2], Nuria Aliaga-Alcalde[3] and Christian A. Nijhuis[4]; [1]Kings College London, United Kingdom; [2]Universitat de Barcelona, Spain; [3]Institut de Ciència de Materials de Barcelona, Spain; [4]University of Twente, Netherlands

Bioelectronics is rapidly moving towards designing nanoscale electronic platforms that allow in vivo determinations. Such devices require interfacing a complex biomolecular moiety as the active sensing unit to an electronic platform for signal transduction. Inevitably, a true systematic design goes through a bottom-up understanding of the structurally related electrical signatures of such hybrid biomolecular circuits, which will ultimately lead us to tailor its electrical properties and exploit them as high performance bioelectronic devices with a wide variety of applications in organic electronics, sensing, biomanufacturing, *etc*.

In this contribution, we will present our latest efforts on trying to understand and control charge transport in a single-protein junction. Our approach relies on trapping individual redox proteins in a tunneling junction under electrochemical control to characterize their main electrical signatures. The method can capture very fine details of the charge transport mechanisms across proteins in an aqueous environment [1,2]. Our studies started on a benchmark redox protein model such as a bacterial blue Cu-Azurin. We will show first the main observed electrical signatures of these systems that make them particularly efficient in transporting charge. We then bioengineer the outer protein surface using point-site mutagenesis as a mean to get a more detailed picture of possible electron pathways through the protein backbone [2,3]. Our results suggest that the protein might not use distinct physical electron pathways across its structure, but transport mechanism can be switched upon quenching of particular motions in the protein structure via mutations. We then compare the above model system to a natural molecular wire, a multiheme protein. Multiheme proteins have been recently discovered as the building blocks in highly conducting pili and transmembrane structures of certain species of the so called electrical bacteria [4]. Our results suggest a very efficient charge transport process along the multiheme main axis with a very shallow electron decay constant.

Summing up, the above work shows the potential of electrochemically controlled nanoscale protein junctions to both elucidating charge transport mechanisms in biological systems as well as in enabling a bottom-up design of electrode/protein interfaces for the future generations of bioelectronic devices.

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SESSION EL10.10: Analysis Methods and Modeling of Junctions
Session Chairs: Maria El Abbassi and Christian Nijhuis
Friday Afternoon, April 14, 2023
Moscone West, Level 3, Room 3014

1:30 PM *EL10.10.01
Machine Learning Tools for the Measurements and Analysis of Quantum and Molecular Devices Maria El Abbassi, Frederik Van Veen, Luca Ornago and Herre S. van der Zant; TU Delft, Netherlands

A deep understanding of the electrical properties of quantum materials and molecular junctions remains very challenging and is currently limited to a small selection of non-reproducible devices which show large device-to-device fluctuations. Understanding the details of every single device remains difficult, time consuming and impossible to scale up. Fast screening of different materials including molecules, as well as precise understanding and control of their electronic properties will open the way to a large number of applications including quantum computing, sensing, etc. However, one of the main challenges of quantum hardware is the poor understanding and control of the properties of the material and its interfaces/surface.

In this talk, I will share our results on using benchmark systems and large dataset combined with machine learning tools to gain more insights into the understanding of transport properties in molecular devices. By developing high-throughput platforms, we could optimize the fabrication of graphene nanogaps to contact molecules and achieve the first stable and reproducible graphene molecular junction by decoupling the electronic properties of the junction from its mechanical anchoring and stability [1]. Combining large statistics allowed by mechanically controlled break junction and clustering techniques [2,3, we could also unravel several electronic paths through porphyrin molecules [4] as well as benchmark transport properties of alkane molecules [5]. I will conclude the talk with advance on the fabrication and measurements of carbon nanotube based spin qubits.

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2:00 PM EL10.10.02
Molecular Structure and Substrate Effects on Single-Molecule Thermoelectric Properties Tim Albrecht[1] and Joseph M. Hamill[1,2]; [1]University of Birmingham, United Kingdom; [2]University of Copenhagen, Denmark

The ability to tailor the electronic transmission function in molecular materials with the help of chemical design opens exciting prospects towards

optimising their electronic and thermal transport properties as well as the thermopower. For example, it is now well-established that quantum interference effects, the targeted introduction of substituents or even the exchange of individual atoms in a molecular structure are factors that allow for finetuning of the energetic structure of the junction.[1,2] The notion of a "Molecular" Quantum Technology is emerging, here in the context of materials design with increasing evidence that favourable thermoelectric properties at the single-molecule level can be translated to "many molecule" devices.
Employing Scanning Tunnelling Spectroscopy in combination with advanced data analysis tools,[3-5] we have recently started to explore different classes of molecules in this context. Based on a variation of distance-dependent I/V spectroscopy, we have measured the thermopower for simple organic molecules as well as new and more complex molecular designs. Specifically, our results agree well with previously reported values for 1,8-octanedithiol, 4,4'-bipyridine and OPE3,[6] while we also find interesting quantum interference and substrate effects for a series of anthracene-based molecules.[7] To this end, we observe a “pinning effect” for asymmetrically coupled molecules, where the stronger anchor dictates the overall charge transport and thermoelectric behaviour, and inversion of the thermopower for weakly bound molecules in Au/Au vs. Au/Pt junctions. In connection with recent thin-film studies, the latter lend themselves to a detailed comparison of thermoelectric performance at the single-molecule and thin-film levels.[8,9]

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2:15 PM EL10.10.03
Dynamic Disorder Design Rules for Small-Molecule Organic Semiconductors Makena Dettmann[1], Lucas Cavalcante[1], Luke L. Daemen[2] and Adam J. Moule[1]; [1]University of California, Davis, United States; [2]Oak Ridge National Laboratory, United States

Small-molecule organic semiconductors are promising materials for applications ranging from solar cells to medical sensors. Their nearly infinite design space means that, in theory, it is possible to tailor the material to the exact specifications of a particular application. In reality, however, design rules to improve mobility (μ) remain elusive because of the complex calculations required to understand its limiters. Transient localization theory posits that charge carriers are slowed down by the collective phonon motions, called dynamic disorder, which localize charge carriers temporarily. Here, we present a streamlined simulation workflow that simplifies simulation of dynamic disorder and enables engineering of new molecular structures based on phonon dynamics. We combine this workflow with a novel visualization technique that enables per-atom insights into how μ is limited. We apply this workflow and analysis to a series of -acenes and a series of BTBT-based molecules. Then we identify design rules in each series that identify possible ways to improve the μ beyond current experimental limits using phonon engineering.

2:30 PM BREAK

SESSION EL10.11: Functional Devices
Session Chairs: Lapo Bogani and Bingqian Xu
Friday Afternoon, April 14, 2023
Moscone West, Level 3, Room 3014

3:00 PM *EL10.11.01
A Wave of Quantum Carbon Lapo Bogani; University of Oxford, United Kingdom

Graphene ribbons with nanometer-scale widths should exhibit half-metallicity, quantum confinement and edge effects. Magnetic edges in graphene nanoribbons have undergone intense theoretical scrutiny, because their coherent manipulation would be a milestone for spintronic and quantum computing devices. Experimental investigations are however hampered by the fact that most nanoribbons do not have the required atomic control of the edges, and that the proposed graphene terminations are chemically unstable. Several questions remain unsolved: how can spins be assembled into hybrid structures at the nanoscale? What is the influence of the graphene environment on the spin? How can we create and control coherent currents in such graphene devices? Here we try to provide an answer to these questions, exploring spin-graphene interactions by using atomically-shaped magnetic materials.
We first examine bottom-up shaping of molecular graphene quantum systems. We then show that, while the static spin response remains unaltered, the quantum spin dynamics and associated selection rules are profoundly modulated. [1] We then show how graphene nanoribbons made via molecular routes can be functionalized to create almost-ideal magnetic structures to test a decade of theoretical work. We observe the predicted delocalized magnetic edge states, and comparison with a non-graphitized reference material allows clear identification of fingerprint behaviours. We then examine how these systems can be considered excellent candidates for the observation of topological states, and unconventional types of magnetism such as Stoner interactions. We quantify the spin-orbit coupling parameters, define the interaction patterns, and unravel the spin decoherence channels. Even without any optimization, the spin coherence time is in the μs range at room temperature, and we perform quantum inversion operations between edge and radical spins.[2] The use of topological engineering and quantum decoupling sequences allows pushing coherence times up to almost ms at room temperature [3].
Eventually we discuss how these systems can push the limits of quantum electronic devices, showing spintronic[4] and electron-vibrational coupling effects[5], which can make them excellent emitting systems for carbon-based optical and optoelectronic devices.

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3:30 PM *EL10.11.02
Molecular Electronics under Microscope Bingqian Xu, Kun Wang, Sneha Kandapal and Cunlan Guo; University of Georgia, United States

Electron transport through a single molecule is a central theme in molecular electronics. The ability to measure the conductance of a single molecule not only offers a new way to approach many interesting and fundamental problems in nanometer-scale science, but is also a necessary step towards the goal of building devices using single molecules. In order to measure single-molecule conductance, a molecular junction with a single molecule wired up to probe electrodes has to be fabricated. It is also essential to be able to efficiently and precisely control electron transport through such molecular junctions and understand the details of the factors that affect the transport before such devices can be made practical. SPM (STM & CAFM) based break junction (SPM-BJ) methods combing the imaging and measuring capabilities offer excellent capabilities to investigate single molecules transport properties through single molecule imaging and a complete control the junction by a series of modulation modes. This talk will focus on 1) introducing the SPM-BJ experimental platform for detailed junction modulation and control and 2) three exemplary research results obtained using the platform: molecule-electrode contacts issues, DNA structural effects on its conductance, and photo-electronic transport via exciton binding.

4:00 PM EL10.11.03
Demonstration of Terahertz Molecular Switches Imen Hnid[1], Ali Yassin[2], David Guérin[1], Lionel Sanguinet[2], Philippe Blanchard[2], Imane Arbouch[3], Colin Van Dyck[4], Jerome N. Cornil[3], Stephane Lenfant[1] and Dominique Vuillaume[1]; [1]IEMN-CNRS, France; [2]MOLTECH-Anjou, France; [3]Laboratory for Chemistry of Novel Materials, University of Mons, Belgium; [4]Laboratory for Theoretical Chemical Physics, University of Mons, Belgium

We study the electron transport properties under a terahertz (THz) irradiation of three molecules that consist of two conjugated systems, which are coupled through a non-conjugated linker. Due to this non-conjugation between them, each molecule can be seen as two weakly coupled sites in series and a resonant transport occurs only when the energy of the two sites are aligned leading to negative differential resistance (NDR) behaviors[1]. Moreover, it has been theoretically suggested that switching in such systems, between different current states in transport through molecules, is possible and may be triggered by a passing electromagnetic pulse in the THz range[2]. This mechanism relies on a THz-induced resonant electron transfer between the pair of neighboring subunits. As a consequence, the energy of the two sites are misaligned and therefore, the passage of current is turned off by the irradiation pulse and the NDR behaviors are eliminated.

Three molecules that differ by the spacer (phenyl vs. thiophene) and the anchor group (thiol vs. cyanide) were synthesized and corresponding SAMs were formed on very flat template-stripped gold electrodes (RMS<0.5nm). Solid-state molecular junctions (MJs), in which a C-AFM (Conducting-Atomic Force Microscopy) Pt/Ir tip is used as the top electrode, were formed. The electronic properties of the resulting MJs were investigated under an in-situ THz irradiation (30THz), and will be presented for the three molecules.

When the THZ irradiation is OFF, NDR behaviors at the nanoscale (for few tens of molecules) were observed with an unprecedented large peak-to-valley ratios (up to ca. 500 compared to ca. 15 in the MCBJ experiments[1]). To gain more insight into the origin of the NDR effect, we also investigated these molecules using density functional theory (DFT) and the non-equilibrium Green's function formalism (NEGF). The calculations reproduced well the observed experimental NDR behavior, which is explained by breaking the degeneracy of the HOMO and HOMO-1 levels under the effect of the applied voltage.

When the Thz irradiation is ON, the junction is immediately switched and the NDR behaviors are completely suppressed. These phenomena were reproducibly and reversibly observed for all three molecular junctions, whatever the nature of the spacer and anchoring group, and will be presented and discussed.

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We acknowledge J.F. Lampin for the loan of the 30 THz laser and help with its set-up. Financial support by ANR (project EVOLMONET, #ANR-20-CE30-0002).

SESSION EL10.12: Virtual Session I: Molecular Electronics
Session Chairs: Christian Nijhuis and Damien Thompson
Tuesday Morning, April 25, 2023
EL10-virtual

8:00 AM *EL10.12.02
Generic Dynamic Molecular Devices by non-Steady State Proton Coupled Electron Transport Kinetics Xi Yu[1] and Lejia Wang[2]; [1]Tianjin University, China; [2]Ningbo University of Technology, China

Molecular devices operating at a non-steady state with time and history-dependent performance raised new challenges for the fundamental study of microscopic non-steady state charge transport dynamics, as well as functionalities that are not achievable by steady state devices. In this study, we reported a generic dynamic operation mode of molecular devices by addressing the transient redox state of ubiquitous quinone molecules by proton/water transfer. The diffusion limited slow proton transfer modulated fast electron transport, leading to a non-steady state transport process, as manifested by the negative differential conductance (NDR), dynamic hysteresis, and memory-like behavior. A theoretical model was further developed, which, combing transient state characterization, quantitatively revealed the non-steady state charge transport kinetics and the principle of the dynamic behavior of the device. At applying pulse stimulation, the dynamic device emulated the neuron synaptic response with frequency dependent depression and facilitation, implying a great potential for future non-linear and brain-inspired devices.

8:30 AM *EL10.12.03
Electrical Driven Hot Carriers Generation and Light Emission in Molecular-Scale Plasmonic Junctions Longji Cui; University of Colorado Boulder, United States

Molecular scale plasmonic nanojunctions have attrached much interests recent years as they have great potential to create the smallest on-chip light sources and sensitive photodetectors. It is crucial to understand the role of electrically generated hot carriers in these structures at the size limit of light matter interaction. This talk will present a series of our recent work and provide both experimental and theoretical insights into this topic. In particular, I will present our observation of above-threshold light emission from plasmonic tunnel junctions and our model that describes electrically driven hot carrier generation and enhanced light emission mechanisms. Further, I will present our recent experiments on tuning light emission crossovers, from below-threshold, coherent multielectron tunneling, to hot carrier enhanced light emission. These results demonstrate rich physics that can be obtained from plasmonic nanojunctions and electrically driven hot carrier geneation in these nanosystems, crucial to numerous future applications.

9:00 AM *EL10.12.04
Single-Molecule Reaction Dynamics Xuefeng Guo; Peking University, United States

This talk will exemplify our on-going interest and great effort in developing efficient lithographic methodologies capable of creating molecular electronic devices through the combination of top-down micro/nanofabrication with bottom-up molecular assembly. These devices use nanogapped carbon nanomaterials (such as single-walled carbon nanotubes (SWCNTs) and graphene) as point contacts formed by electron beam lithography and precise oxygen plasma etching. Through robust amide linkages, functional molecular bridges terminated with diamine moieties are covalently wired into the carboxylic acid-functionalized nanogaps to form stable carbon electrode-molecule junctions with desired functionalities. We have used these approaches to build functional devices that switch their molecular conductance upon exposure to external stimuli, such as ion, pH and light, and realize label-free, real-time electrical detection of chemical reactions at the single-event level for revealing their intrinsic mechanisms towards precise chemistry.
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SESSION EL10.13: Virtual Session II
Session Chairs: C. Frisbie, Christian Nijhuis, Damien Thompson and Herre van der Zant
Tuesday Morning, April 25, 2023
EL10-virtual

10:30 AM *EL10.13.01
Enabling Long-Distance Singlet-Fission, Charge and Triplet-Exciton Transport via Molecular Bridges Spiros Skourtis; University of Cyprus, Cyprus

We discuss three examples of bridge-mediated transport processes where transport is analyzed in terms of dominant pathways and of important intermediate states. The first example relates to recent experiments of very-long-distance DNA charge transport where pathways that do not involve DNA-base states seem to play an important role [1]. The second example relates to recent experiments of bridge-mediated singlet-fission and triplet-exciton separation rates that observe a bridge-resonance enhancement of singlet fission [2]. The third is a proposal for building molecular wires that support very-long-distance coherent triplet-exciton transport that is robust to static and dynamic disorder [3].

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11:00 AM EL10.13.02
Designing of a “Perfect” Porphyrin Molecule for the Mechanically Controllable Break Junction Experiments Diana Dulic; FCFM, Universidad de Chile, Chile

The biggest challenge of molecular electronics is to condense the functionality of an electronic device into a single molecule and to exploit the functional versatility offered by the chemical diversity of molecules for electronic device purposes.
Porphyrins and their related macrocycles are promising building blocks for the construction of bio-inspired molecular devices. Nature itself offers magnificent examples of porphyrin's usefulness, such as activating and transporting molecular oxygen in mammals and harnessing sunlight in plant photosynthetic systems.
In spite of their potential, obtaining well-defined single-molecule conductance features is a difficult task. Due to π-stacking porphyrins can form a variety of junction configurations, leading to a large spread in conductance values using the mechanically controllable break junctions (MCBJ) technique. This limits further progress in investigating the molecular functionalities on a single molecule level in porphyrin molecules.
In this presentation, I will show that by close interaction between synthetic chemists and physicists a “perfect” porphyrin molecular design for mechanically controllable break junctions can be achieved, leading to well-defined, highly conducting molecular junctions. This opens further prospects for “porphyronics” – porphyrin-based molecular electronics.

11:15 AM EL10.13.03
Spin-Dependent Charge Transport in Single Chiral-Molecule Junctions Anil K. Singh[1], Kévin Martin[2], Maurizio Mastropasqua Talamo[2], Narcis avarvari[2] and Oren Tal[1]; [1]Weizmann Institute of Science, Israel; [2]University of Angers, France

The experimental observation that electrons transferred through a chiral molecule favors a particular electronic spin orientation is known as the chiral-induced spin selectivity (CISS) effect. This effect has been extensively studied both experimentally and theoretically. However, the mechanism of this effect is still not fully understood. Here, we report on spin filtering by molecular junctions based on a single pi-conjugated chiral molecule suspended between a nickel electrode and a non-ferromagnetic electrode. The effect depends on the molecule chirality, applied voltage polarity, and the non-ferromagnetic metal type. We ascribe our observations to the CISS effect at the quantum coherent transport regime and discuss the influence of the electrode properties on the CISS effect.

11:30 AM *EL10.13.04
Quantum Interference Beyond Single-Molecule Transport Gemma C. Solomon; University of Copenhagen, Denmark

Over the last ten years, there has been a growing interest in quantum interference effects observed in molecules. Remarkably, given their fragility in mesoscopic physics, quantum interference effects can be readily observed in molecules at room temperature in solution. This robustness comes from the extremely small size of the molecular components (1-2nm) and thereby the small dimensions over which phase coherence is required. In this talk I outline our efforts to explore molecular quantum interference effects beyond single molecules and to use these effects for more than simply switching current on/off.
Firstly, I will outline our efforts to understand quantum interference beyond single molecules by studying clusters of molecules and monolayers of varying density. These studies indicate that current suppression at low bias due to destructive quantum interference may be either more or less pronounced for the same molecule, depending on whether the measurement is made on a single molecule or a monolayer.
Secondly, I will outline our efforts exploring the potential for molecules exhibiting destructive quantum interference effects to be employed as dielectric materials, for example as gate dielectrics in organic transistors. Our initial studies show that it is possible to increase the dielectric constant of the monolayer, while maintaining low levels of current, but challenges remain in developing chemical insight as to how best to tune these properties.

12:00 PM EL10.09.03
Self-Assembled Monolayers of Alkylselenolates on Gold with Lifetime Over Two Hundred Days Ningyue Chen and Yuan Li; Tsinghua University, China

Self-assembled monolayers (SAMs), based on thiol-metal chemistry, are widely investigated in multiple fields such as optics, biochemistry and organic electronics due to their simplicity, repeatability and controllability. The thiol-based SAMs, however, go no further than laboratory studies due to their weak property against oxidation. Therefore, it is necessary to pursuit an alternative anchoring group, which is expected to form similar supramolecular structure as thiol-SAMs and meanwhile, possesses air-stability with long lifetime. Here, we proposed diselenide as an advantageous candidate since selenium has similar properties as sulfur which enables it to be a promising precursor for well-ordered SAMs. By spectroscopy and tunnelling current, we demonstrated the chemisorbed and densely packed selenium-SAMs has, indeed, been fabricated. Notably, when we stored the selenium-SAMs in ambient condition, they own rigorously long-lifetime in ambient conditions over 200 days by the reason of the strong selenium-gold bond. We surveyed the stability of selenium-SAMs by the observations of a minor fluctuations of tunnelling current and the value of decay coefficient through SAMs as a function of days. Additionally, spectroscopy provides detailed structural characterization as the oxidation is much slow with selenium-gold bond and there was nearly no desorption of alkylselenolates during this process. Finally, we performed DFT calculations and the results illustrate the stronger binding energy and weaker affinity to oxygen of selenium-SAMs compared with thiol-SAMs, leading to the merely impossibility of peroxidation of selenium-gold bond.

12:15 PM EL10.09.04
A Conductive Ionogel Top-electrode for SAM-based Junctions Conducted in Liquid Environment Xiyue Bai and Yuan Li; Tsinghua University, China

Study of the charge transport through molecules in liquid environment is important for understanding the fundamental of complicated system such as electrochemistry, catalytic reaction, and biological activities in physiological environment. In this work, we designed a flexible and conductive top-electrode composed of ionic liquid and carbon powder wrapped with polymers (we call it ionogel-carbon black electrode, in short IG-CB) to form top-contact on a self-assembled monolayer (SAM) on Ag or Au bottom-electrode, at environmental conditions of solid states, pure water or other liquid. This IG-CB electrode is capable of measuring charge transport through SAMs of alkanethiolates with long stability and high reproducibility. We tested molecules with different hydrophilicity and lipophilicity in air, polar and non-polar solvent to discover the mechanism of electron tunneling in liquid environment. IG-CB electrode can reflect more molecular information and interfacial interaction compared to EGaIn due to the ability of IG-CB electrode to produce stable traces in different environments. The greatest advantage of IG-CB electrode is the tunability of chemical properties, which cannot be achieved by other top-electrodes. We demonstrated that the current density is highly dependent on both the hydrophobicity of the electrode and SAMs. One of the reasons for the correspondence is mainly from the mutual effect between the surface dipole of SAMs and polarity of the solvent.
Next we fabricated samples with the monolayer of proteins (three kinds of proteins with different numbers of heme groups inside) supported by SAM. The junction measurements show activationless behaviors of three proteins when they are in solid states, but, when the junctions immersed in pure water they become temperature dependent. We found that it requires about 100−120 meV for electrons passing through one heme group inside a hydrated protein molecule for the first time. We also show that the threshold voltage for heme group to be oxidized is −0.6 V in our system, and below that it is likely only involving reorganization of surrounding dipoles in water. Therefore, we provide a new approach to study the role of water in electron flowing through SAM in liquid environment, the mechanism of charge tunneling in proteins and could promote the study in electron transfer, enzymatic reaction and etc.

SYMPOSIUM

April 11 - April 27, 2023

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SESSION EL11.01: OLED Device I
Session Chairs: Jun Yeob Lee, Jian Li, Lin Song Li and Biwu Ma
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3024

10:30 AM *EL11.01.01
The Long Path to Long Lifetime Deep Blue Phosphorescent OLEDs Stephen R. Forrest and Haonan Zhao; University of Michigan, United States

Perhaps the single most important problem confronting the development of OLED displays and lighting today is how to achieve sufficiently long triplet-controlled emission device lifetime to prevent rapid color change during operation, while achieving 100% internal emission efficiency. It has been shown[1] that bimolecular (e.g. triplet-polaron, triplet-triplet) annihilation provides a source of energy sufficient to destroy the blue triplet chromophore (whether a phosphor or a TADF molecule) or its host. Since that time, many materials, structures and strategies to extend blue emission lifetime based on this understanding have been demonstrated. Furthermore, various molecular fragments have been identified whose presence leads to the observed luminance loss. Unfortunately, a fully satisfactory solution has not been shown where blue triplet emitter lifetime is sufficient to meet the standards of high performance displays, although white OLED illumination sources may now have adequate lifetime to meet industry standards. In this talk I will discuss progress in extending blue phosphorescent OLED (PHOLED) lifetime, and in understanding of the limitations to extending the lifetime of blue triplet emitters. In particular, I will focus on the relationship between radiative state lifetime, exciton density, and the longevity of the PHOLED. I will review efforts to shorten the radiative lifetime via emitter design and optical cavity engineering. Prospects for future advances will be discussed.

"Intrinsic luminance loss in phosphorescent small-molecule organic light emitting devices due to bimolecular annihilation reactions". N.C. Giebink, B.W. D'Andrade, M.S. Weaver, P.B. Mackenzie, J.J. Brown, M.E. Thompson, and S.R. Forrest, *J. Appl. Phys*., **103**, 044509 (2008).

11:00 AM *EL11.01.02
Addressing Fundamental Limits to Blue OLED Stability Marc Baldo; Massachusetts Institute of Technology, United States

Phosphorescence and triplet-triplet annihilation are two of the leading approaches to realizing more efficient and stable blue organic light emitting devices. To address the stability of blue phosphorescence, we modulate the exciton lifetime of the emitters without drastically decreasing the light extraction efficiency using plasmonic light extraction structures. The results are compared to all-optical studies suggesting very strong dependence of OLED stability on excitonic lifetime.

Increasing the fraction of singlet excitons generated from triplet-triplet annihilation (TTA) remains the major challenge confronting applications of solid-state excitonic upconversion in OLEDs. We will describe two recent efforts addressing this problem. First, we investigate rapid intersystem crossing (ISC) of high energy triplets (T_2) to the desired singlet state (S_1). Generating more singlet excitons is expected to improve efficiencies, but this approach comes with a tradeoff. Rapid ISC can exacerbate losses due to faster relaxation of the original triplet states (T_1) back to the ground state (S_0), as well as faster relaxation of $T_2 \rightarrow T_1$. We describe the computational design and experimental characterization of new TTA materials with predicted ISC rates more than three orders of magnitude faster than ISC in the classic material 9,10-diphenylanthracene (DPA). Experimentally, we find that the upconversion efficiency *doubles* in the limit of large enhancements in ISC, confirming that tuning the $T_2 \rightarrow S_1$ ISC rate can indeed provide a strategy for the systematic improvement of TTA materials, and demonstrating promising new materials for applications. Second, we show that the tailorability and highly porous, but ordered structure of metal-organic frameworks (MOFs) combine to minimize inter-triplet exchange coupling and engineer effective spin mixing between singlet and quintet triplet-triplet pair states. We demonstrate singlet-quintet coupling in a pyrene-based MOF, NU-1000. An anomalous magnetic field effect is observed from NU-1000 corresponding to an induced resonance between singlet and quintet states that yields an increased fusion rate at room temperature under a relatively low applied magnetic field of 0.14 T. Our results suggest that MOFs offer particular promise for engineering the spin dynamics of multi-excitonic processes and improving their upconversion performance.

11:30 AM EL11.01.03
The Role of Emissive Layer Spontaneous Orientation Polarization in Charge Accumulation and Exciton Quenching in Phosphorescent OLEDs
Evgeny Pakhomenko and Russell J. Holmes; University of Minnesota, United States

Many common organic semiconductor materials employed as active layers in organic light-emitting devices (OLEDs) possess an appreciable permanent dipole moment that can preferentially align forming a bound polarization charge, a phenomenon known as spontaneous orientation polarization (SOP). Intrinsic polarization of the film alters the device internal electric field, resulting in charge accumulation even at voltages below the turn-on. The presence of this additional charge impacts OLED efficiency and lifetime, with prior findings demonstrating a ~20% reduction in peak efficiency and a threefold reduction in lifetime when the SOP is present in the electron transport layer (ETL). While these findings highlight the impact of polar transport layer on OLED performance, the role of SOP in the emissive layer has not been considered in detail. Here, we demonstrate the significance of emissive layer SOP by systematically probing the polaron accumulation and exciton-polaron quenching in green phosphorescent OLEDs with various polar hosts. A comparative analysis of displacement current measurements (DCM) reveals that the presence of SOP in the host alters the accumulated charge distribution, with the majority of the charges still residing in the device emissive layer. By probing the emitter photoluminescence during device operation, the amount of exciton-polaron quenching is found to be compatible to the OLEDs with polar ETLs, and kinetic modeling of this phenomenon reveals additional details on the location of the accumulated charges. Finally, we implement a method to tune the location of accumulation and thus the amount of quenching by introducing an energy barrier at one of the active layer interfaces. This study improves the current understanding of how SOP impacts OLED performance by studying the exciton-polaron quenching induced by emissive layer SOP and developing means to manipulate the accumulated charge location to tune this quenching.

11:45 AM EL11.01.04
Engineering Polarization-Induced Quenching in Organic Light-Emitting Devices via Thin Film Processing Conditions Siliang He, Evgeny Pakhomenko and Russell J. Holmes; University of Minnesota Twin Cities, United States

Due to structural asymmetry, some molecules actively used as the electron transport layer (ETL) in organic light-emitting devices (OLEDs) have appreciable permanent dipole moments (PDMs). Preferential molecular orientation can lead to PDM alignment and net polarization, a phenomenon known as spontaneous orientation polarization (SOP). Prior work has shown that SOP leads to a macroscopic surface potential that can induce significant charge accumulation in an OLED. Accumulated charge densities can be large enough to quench excitons, significantly limiting peak device efficiency. Varying film processing conditions, like substrate temperature and deposition rate, have been previously shown to impact molecular orientation and SOP. In this work, OLED performance is enhanced by suppressing SOP-induced exciton-polaron quenching via an appropriate choice of processing conditions. More importantly, the impact of temperature and deposition rate are unified in a single framework that quantitatively considers the vapor-deposited film as a supercooled glass. The impact of varying relative temperature and deposition rate are understood as means to frustrate the ability of molecules in the film to relax to an equilibrium, isotropic configuration. This unification offers a useful and generalized approach to engineering the impact of SOP on OLEDs via variations in processing conditions.

SESSION EL11.02: OLED Materials I
Session Chairs: Jun Yeob Lee, Jian Li, Lin Song Li and Biwu Ma
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3024

1:30 PM *EL11.02.01
Blue Phosphorescent OLED Stability Study Jason Brooks; Universal Display Corporation, United States

Today organic light-emitting devices (OLEDs) are used in billions of displays generating $38 billion in annual revenue in 2021. In 1986 the demonstration of an efficient planar heterojunction device (1) started OLEDs on a path to commercialization. Further efficiency improvements were realized by utilizing a fluorescent guest and host emissive layer (EML) system (2). The internal quantum efficiency (IQE) of these early fluorescent OLEDs was limited to approximately 25% as triplet excitons cannot emit radiatively in these materials. In contrast, in a phosphorescent OLED (PHOLED) system, first demonstrated in 1998, all the singlet excited state excitons are converted into the triplet excited state through inter-system crossing (S_1 to T_1) via the presence of a heavy metal atom (3).
Red and green PHOLEDS, pioneered by Universal Display Corporation (UDC), have been used in commercial OLED applications for several years now, however the device lifetime of high efficiency blue has until recently been a challenge. Here we will present a case study on a series of blue emitting imidazo-phenanthridine benzimidazole iridium (III) complexes, where an aromatic carbon is replaced with nitrogen on the ligand resulting in a dramatic blue shift in emission. The effect on device stability was probed by substituting aryl and alkyl groups on the ligand in close proximity to the nitrogen lone pair. Further modifications required to improve sublimation for the preparation of vacuum deposited devices through the use of ancillary ligands will also be described. Our results show that device stability is highly dependent on the type of substituent near the nitrogen, indicative of its reactivity in device operation.

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Baldo, M., A., O'Brien, D. F., You, Y., Shoustikov, A., Sibley, S., Thompson, M. E., Forrest, S. F., *Nature*, 395 (6698), 151–154 (1998).

2:00 PM EL11.02.03
Blue Emitting Square Planar Metal Complexes for Displays and Lighting Applications Jian Li; Arizona State University, United States

The successful development of efficient and stable molecular blue emissive materials will have a significant impact on the continued deployment of organic light emitting diodes (OLEDs) technology for display and lighting applications. Moreover, the successful development of alternate low cost technology for current solid state lighting devices will have a significant impact on the U. S. economy and national security. In this presentation, we will discuss our continuing efforts on the design, synthesis and characterization of novel platinum and palladium complexes for displays and lighting applications. The photo-physics, electrochemistry, electroluminescent properties and operational stability of these novel metal complexes, including deep blue narrowband emitters and amber emitting phosphorescent molecular aggregates, will be discussed.

2:45 PM BREAK

SESSION EL11.03: OLED Materials II
Session Chairs: Jun Yeob Lee, Jian Li, Lin Song Li and Biwu Ma
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3024

3:15 PM *EL11.03.01
OLEDs – Beyond Displays Franky So; North Carolina State University, United States

In contrast to inorganic light emitting diodes (LEDs) which require epitaxial growth on single crystal wafers, organic LEDs (OLEDs) can be fabricated virtually on any substrates without size limitation. When OLEDs are made on flexible substrates, they can be made very thin to replace conventional liquid crystal displays. Because of the form factor and flexibility, they can be used in applications which cannot be realized by conventional LCDs. Today, OLED technology has been developed to the point that it has become a mainstream display technology for mobile devices as well as televisions. In addition to displays, OLEDs are also being considered for lighting and sensing applications. In this presentation, we will describe the challenges and opportunities in OLED lighting. We will also present the opportunities in different imaging applications using OLEDs.

3:45 PM *EL11.03.02
Electrophosphorescence Generated from Ir(III) Carbene Phosphors and Respective Hyperluminescence Yun Chi; City University of Hong Kong, Hong Kong

Organic light-emitting diode (OLED) is considered as one most promising technology to facilitate visual communication in the form of monitors and wearable and head-mounted display devices. Therefore, much efforts have been devoted in improving their performances and, as the result, better and more reliable materials, particularly the emitters, have been developed in both academic and industrial sectors. Among the emissive materials, Ir(III) metal complexes have been recognized for their remarkable stability and efficient green and red luminescence and, nowadays, they have been employed as an integral component of commercially viable OLED devices. However, much less progresses have been made on the respective blue emitters. This shortfall prompted more research on both the blue emissive transition-metal based phosphors for future advancement of OLED technology.

In general, the Ir(III) metal atom is capable to promote the facile intersystem crossing facilitated by spin-orbit coupling, allowing full utilization of both the electro-generated singlet and triplet excitons. There are two possible class of Ir(III) complexes suitable for making the demanded blue phosphors. One involves functional cyclometalating chelates linked to N-donor fragment such as pyridine, pyrazole or imidazole, in the form of either the homoleptic or heteroleptic derivatives Ir(C^N)$_3$ and Ir(C^N)$_2$(L^X), C^N = N-containing aromatics and L^X = anionic ancillary. The alternative designs contain the Ir(III) complexes with N-aryl carbene cyclometalates which can be represented by the generalized formula *m*-Ir(C^C)$_3$ and *f*-Ir(C^C)$_3$, where *m*- and *f*-indicated the meridional and facial coordination arrangements, respectively.

Recently, we reported the successful preparation of several class of homoleptic Ir(III) carbene complexes and employed the same for fabrication of blue OLED devices. Their emission peak max. occurred in the region between 420 to 500 nm in solution state at RT. We believed that they are capable to display the genuine true-blue emission hue and to serve as the chosen blue emitter and sensitizer (or donor) in fabrication of phosphorescent and hyperluminescent OLED devices. Now, this task has been partially accomplished, to which the corresponding syntheses and applications will be discussed in this presentation.

4:15 PM EL11.03.03
Design and Synthesis of Asymmetric Au(III) Complexes Exhibiting Bright Anisotropic Emission for High-Performance Organic Light-Emitting Diodes Hsin-Hung Kuo[1,2], Sudhir Kumar[1], Rashen Lou Omongos[3], Marc E. Usteri[1], Michael Wörle[4], Daniel Escudero[3] and Chih-Jen Shih[1]; [1]ETH Zurich, Switzerland; [2]University of Cambridge, United Kingdom; [3]KU Leuven, Belgium; [4]ETH Zürich, Switzerland

Organic light-emitting diodes (OLEDs) are emerging as one of the most promising candidates for next-generation optoelectronics. However, most commercial OLEDs are based on rare-metal organometallic emitters, which bring challenges towards sustainable technology. Recent development of earth-abundant gold complexes has drawn a lot of attention, whereas the device efficiencies remain lower than the rare-metal counterparts. Here, we present rational molecular design of a series of Au(III) organometallic complexes consisting of asymmetric C^C^N ligands and carbazole moieties functionalized by phenyl or mesityl groups. The synthesized complexes exhibit shortened radiative lifetimes, and reach improved photoluminescence quantum yield, η_{PL}, of greater than 93% in thin films. Moreover, the asymmetric molecular design induces anisotropic emission with a high ratio of horizontally oriented transition dipole moment of up to 82% in host-guest films. Our computational results corrborated our experiemtnal data. It suggested that the asymmetric motifs of emitters give rise to pertubation in eletrostatic potential distribution. As a result, our chemically asymmetrical Au(III) complexes orient horizontally in bipolar host, 26DCzPPy, enchancing light out-coupling efficiency. Accordingly, we demonstrate high-performance OLED devices with record-high external quantum efficiencies, η_{ext}, and current efficiencies, η_{CE}, of up to 27% and 89 cd A^{-1}, respectively. We believe that the molecular design of anisotropic Au(III) emitters will be greatly facilitated by the fundamental principles and theoretical analysis presented here.

4:30 PM EL11.03.04
Planar Chirality Enables Narrow Bandgap Conjugated Polymers with Red Circularly Polarized Luminescence Teodora Moiseanu[1], Rituparno Chowdhury[1], Juan Manuel Moreno Naranjo[2], Larissa Hogenhout[1], Robert Phipps[1], Matthew J. Fuchter[2], Richard Friend[1] and Hugo Bronstein[1,1]; [1]University of Cambridge, United Kingdom; [2]Imperial College London, United Kingdom

Materials with chiroptical properties have garnered interest in the field of optoelectronics due to their applications in circularly polarized (CP)-OLEDs, sensing, spintronics, optical quantum information, and many others. Chiral small molecules have been investigated, however they typically display very low dissymmetry factors on the order of 10^{-3}. The potential of supramolecular structures such as conjugated polymers to self-assemble presents an opportunity for much stronger chiroptical properties.

Previous work on chiral conjugated polymers has been restricted to wide bandgap materials due to a focus on chiral side chain polyfluorenes and weakly conjugated polymers. There is a lack of narrow band gap conjugated polymers with strong chiral emission within the field.

Here it is demonstrated that planar chirality holds the potential to obtain chiroptical behaviour alongside the strong main-chain conjugation essential to obtain narrow bandgap polymers. A series of polymers were investigated, endowed with planar chirality from paracyclophane moieties. Polymers with emission across the visible spectrum were assessed for their chiral response in solution and thin-film by circular dichroism (CD), and chiral photoluminescence (CPL). The novel materials display high dissymmetry factors, with g_{abs} reaching 0.1 in film for fluorene-based copolymers, and g_{lum} reaching 0.08 for thiophene-based copolymers. To the best of our knowledge, these are the highest values recorded for CD and CPL for planar chiral polymers with main-chain conjugation, to date, with strong potential to be applied in CP-OLEDs.

4:45 PM EL11.03.05
High-Performance Saturated-blue OLEDs Employing [3+2+1] Iridium Complexes as the Phosphorescent Sensitizer Chengcheng Wu[1,2] and Guodan Wei[1,2]; [1]Tsinghua-Berkeley Shenzhen Institute (TBSI), Tsinghua University, China; [2]Institute of Materials Research, Tsinghua Shenzhen International Graduate School, Tsinghua University,, China

By introducing the trimethylsiliyl (TMS) groups on the 2′,6′-difluoro-2,3′-bipyridine (dfpypy) main ligand, two promising [3+2+1] coordinated saturated-blue emitting iridium complexes are designed and synthesis to investigate their structural, photophysical and electrochemical properties. The existence of the inter/intramolecular interactions (C-F···H/C-N···H) are considering as an effective path to accelerate energy transfer and improve the photoluminescence quantum yield (PLQY) of the luminescent materials. Both the complex **B-4-TMS** and **B-5-TMS** functionalized the TMS on dfpypy ligand exhibited PLQY close to 90%, and the vibronic emission peak at 443/465 nm with rapid decay down to 0.36 μs in toluene solution, emerging high radiative decay (k_r) of up to 2.5×10^6 s^{-1}. The phosphorescent OLEDs based on the two phosphors exhibited the maximum external quantum efficiency (EQE$_{max}$) of 25.49% for device A, 27.77% for device B, respectively. To boost the color quality and efficiency, the hyper-OLEDs employing the two iridium complexes to sensitize the terminal emitter of *v*-DABNA are achieved in terms of the efficiency as high as 33.01% with the full width at half maximum (FWHM) of 17 nm and the CIEy values down to 0.123 as well as the LT_{50} close to 5000 h at an L_0 of 100 cd m^{-2}, demonstrating the mechanism of Förster resonance energy transfer (FRET) process. Such results which have been the among the highest efficiency reported for phosphor sensitized saturated-blue hyper-OLEDs.

SESSION EL11.04: OLED Optics I
Session Chairs: Jun Yeob Lee, Jian Li and Lin Song Li
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3024

8:30 AM *EL11.04.01
Efficient and High-Brightness Microcavity OLEDs—Overcoming Angular Color-Shifts Through Strong Light-Matter Coupling and Monolithic Integration of OLEDs for Minimally Invasive Brain Implants Malte C. Gather[1,2]; [1]University of St. Andrews, United Kingdom; [2]University of Cologne, Germany

With ever more stringent color requirements in the display industry (such as BT.2100) and the requirement for monochromatic emission in many emerging applications of OLEDs (such as fluorescence-based sensing), there is a growing need for OLEDs with narrow-band, saturated-color emission. While the peak emission wavelength of OLEDs can be adjusted via chemical modification of the emissive material, it has proven challenging to design emitters with extremely narrowband luminescence spectra. Micro-cavity OLEDs by contrast offer narrowband emission but show an intrinsic and often substantial and undesired change in spectrum and color with observation angle.

Here, we overcome these limitations by combining the concept of microcavity interference with the angle independent light absorption/emission of molecules in an efficient and synergistic manner. By introducing an assistant absorber layer into a microcavity OLED, we create a strongly coupled hybrid light-matter state (i.e., an exciton polariton) that inherits the angle insensitivity of molecular absorption and the narrow linewidth of the cavity mode. This new device architecture enables efficient OLEDs with angle-independent, narrowband emission (EQE >10%, FWHM <20nm, angle shift <10nm @60° tilt).

Besides the display industry, the unique properties of OLEDs – in particular their ability to monolithically integrate with a wide range of substrate materials – lend themselves favorably for next generation bioimplants that provide targeted and minimally invasive light delivery deep in living tissue. This is of particular interest for neuroscience, where the recently developed method of optogenetics has enabled new ways of studying neuronal networks. However, the delivery of light to the cells of interest in animal models remains an open challenge. We show how integration of high-brightness microcavity OLEDs on needle-shaped CMOS chips allows controlled light delivery through a minimally invasive implant with 1024 individually addressable pixels, each with a size comparable to a single neuron.

9:00 AM EL11.04.02
Highly Efficient Top-Emission Organic Light-Emitting Diodes Based on Ampicillin Micro-Structure Donghyun Kim, Changmin Lee, Amjad Islam, Geonwoo Jeong, Dong Hyun Choi, Tae Wook Kim, Sye Hamad Ullah Shah, Hyun Woo Jo, Yeong Beom Kim, MinJae Park, Keum-Jin Ko and Seung Yoon Ryu; Korea University, Korea (the Republic of)

The effort to enhance the efficiency of organic light-emitting devices (OLEDs) has led to the improvement of advanced materials with multiple advantages property. Herein, we present the robust contribution of a widely used antibiotic; ampicillin (Amp) in optoelectronics. The optimum fusion of Amp with poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) considerably improved the device efficiency of a single-unit green phosphorescent OLED. The addition of 25% Amp in PEDOT:PSS provided a horizontal interfacial dipole. The dipole suppressed the hole injection by lowering the work function of the anode and improved the charge balance. Moreover, the parallel arrangement of molecules facilitated the generation of J-aggregations which contributed additional/extra excitons to the device. Additionally, to decrease the deviation in the efficiency and stability of Amp based OLEDs, we reinforced the microcavity effect through the top-emission OLED (TEOLED) structure and optimized the annealing conditions. Amp microstructures (Amp-MSs) of various sizes and shapes (α-/β-phase) are induced due to the increase of annealing temperature annealing temperature, time, and pH level, which led to different degenerated energy states and improved device stability. Amp-MSs induce photoluminescence (PL) and electroluminescence (EL). Additionally, Amp-MSs can adjust the charge-balance by Fermi-level (E_F) alignment, thereby decreasing the leakage current and Amp-PEDOT:PSS layer prevented In diffusion. Moreover, the Amp-MSs triggered light scattering through diffuse reflectance, as indicated by angle-resolved reflectance and optical simulations. Therefore, the wave-guided modes were significantly reduced. It can enhance the light-outcoupling through optical-scattering. As a result, it is suggested that high efficiency can be obtained by using carrier harvesting and photon harvesting through electroluminescence, photoluminescence and light scattering based on Amp-MSs. The TEOLED demonstrates an extraordinarily high current efficiency (CE) (maximum ~ 281.3 cdA^{-1} and average ~ 264.3 cdA^{-1}) and EQE (maximum ~ 68.7% and average ~ 63.4%) with a wide color gamut (~118%). The color coordinates were compensated owing to the extension of the spectrum by the Amp-MS (red-shifted by J-aggregated excitons). Moreover, the deconvoluted EL spectra systematically revealed each contribution of Amp-MS in the device EQE enhancement. These findings are expected to enable the development of high-performance optoelectronic/bioelectronic devices.

9:15 AM EL11.04.03
Using the Microcavity Effect to Understand the Light-Emitting Electrochemical Cell Joan Ràfols-Ribé, Xiaoying Zhang, Christian Larsen and Ludvig Edman; Umeå University, Sweden

The thin-film and planar architecture of electroluminescent devices such as the light-emitting electrochemical cell (LEC) and the organic light-emitting diodes (OLED) make them highly sensitive to microcavity effects. In OLEDs, the microcavity can be carefully designed to maximize the light outcoupling by fabricating a multilayered stack with the emission layer at its optical maximum position. In LECs, however, this microcavity control is more challenging due to its in situ formation of an emissive p-n junction by electrochemical doping upon an applied voltage. Here, we take advantage of microcavity effects to extract relevant parameters of a polymer-based LEC. First, we show that it is possible to shift the emissive p-n junction to a preferred position by the straightforward inclusion of an easily tuned additive in the active material. [1] Second, we show that the position of the emissive p-n junction shifts with time during LEC operation. Third, we discuss how the width and the dipole orientation of the emissive p-n junction can be determined and tracked over time with a “dark” device. Finally, we discuss how these results can be utilized to better understand the physics behind the LEC operation and to improve the device performance.

References
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9:30 AM EL11.04.04
Singlet Oxygen Production by OLED Irradiation in Photodynamic Therapy Assay Using Metallic Nanoparticles Rafael d. Carvalho, Aline M. dos Santos, Arthur R. Barreto, João Paulo C. do Carmo, Tomás B. Duarte, Mariana G. dos Santos, Guilherme C. Concas, Tahir Jan, Tommaso Del Rosso and Marco Cremona; Pontifical Catholic University of Rio de Janeiro, Brazil

Nanotechnology is considered one of the key technologies for the future. One of the most strategic subjects of the century is the research on nanostructured materials for the development of new electronic devices towards to a more advanced society. Nanostructured materials can present both physics and chemical properties completely different from either solids or microscopic materials. Therefore, the capability of manipulation and control of such materials represents an actual challenge to the scientific and technological community. Furthermore, in the last few years, phototherapy have been calling attention due to recent development in scientific research that involves interactions of an incident photon over a chromophore present in a biological environment. Here stands out the photodynamic therapy (PDT) mechanism as a growing field of application of phototherapies with high relevance. Noble metal nanoparticles (NPs), such as AuNPs and AgNPs, plays an important role in the future of photomedicine experiments based on PDT, due to the concentration of light caused by the Localized Surface Plasmon Resonance (LSPR), and low citotoxicity. In particular, some metal oxide NPs synthesized by pulsed laser ablation (PLA) in water, can also produce via *water splitting* H_2 and O_2 gas phase that could enhance the free oxygen content. The PDT mechanism is non-invasive treatment for surface lesions, such as human skin, which uses visible light to excite a photosensitizer (PS), which is a photosensitive drug. The PS molecule in its ground state (S0) can absorb a photon and pass to its excited state (Sn) and, through vibrational and internal conversion processes, pass to the singlet excited state (S1). Furthermore, the PS molecule can go from the S1 state to the triplet excited state, via intersystem crossing. This triplet state has at least two reaction mechanisms known as type I and type II. Both mechanisms generate ROS and the production of singlet oxygen (type II mechanism) is the most relevant in treatments involving photodynamic therapy. In the absence of the irradiation light, the photosensitizer is non-toxic. The oxygen produced is reactive and can destroy nearby cells such as bacteria, fungi, and tumor cells. In a PDT treatment, the incident light must be within the therapeutic window, approximately between 600 nm and 1000 nm, which allows penetration of human tissue into deeper regions, between 5 mm and 20 mm, avoiding invasive treatments. In this work, we investigate the production of singlet oxygen using a PDT assay platform based on organic light-emitting diode (OLEDs), as light source with emission in the therapeutic windows, seeking applications in biological environments. The PDT assay consists of monitoring, as a function of time, the absorption spectra of a solution (phosphate buffer) with a photosensitizer, NPs, and a probe molecule. With the incidence of light in the range of the therapeutic window, PS can produce singlet oxygen modifying the probe while NPs can increase this effect. The influence of *water splitting* mechanism in the singlet oxygen consumed by the probe molecule is also investigated. Thus, it's possible to indirectly access information on the amount of singlet oxygen produced by OLED irradiation as well as on the efficiency of the PDT assay. Here we investigate the production of singlet oxygen dependence on: (i) the concentrations of different PS used; (ii) concentration and size of AuNPs and AgNPs and other metal-oxide NPs; (iii) the concentration of probe molecule; and (iv) the emitted light (wavelength and light power) of the OLEDs with different emissions.

9:45 AM EL11.04.05
High-Resolution Imaging and Statistical Analysis of Clustering in Phosphorescent OLED Materials Roland A. Bennett[1], Paul Niyonkuru[1], Michael Zachman[2] and Jeramy D. Zimmerman[1]; [1]Colorado School of Mines, United States; [2]Oak Ridge National Laboratory, United States

Since the early days of OLED research, emissive properties have indicated that guest clustering likely occurs in certain systems, but very few direct measurements of guest morphology have been published for vacuum-thermal-evaporation based OLED devices.

Here, we report on morphology measurement performed using atom probe tomography (APT)[1] and high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) imaging of conventional phosphorescent guests (e.g., Ir(ppy)$_3$ and Ir(ppy)$_2$(acac)) in various host materials. The morphology measurements are analyzed using spatial statistical analyses, such as Ripley's K-function and G-function, and compared against statistical simulations of morphology to identify various aspects of morphology.[2-4]

We will present direct evidence for vertical stacking of guest molecules during growth, as well as variations in guest density over 5-10 nm scales in certain systems, and discuss principles governing these morphologies, bringing insight into long-standing questions surrounding morphology in nominally amorphous phosphorescent OLED systems.

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10:00 AM BREAK

SESSION EL11.05: OLED Optics II
Session Chairs: Jun Yeob Lee, Jian Li and Lin Song Li
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3024

10:30 AM *EL11.05.01
Development of Deuteration Technology to Improve Lifetime of OLED EX and Identification of Stability of Deuterated Materials Ji-Ho Baek; LG Display Co., Ltd., Korea (the Republic of)

LG Display has recently completed the development of 'EX Technology' and is focusing on technological innovation. EX Technology, which consists of deuterium technology and presonalization algorithms, increases screen brightness (luminace) by 30% compared to existing OLEDs and reproduces natural colors more precisely.In this paper, we will explain the effect of improving the lifetime of OLED products through the developement of deuterium technology and the mechanism for the degradation phenomenon of deuterated materials. With substituting C-D bond for C-H bond, Isotope species show electrochemical stability, which leads to increasing device lifetime.

11:00 AM EL11.05.03
Strategies for High-Efficiency Simple Fluorescent Emitters in OLEDs Le Yang; Institute of Materials Research and Engineering, Singapore

For functionally viable single-colour organic light emitting diodes (OLEDs), we advocate that that they must satisfy three criteria: efficiency, lifetime, and colour (sharpness, gamut). The significant advances over the past decade has seen materials and device systems such as TADF take off, along with the earlier phosphorescent emitters – they have easily overcome the efficiency inadequacy of OLEDs. However, they often tend to have less decent stability and colour sharpness. First generation simple fluorescent emitters tend to have, in general, better lifetimes and emission sharpness, but they are severely limited by their internal quantum efficiencies of 25%, due to spin-statistics. In this talk, we would like to share and explore two main strategies in overcoming the efficiency bottleneck in these simple fluorescent OLEDs, to make them a competitive candidate in display tech. First we look at a dual-dopant system, lifting rubrene-derivative based OLEDs to unprecedented >20% external quantum efficiency.[1,2] Next, we look at single-dopant devices, in triplet fusion mechanism, by drawing parallels to (optically-excited and two-dopant) triplet-triplet annihilation upconversion, and how to enhance device efficiency ceiling.[3,4]

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2. Di, D., Romanov AS, Yang, L, *et al.* High-performance light-emitting diodes based on carbene-metal-amides. *Science.* **356**, 159–163 (2017).
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11:15 AM EL11.05.04
Predicting Photoluminescence Properties of OLEDs for High Throughput Screening Felix Therrien[1,1], Alexander Davis[1,1], Suhas Mahesh[1], Jeffrey Cheung[1], Brandon Sutherland[1], Eli Zysman-Colman[2], Edward H. Sargent[1] and Oleksandr Voznyy[1]; [1]University of Toronto, Canada; [2]University of St Andrews, United Kingdom

Widespread adoption of organic light emitting diodes (OLEDs) displays is hindered by the short operational lifetime of blue emitters in comparison to red and green ones despite their high energy efficiency, color contrast and the possibility for flexible and transparent displays. The discovery of new photoluminescent molecules that emit in the 450-465~nm range can be accelerated by high throughput screening (HTPS) and matter modeling. However, existing first principle prediction models have only been applied to a limited number of specific systems and are not suitable for HTPS. In this article, we develop a systematic methodology to predict wavelengths and photoluminescence quantum efficiency (PLQY) from first principle for any blue-green irridium complexes using density functional theory. We validate our predictions on a set of 450 molecules for which in-solution emission wavelengths and PLQY have been reported in literature. We show that our methodology is sufficiently versatile, efficient and accurate to be utilized on large amounts of data and suitable for large scale data generation for machine learning training.

SESSION EL11.06: QD-LED I
Session Chairs: Jun Yeob Lee, Jian Li and Lin Song Li
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3024

1:30 PM *EL11.06.01
Blue Emissive Light Emitting Diodes Using ZnO-Graphene Oxide (GO) and ZnO-Polyaromatic Hydrocarbons Hybrid Quantum Dots Won Kook Choi[1,2] and Hong Hee Kim[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]University of Science and Technology, Korea (the Republic of)

A self-emissive electroluminescent quantum dots (ELQDs) LED display is highly expected as a next generation flexible display. are highly demanded for achieving eco-friendly ELQDs. Ecofriendly ZnO semiconductors has a band gap of 3.37 eV and large exciton binding energy (~60 meV) at RT and thus expected to be good candidates for non-harmful Cd and inexpensive In-free blue QDs. ZnO QDs are hybridized with graphene oxide QDs (GO) [1] and functionalized poly-aromatic hydrocarbonds (f-PAHs) [2] to control the intrinsic defects located on ZnO surfaces causing green emission. From time-resolved PL (TRPL) for ZnO and ZnO-GO QDs reveals that conventional green emission of ZnO QDs has a longer lifetime by 10^3 times than ~ns of blue emission and disappear by hybridization with GO. Type I ZnO-GO QLEDs show deep-blue electroluminescence (EL) at 438 nm, brightness of 1980 cd m^{-2}, and an external quantum efficiency (EQE) of 2.78% with CIE (0.16, 0.11) without green emission. In a similar way, quasi type II ZnO/1-aminopyrene hybrid QDs-based QLEDs show EL of 3379 cd m^{-2} at $\lambda = 441$ nm with a full width at half maximum of 41.7 nm, a luminous efficacy (LE) of 3.32 cd/A, EQE of 2.35%, and remarkably long lifetime T_{50} of >17830 h at 100 cd/m^2.

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2:00 PM EL11.06.03
Efficient Short-Wave Infrared Light-Emitting Diodes based on Heavy-Metal-Free Quantum Dots Li Jun Lim and Zhi Kuang Tan; National University of Singapore, Singapore

Short-wave infrared (SWIR) light emission is important for a diverse range of modern applications, such as eye-safe depth sensing, light detection and ranging (LiDAR), facial recognition, eye tracking, optical communication, and health-monitoring technologies. However, there are a very limited number of known semiconductors that can emit efficiently in the SWIR spectral range. Presently, SWIR light-emitting diodes (LEDs) based on colloidal quantum dots (CQD) are dominated by lead chalcogenide systems (PbS and PbSe CQDs), despite the presence of heavy metal and modest efficiencies (~8%). Here, we report highly efficient SWIR LEDs based on heavy-metal-free In(Zn)As-In(Zn)P-GaP-ZnS core-shell CQDs. The shell layers were judiciously chosen to possess decreasing lattice constant which allowed the lattice strain caused by mismatch to be gradually relaxed across the core–shell structure and was crucial in passivating surface traps in the In(Zn)As core which resulted in a constant increase in the PLQE from 2% to 10%, 30%, and 73% upon the growth of the In(Zn)P, GaP, and ZnS shells, respectively.

Using solution processing methods, an indium–tin oxide (ITO)/zinc oxide (ZnO)/ poly(9-vinylcarbazole) (PVK)/polyethylenimine ethoxylated (PEIE)/CQDs/poly(N,N′-bis-4-butylphenyl-N,N′-bisphenyl)benzidine (poly-TPD)/molybdenum trioxide (MoO_3)/silver (Ag) electroluminescent device was also fabricated using the synthesized CQDs. The implementation of an otherwise hole-transporting PVK layer on the electron-injecting side of the device stack led to a surprising enhancement in device performance, giving high external quantum efficiencies (EQE) of 13.3% at long emission wavelengths of 1006 nm. Single-carrier device and optical investigations reveal the origins of enhancement to be the electronic decoupling of the CQD layer with the electron-injecting ZnO layer, which mitigated luminescence quenching and improved charge balance. This work marks one of the highest efficiencies reported for heavy-metal-free solution-processed LEDs in the SWIR spectral region (>1000 nm), and could find significant applications in emerging consumer electronic technologies.

2:45 PM BREAK

SESSION EL11.07: QD-LED II
Session Chairs: Jun Yeob Lee, Jian Li and Lin Song Li
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3024

3:15 PM *EL11.07.01
Quantum Dot Light Emitting Diodes for Next Generation Display Zhuo Chen, Yanzhao Li, Dong Li, Yuanming Zhang, Jingwen Feng, Yang Gao, Haowei Wang and Xiaoyuan Zhang; BOE Technology Group Co Ltd, China

Display is the central window for people to get information, while people's demanding for high quality display is never ending. As a type of semiconducting nanoparticles, quantum dots have unique advantages such as tunable emission with sizes, narrow emission, high stability, etc. Quantum dot light emitting diodes (QLED) is one of the most competitive technologies for next generation display. In this presentation, I will introduce the research and progress in the field of QLED in BOE Technology Group.
(1) Inkjet Printing
Inkjet printing is a drop-on-demand technique for pixelated patterning, which has maximal material utilization in theory. The ink stability, the quality of ink droplet, the accuracy of IJP equipment, as well as the morphology of printed film are the key factors in the IJP process. Via inkjet printing process, we have successfully fabricated 55-inch 4K and 8K AMQLED TV demos, whose color gamut reaches 119% NTSC and the contrast ratios are higher than 1,000,000:1.
(2) Sacrificial Layer Assisted Photolithography
To achieve higher pixel density, photolithography technique is considered to prepare the high resolution quantum dot patterns. Quantum dot damage, interfacial contamination, color mixing from residues of other colors and other factors should be considered in quantum dot photolithography. We developed a sacrificial layer assisted patterning (SLAP) technique. In this approach, in order to protect the quantum dot layer and QD/ET interface during the photolithography process, we introduced a sacrificial layer to isolate QD layer and photoresist. We achieved a 500 PPI R/G/B full-color device via the SLAP approach, in which the subpixels are without color impurity and color gamut reaches 114% NTSC.

3:45 PM EL11.07.02
Ecofriendly Solvent for Green QD-LED Fabrication Jang-Kun Song and Hyo-Bin Kim; Sungkyunkwan University, Korea (the Republic of)

Quantum-dot light emitting diode (QDLED) displays have been attracted great attention because of their high potential as a future display technology. The color performance and theoretical quantum efficiency of QDLEDs far exceed those of OLEDs, and solution processability is also regarded as an important advantage for low-cost manufacturing capabilities. However, the use of toxic and environmentally hazardous organic solvents is the dark side of solution processable QDLEDs. Chlorobenzene, chloroform, 1-4 dioxane, and 1,2-dichlorobenzene are representative toxic solvents for the manufacture of QDLEDs, and these are mainly used as solvents in the hole transport layer (HTL). For example, chlorobenzene is known as a solvent with long-term toxic effects on human causing dizziness and neurasthenia, central nervous system disease and renal degeneration, and also affects aquatic life if it enters rivers and seas. Therefore, it is important to find an environmentally friendly solvent for (HTL), but to date, this has not been studied. In this presentation, we report a new methodology for finding solvents that are environmentally friendly, have good processability, and have solvent orthogonality with adjacent layers. Using the proposed methodology, which is designed based on Hansen solubility parameters (HSPs) and solvent selection guidelines (SSGs), an alternative green solvent for HTL was found and an all-solution processed eco-friendly QDLED device was fabricated. The HTL layer fabricated using the green solvent exhibits lower roughness and does not have interlayer mixing; as a result, the device shows superior electro-optical performance compared to the reference device using chlorobenzene solvent. Thus, the new solvent selection method can provide a green solution for future QDLED displays.

4:00 PM EL11.07.03
Deterministic Quantum Light Arrays from Giant Silica-Shelled Quantum Dots Hao A. Nguyen and Brandi Cossairt; University of Washington, United States

Colloidal quantum dot (QD) single-photon sources are important for their applications in photonic quantum information technologies. To fully realize their potential applications, scalable deterministic placement of stable single QD emitters is required. In this work, we synthetically increase the QD size via silica encapsulation to facilitate deterministic positioning of single QDs into large arrays while maintaining their photostability and single-photon emission properties. By using different integration methods including template-assisted self-assembly and inkjet printing, giant silica-shelled QDs can be precisely positioned into order arrays with high yield. Finally, second order photon correlation measurements are used to confirm their single-photon emission. This work shows that giant silica-shelled QDs are a flexible class of materials that may be compatible with other device fabrication techniques to achieve deterministic single particle positioning in complex quantum photonic platforms.

4:15 PM EL11.07.04
Electrical Doping of Colloidal Semiconductor Nanocrystals—Electron-Only-Device & Hole-Only-Device Hakjune Lee[1], Jaemin Lim[2], Doyoon Shin[2], Seongbin Im[2], Wan Ki Bae[2] and Jong Ah Chae[2]; [1]Seoul National University, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of)

Auger recombination, whereby exciton recombination energy is transferred to a third carrier instead converted to a photon, in colloidal semiconductor

quantum dots (QDs) have complicated to accomplish high-performance optoelectrical applications. For analyzing dynamics of QDs inside applications, previous studies have primarily focused on bi-exciton states and negatively charged exciton states, whereas positively charged exciton states are hardly investigated due to difficulties in adding and stabilizing extra holes in QDs.
Herein, we demonstrate electronic systems, electron-only-device (EOD) and hole-only-device (HOD), injecting extra carriers to QDs and analyze auger lifetime spectroscopy in chorus with electrical characteristics. This method adds extra carriers to CdSe/CdS heterostructured QDs whose multi-carrier states are well studied for long time, so exhibits the key spectroscopic signatures including development of fast decay, 1S bleach, auger quenching of photoluminescence (PL), and PL spectra shift. We assign dynamics to three distinct states of different lifetimes attributed to single exciton, energy transfer to metal, and charged exciton respectively, and the expected PL intensities from the lifetime accord precisely with measured PL intensities. Additionally, these spectroscopic and electronic changes are recovered totally, just discharged without any bias. Out method offers a universal tool of creating multicarrier states of QDs in a non-destructive manner and opens a new prospect in analyzing positively charged trion in veil before.

4:30 PM EL11.07.05
Nondestructive Photopatterning of Quantum Dots via Ligand Crosslinking Moon Sung Kang; Sogang University, Korea (the Republic of)

Electroluminescence from quantum dots (QDs) is a suitable photon source for futuristic displays offering hyper-realistic images with free-form factors. Accordingly, a nondestructive and scalable process capable of rendering multicolored QD patterns on a scale of several micrometers needs to be established. In this talk, two different nondestructive direct photopatterning methods for QDs are introduced, both of which exploit crosslinking reaction between the ligands of neighboring QDs. The first method exploits an additive that can crosslink with native aliphatic QD ligands. This additive is referred to as light-driven ligand crosslinker (LiXers) [1]. Specifically, we employ LiXers in branched structure containing multiple azide units [2]. The branched LiXers effectively interlock heavy-metal-free QD films via photocrosslinking native aliphatic QD surface ligands without compromising the intrinsic optoelectronic properties of QDs. Using branched LiXers with six sterically engineered azide units, we achieved RGB QD patterns on the micrometer scale. The photocrosslinking process did not affect the photoluminescence and electroluminescence characteristics of QDs and extended the device lifetime. Alternatively, QD ligands by themselves containing a photocrosslinkable moiety (that can also directly crosslink with native aliphatic ligands of neighboring QDs) can be anchored onto QD surface [3]. Specifically, photocrosslinkable ligands (PXLs) based on benzophenone derivative are exploited. The use of PXL permits employing a secondary ligand system (which is referred to as dispersing ligand, DL) that is devised to control the solubility of QDs to solvent. Based on a dual-ligand passivation system comprising PXL and DLs, we demonstrate that QDs can be direct patterned on various substrates using commercialized photolithography (i-line) or inkjet printing systems without compromising the optical properties of the QDs or the optoelectronic performance of the device. Our approaches offer versatile ways of creating various structures of luminescent QDs in a cost-effective and non-destructive manner. This could be implemented in nearly all commercial photonics applications where QDs are used.

SESSION EL11.08: Perovskite-LED I
Session Chairs: Jun Yeob Lee, Jian Li, Lin Song Li and Biwu Ma
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3024

8:30 AM *EL11.08.01
Two Distinct Populations of QDs in QD-LEDs Vladimir Bulovic; Massachusetts Institute of Technology, United States

Electroluminescence of a colloidal quantum dot LED (QD-LED) originates from an electrically-excited thin QD film within it, which is just few QD layers in thickness. We show that within this QD film two distinct populations of QDs are formed, as manifested by their distinct responses to optical and electrical excitations. Our measurements are done on thin films of InP/ZnSe/ZnS (core/shell/shell) QDs on glass substrates and on forward and reverse biased QD-LEDs. We show that the nano-scale morphology of the QD layer can affect the QD-LED operation.

9:00 AM *EL11.08.02
Perovskite Nanocrystal Emitters for Efficient, Bright, and Stable Light-Emitting Diodes Tae-Woo Lee; Seoul National University, Korea (the Republic of)

Metal halide perovskites (MHPs) are attracting great attention as promising next-generation light emitters because of their high color purity (FWHM ~ 20 nm) and low process cost. Although a lot of strategies have been reported, electroluminescence efficiency and stability of MHP still lag behind existing light-emitting diodes (LED). In this talk, advantages and strategies for the realization of efficient, bright, and stable PeLEDs will be delivered.
First, we report a comprehensive material strategy for the suppression of defect states in colloidal perovskite nanocrystal (PNC). Doping of guanidinium (GA^+) cation with additional hydrogen bonding compared with formamidinium (FA^+) into formamidinium lead bromide ($FAPbBr_3$) PNCs yields limited bulk solubility while creating an entropy-stabilized phase in the PNCs and leading to smaller PNCs with more carrier confinement. Furthermore, a PNCs surface-stabilizing bromine-based small molecule, 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (TBTB), was applied as a halide vacancy healing agent. In addition, by applying the modified-bar coating method, we fabricated large-area devices which have similar efficiency with small-area devices made by the spin-coating method. Through these strategies, highly efficient large-area perovskite light-emitting diodes were achieved.
Next, we developed core/shell structured perovskite nanocrystals obtained using the simple in situ reaction of organic shell additive with 3D polycrystalline perovskite films. Large 3D crystals are split into nanocrystals and the shell molecule surrounds the nanocrystals, achieving strong carrier confinement while maintaining good charge-transport properties of 3D perovskites. With efficient charge confinement and transport at the same time, we demonstrated simultaneously efficient, bright, and stable PeLEDs. Our work sheds great light on the possibility that PeLEDs can be commercialized in the future display industry.

9:30 AM EL11.08.03
Efficient and Stable Blue Light Emitting Diodes Based on Surface Passivated $CsPbBr_3$ Nanoplatelets He Liu, Michael Worku, Animesh Mondal, Tunde Shonde, Maya Chaaban, Azza B. Akacha, Sujin Lee, Fabiola Gonzalez, Oluwadara J. Olasupo, Xinsong Lin, J.S. Raaj V. Winfred, Yan Xin, Eric Lochner and Biwu Ma; Florida state university, United States

Metal halide perovskite nanocrystals (NCs) have emerged as highly promising light-emitting materials for various applications, ranging from perovskite light-emitting diodes (PeLEDs) to lasers and radiation detectors. While remarkable progress has been achieved in highly efficient and stable green, red, and infrared perovskite NCs, obtaining efficient and stable blue emitting perovskite NCs remains a great challenge. In this talk, I will present our recent efforts in the development of efficient and stable blue PeLEDs based on perovskite NCs. First, a facile synthetic approach for the preparation of blue emitting

$CsPbBr_3$ nanoplatelets (NPLs) will be introduced, in which treatment by an organic sulfate, 2,2-(ethylenedioxy) bis(ethylammonium) sulfate ($EDBESO_4$), significantly enhances the photoluminescence quantum efficiency (PLQE) and stability. Detailed structural characterizations reveal that $EDBESO_4$ treatment affords surface passivation of $CsPbBr_3$ NPLs by both $EDBE^{2+}$ and SO_4^{2-} ions, which helps to prevent the coalescence of NPLs and suppress the degradation of NPLs. A simple PeLED with emission peaked at 462 nm has been fabricated to exhibit an external quantum efficiency (EQE) of 1.77% with a luminance of 691 cd m^{-2} and a half-lifetime of 20 min, which is the brightest pure blue PeLEDs based on NPLs reported to date. Secondly, to further improve the device performance of PeLEDs based on $CsPbBr_3$ NPLs, we have introduced semiconducting organic salts, the triphenyl(9-phenyl-9H-carbazol-3-yl) phosphonium sulfate ($TPPcarz_2SO_4$) and triphenyl(9-phenyl-9H-carbazol-3-yl) phosphonium bromide (TPPcarzBr) as surface passivation agent for blue emitting $CsPbBr_3$ NPLs. The charge transporting phenylcarbazole unit in $TPPcarz_2SO_4$ and TPPcarzBr is found to improve the conductivity and energy alignment of surface passivated $CsPbBr_3$ NPLs when they are used as a light emitting layer. PeLEDs based on dual semiconducting organic passivated $CsPbBr_3$ NPLs have been fabricated to exhibit EQEs of up to 2.44% and a half-lifetime of 100 min, providing a novel and effective strategy to make high efficiency and long operating lifetime PeLEDs. Our work shows clearly the potential of using properly surface passivated perovskite NPLs as emitters for highly efficient and stable PeLEDs.

9:45 AM EL11.08.04
Progress in Lead-free Hybrid Organic-Inorganic Metal Halides for Optoelectronic Applications Jonathan E. Halpert, Yanyan Li and Zhicong Zhou; Hong Kong University of Science & Technology, Hong Kong

Lead-based perovskites have advanced tremendously over the last decade, producing solar cells with PCE > 24% and LEDs with EQE over 20 % for both red and green. However, the toxicity and instability of lead halide perovskites will likely limit their use in many instances. Here we have synthesized a novel class of copper-based micro- and nanomaterials that have high QY, up to 100%, and are long lived when packaged under nitrogen. We show recent improvements in copper-based self-trapped excitonic (STE) emitters, to produce highly luminescent, long lived emitters with red to near-IR emission peaks. In particular, we report alkali copper(I) iodide (ACuI)-based (A = Na, K, Rb, and Cs) organic-inorganic hybrid materials with different structures and emission peaks by adjustment of the alkali atoms and organic molecules. We can also substitute bromide and chloride for pure and mixed halides, such as red emissive lead-free hybrid organic-inorganic copper halides $A_6(C_4H_8OS)_{12}[Cu_8X_{13}][Cu_4X_4(OH)(H_2O)]$ (ACX-THTO, A = K, Rb, and Cs; X = Cl, Br; THTO = C_4H_8OS). These compounds possess strong photoluminescence with emission peaks in the range of 530-660 nm with a highest PLQY of nearly 100%. In addition to copper based compounds we examined one-dimensional (1D) $Na_3SbBr_6(C_2H_6OS)_6$ and $Na_3SbBr_6(C_4H_8OS)_6$ single crystals, which exhibit bright yellow and orange emission with PL peaks at 610 nm and 664 nm, respectively, and a high photoluminescence quantum yield (PLQY) of 86% was obtained for $Na_3SbBr_6(C_2H_6OS)_6$. These two compounds can be reversibly converted into each other by the removal and addition of the organic components. In general, the technique for producing hybrid organic inorganic copper halides can be extended to several members of the family, with increasing stability, in order to synthesize a wide array of emissive species, covering the visible spectrum. Green, yellow, and red down-conversion light emitting devices (LEDs) can be fabricated by using these materials, and a white LED based on all-copper iodide phosphors is demonstrated with a high color rendering index (CRI) of 93 by utilizing a mixture of blue-emissive $Cs_3Cu_2I_5$ and yellow-emissive $Rb_2Cu_2I_4(C_4H_8OS)_3$ powders. With high brightness and large absorption cross sections in the UV, these materials are ideal for white light arrays, and could be used as well in displays where visible wavelength transparency is more critical than color purity of emission.

10:00 AM BREAK

SESSION EL11.09: Perovskite-LED II
Session Chairs: Jun Yeob Lee, Jian Li, Lin Song Li and Biwu Ma
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3024

10:30 AM *EL11.09.01
Metal Halide Perovskite LEDs as Bright Thin Film Emitters Barry P. Rand; Princeton University, United States

Hybrid inorganic-organic lead halide perovskites have captured significant interest in the thin film optoelectronics community due to their impressive optical and electrical properties. For light emitting diodes (LEDs), our group is exploring their operation under very high current densities, for high-brightness applications, exploring whether they can operate at brightness akin to inorganic LEDs. We demonstrate high brightness, and show that Joule heating and voltage-induced electrochemical interface reactions present substantial challenges to these operating conditions for sustained periods of time.

11:00 AM *EL11.09.02
Suppressing Ion Interdiffusions in Halide Perovskite Devices Hanwei Gao and Brendon Jones; Florida State University, United States

Halide perovskites showed great potential for cost-effective optoelectronics. Low activation energy of ion migration, however, posed a challenge to implement viable devices with desirable lifetime. Not only were the ions mobile within the perovskite layer, they would also diffuse across heterogeneous interfaces in devices and degrade the charge transport layers and electrodes. In this work, we demonstrated that ultrathin, inorganic interlayers could suppress such interdiffusions without compromising the optoelectronic performance of the devices.

SESSION EL11.10: OLED Device II
Session Chairs: Jun Yeob Lee, Jian Li, Lin Song Li and Biwu Ma
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3024

1:30 PM *EL11.10.01
(carbene)M(amide) Complexes as TADF Emitters in OLEDs Mark E. Thompson[1], Jonas Schaab[1], Collin Muniz[1], Peter Djurovich[1], Haonan Zhou[2] and Stephen R. Forrest[2]; [1]University of Southern California, United States; [2]University of Michigan, United States

I will focus on the photophysical and electroluminescent properties of two-coordinate copper, silver and gold carbene complexes, *i.e.* (carbene)M^I(donor), where the carbene acts as an acceptor and the donor is an amide group. These complexes show high phosphorescence quantum yield (F_{PL} = 0.7 – 1.0), with radiative lifetimes in 0.2-3 ms regime, with emission lines spanning from the violet to red. The "tuning" of emission between violet and red involves careful manipulation of the carbene-acceptor and donor ligands to control the donor-acceptor energy difference. Binuclear analogs show a further increase in radiative rate. Cryogenic photophysical measurements show these complexes emit via thermally assisted delayed fluorescence (TADF) with properties rivaling the state-of-the-art iridium based phosphors. The high radiative rates are due predominantly to the small singlet-triplet energy gaps in these materials. Interestingly, these materials maintain a high radiative rage out of their singlet state, even with the small exchange energy that leads to the small singlet-triplet gap. This is not typically observed in organic TADF materials, which give very low singlet radiative rates. We have prepared organic LEDs with these dopants and achieved ~ 100% EL quantum efficiency for blue and green emissive OLEDs at comparatively low drive voltages. By careful ligand design we have achieved radiative lifetimes (carbene)M^I(donor) complexes as low as 250 ns, while maintaining a high F_{PL}. I will talk about our recent results of these fast phosphors in high efficiency OLEDs.

2:00 PM EL11.10.02
Achievement of Highly Efficient and Strong Emission of Eu(III) Complex in a Host-Guest Film by Triplet Sensitization Shiori Miyazaki[1], Kiyoshi Miyata[1], Kenichi Goushi[1], Yuichi Kitagawa[2,2], Yasuchika Hasegawa[2,2], Chihaya Adachi[1] and Ken Onda[1]; [1]Kyushu University, Japan; [2]Hokkaido University, Japan

Trivalent lanthanide (Ln(III)) materials are ideal for luminescence applications owing to their narrow-band emission and superior color purity. However, they suffer from the inherent drawback of the tiny absorption coefficient. To overcome their tiny absorption coefficient due to the forbidden f-f transitions, tremendous effort has been devoted to developing photoluminescent Ln(III) complexes using molecular technology focused on realizing efficient energy transfer from antenna ligands to Ln(III) as well as strong light absorption of the antenna ligands. However, the development of antenna ligands that can be used for sensitization is limited due to difficulties in controlling the coordination structures of lanthanides.
In this study, we overcame the challenge by a simple strategy using solution-processed host-guest films: host-molecule-based sensitization of trivalent europium (Eu(III)) via triplet exciton. When compared to conventional luminescent Eu(III) complexes, a system composed of mT2T (2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine) host molecules and $Eu(hfa)_3(TPPO)_2$ (hfa: hexafluoroacetylacetonato, TPPO: triphenylphosphine oxide) significantly increased overall photoluminescence intensity (I_{PL}). We achieved a 500-fold enhancement of the I_{PL} of an Eu(III) complex with a common ligand. Moreover, the combination realized sensitization from more than 40 host molecules per Eu(III).
To investigate the source of the relatively high I_{PL}, we used time-resolved photoluminescence spectroscopy (TR-PL) and femtosecond transient absorption spectroscopy (fs-TAS) in a multiscale temporal range from sub-picoseconds to hundreds of microseconds and investigated the emission mechanisms of the host-guest film. Beginning with the initial excitation of the host molecules and ending with the emission of the Eu(III) complex, we elucidated the mechanisms of all processes in the film: (1) the intersystem crossing (ISC) in the host molecule, (2) the inter-molecular energy transfer process from the host molecules to the ligands of the guest Eu(III) complex, (3) the intra-molecular energy transfer process from the ligands to Eu(III), and (4) the emission processes of f-f transitions in Eu(III). Furthermore, we discovered that the yields of all energy transfer processes, (1)-(3), are nearly unity and that the yield of the Eu(III) emission process (4) determines the overall quantum yield of the film. This highly efficient photoluminescence is attributed to the ideal triplet sensitization processes: rapid and efficient ISC in mT2T results in efficient triplet-triplet inter-molecular energy transfers with no loss. Finally, we propose clear design strategies for efficient light harvesting of Eu(III): the host-guest system with host molecules (1) which shows efficient ISC, and (2) whose triplet state energy matches that of the ligand of the Eu(III) complex.
Our discovery paves the way for efficient light harvesting of Eu(III) complexes with simple fabrication using a solution process.

2:15 PM EL11.10.03
Highly Crystalline Rubrene Light-Emitting Diodes with Epitaxial Growth Shu-Jen Wang, Anton Kirch, Hans Kleemann, Sebastian Reineke and Karl Leo; TU Dresden, Germany

Conventional organic optoelectronic devices suffer from low carrier mobility limited by static and dynamic disorder. Organic crystals with long-range order can circumvent the effects of disorder and significantly improve the charge transport. While highly ordered organic crystals offer the desirable electronic coupling strength and charge transport, their integration into large-area optoelectronic devices remains a challenge. Here, we introduce monolithic integrated triclinic crystal rubrene light-emitting diodes (LEDs) using epitaxial growth with functional additives being engineered into the films. We demonstrate superior charge transport, excellent operational and long-term stability in our light-emitting devices. By comparing two rubrene-based LEDs, one made from amorphous and one from crystalline rubrene layers, their exciton dynamics is analyzed by using comprehensive transient electroluminescence simulation. Finally, we provide an outlook on the potential applications of rubrene and/or its derivatives crystalline films for enhancing the performance of organic and hybrid optoelectronic devices as well as the prospect on extension of this fabrication process to other organic semiconductor materials.

SESSION EL11.11: Poster Session
Session Chairs: Jian Li and Lin Song Li
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL11.11.04
Enhanced Performance of Quantum Dot Light-Emitting Diodes Using Self-Assembled Monolayer Treated ZnO Taewoong Yoo and Jeonghun Kwak; Seoul National University, Korea (the Republic of)

Among various types of quantum dots (QDs), InP-based QDs are spotlighted as the emitting materials for commercial quantum dot light-emitting diodes (QLEDs) due to their environmentally benign features. However, the efficiency of InP-based QLEDs is restricted because the excess injection of electrons compared to that of holes can induce charge imbalance. In this study, self-assembled monolayers (SAMs) were treated on the ZnO electron transport layer (ETL) in order to form molecular dipoles and improve the charge balance. To investigate the effects of molecular dipoles on the device properties depending on the materials consisting of SAM, 4-methoxybenzoic acid (4-MBA) and 4-cyanobenzoic acid (4-CBA) having the opposite dipole moments are adopted. Compared to pristine ZnO, the valence band maximum (VBM) and the conduction band minimum (CBM) of 4-MBA coated ZnO were reduced by 0.1 eV. This resulted in the suppression of excess electrons and improvement in the charge balance. Furthermore, surface defects of ZnO which induce non-radiative recombination were passivated by the carboxyl group in the benzoic acid. As a result, our InP-based QLED with 4-MBA exhibits a maximum external quantum efficiency of 5.3%, which is 15% improvement compared with that of pristine device. The result implies that appropriate SAM treatment between the ETL and the EML is an effective method to optimize the charge balance of the QLED device.

5:00 PM EL11.11.05
The Magnetic Filed Effect of the Singlet Fission and Triplet-Triplet Annihilation Reactions in Polycrystalline Tetracene-Based Diodes Tzung-Fang Guo and Shi-Hong Lou; National Cheng Kung University, Taiwan

We characterize the magneto photocurrent (MPC) response in polycrystalline tetracene-based diodes and magneto photoluminescence of the tetracene film and attribute the initially decreasing and then increasing MPC responses to the feature of the singlet fission (SF) reaction. The SF reaction in polycrystalline tetracene active layer is more evident when the device was irradiated with the short wavelength of irradiation. This observation indicates a possible route to utilize the excess exciting energy for the generation of extra excited states (triplet) to contribute the higher photocurrent. Additionally, through the measurement of magneto electroluminescence of tetracene-based diodes operated under the forward bias regime, we are able to characterize the reaction of triplet-triplet annihilation (TTA) to singlet. The TTA process may harvest the energy from triplet to singlet excitons in tetracene active layer and in part contribute the emission to fluorescence especially in the high current density and low temperature regime.

5:00 PM EL11.11.06
Efficient, Color-stable and Long-lived White Organic Light-emitting Diode Utilizing Phosphorescent Molecular-Aggregates Aden S. Seeglitz, Jian Li, Lydia Ameri, Linyu Cao and Xinqiang Zhu; Arizona State University, United States

White organic light-emitting diodes have the potential to become the new form of solid-state lighting used in housing and commericial buildings. Highly efficient and stable single-stack hybrid white organic light-emitting diode (WOLED) devices are developed using two emissive layers, one with amber colored phosphorescent molecular aggregate emission from the Pd (II) complex, Pd(II) 7-(3-(pyridine-2-yl-κN)phenoxy-κC)(benzo-κC)([c]benzo[4,5]imidazo-κN)[1,2-a][1,5]naphthyridine, Pd3O8-Py5, and the other with blue fluorescence emission. An optimized device structure achieved high color stability under various current densities, an external quantum efficiency (EQE) of 45.5%, a power efficiency of 97.4 Lm W^{-1}, and an estimated LT$_{95}$ (operational time to 95% of the initial luminance) of 50,744 hours at an initial luminance of 1000 cd m^{-2}.

5:00 PM EL11.11.07
Ligand-Engineered Emissive Quantum Dots for Direct Patterning Jaemin Lim, Doyoon Shin, Dongju Jung, Hakjune Lee, Seongbin Im, Kahyung Kim and Wan Ki Bae; Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of)

Nanocrystal quantum dots (QDs) are a new class of luminophores that stand at the forefront of nearly all light-emitting applications. Specifically, QDs have become mainstream of display technologies, in which the combinations of primary colors realize images in response to electrical or optical excitation. The success of next-generation QD displays demands multicolor QD patterns on desired substrates over a large area with high-precision and high-definition, and most importantly, without compromising on optical or optoelectronic characteristics of QDs.

Previously, transfer printing, inkjet printing and photolithographic patterning have been suggested to realize such QD patterns, but only marginal success has been awarded. Transfer printing can only cover small area patterns, and standard instruments for its use have yet to be developed. Inkjet printing is effective only for low resolution patterns due to the limitation in the feature size of ejected drops, which in return constrains its use for high-definition QD patterns for near eye display applications (*i.e*, resolution > 3,000 ppi). Photolithography, for which the standard fabrication equipment and procedures are established, promises high-throughput, high-definition QD patterning over a large area. The only problem with conventional photolithography is the use of photoresists and photoinitiators, which deface the optical and electrical properties of QDs.

Here, we devise QD materials that can be processed *via* photolithographic processes without the presence of photoresists and photoinitiators. Specifically, we endow the essential functions for photocrosslink to the ligands that exist at the perimeter of QDs - the surface of QDs is functionalized with the photocrosslinkable ligands and the dispersing ligands. Photocrosslinkable ligands are photoreactive organic scaffolds that recruit structurally engineered benzophenone moieties whose sensitivity to UV-A improved by two orders of magnitude compared to unsubstituted benzophenone molecules. Consequently, even a short exposure time to UV-A irradiation confer the structural robustness to the QD films. Only a small fraction of photocrosslinkable ligand displacement (less than 10 mol%) is necessary for fully crosslinking, which in return leaves room for extending process compatibility with a range of solution-processing techniques by engineering the rest of the majority dispersing ligands. The success in controlling the structure of both ligands allows direct patterning of QDs *via* commercialized photolithography (*i*-line) without altering optical or optoelectronic characteristics of QDs. The advantages of the present approach are well represented by the high-definition QD patterns over a large area achieved by means of standard photolithography equipment (*i.e.*, pixel resolution for primary colors over 15,000 ppi on a 6-inch wafer).

5:00 PM EL11.11.08
Impact of Morphological Inhomogeneity on Excitonic States in ZnSeTe Quantum Dots Dongju Jung[1], Hakjune Lee[2], Doyoon Shin[1], Jaemin Lim[1], Seongbin Im[1], Jeongwoo Park[1] and Wan Ki Bae[1]; [1]Sungkyunkwan university, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)

Colloidal quantum dots (QDs) made of heavy metal free elements can have high quantum efficiency, tunable color, and narrow spectral linewidth, making them suitable for use as light sources. In a recent study, QDs with high luminous efficiency with a color range from purple to blue and cyan were synthesized using ZnSe$_{1-X}$Te$_X$ alloys. However, as the ratio of Te was increased to adjust the color toward the blue region, a sudden increase in linewidth occurred in all previous reports. The lack of understanding of its origin makes it difficult to fabricate blue ZnSe$_{1-X}$Te$_X$ QDs with narrow linewidth. In this study, temporally and spectrally resolved ensemble measurements and single dot measurements were performed on ZnSe$_{1-X}$Te$_X$ QDs with various Te ratios. Through this, it was possible to analyze inhomogeneous and homogeneous broadening which makes it possible to predict the existence of a new state caused by the influence of Te. And through density functional theory, it was found that a hole trap state can occur when two Te exist adjacent to each other in the crystal structure, and this is the reason of the sudden increase in linewidth. These results may suggest future research directions for making blue light-emitting sources through ZnSe$_{1-X}$Te$_X$ QDs.

5:00 PM EL11.11.09
Perovskite Quantum Dot Stabilization Using Molecular Sieves with Water-Selective Trapping Properties of Mesoporous Trap Dong Hwan Wang, Jin Young Kim, Woongsik Jang and Byung Gi Kim; Chung-Ang Univ, Korea (the Republic of)

Recently, lighting and display technologies require the search for materials that emit high-purity colors at high resolutions and realize vivid, natural colors. Quantum dots (QDs) are attracting attention as next-generation functional materials due to their superior color turnability and narrow band emission. Among them, perovskite QDs have been widely used due to their good optical and electronic properties, but still need to be discussed due to their structural issue [1]. In this research, a mesoporous material was introduced into a solvent to maximize the stability associated with surface defects in QDs using perovskite materials [2]. So far, the use of molecular sieves, which are mesoporous structural materials, has not been discussed to improve the efficiency and stability of QDs. For perovskite material, moisture and humidity control in the ambient environment and within the material is important [3].

Therefore, molecular sieves were introduced in the process of dissolving precursors to trap H_2O molecules before the synthesis of perovskite QDs. We used the split-ligand re-precipitation (S-LMRP) method for synthesis in the ambient environment, and tried to trap H_2O of dimethylformamide (DMF), which is the main solvent for dissolving the perovskite precursor and has a high hydration rate [4]. As a result, it was confirmed by FT-IR spectra analysis that H_2O molecules were declined in DMF, and it was also confirmed that H_2O was declined in the synthesized QDs using the dehydrated DMF. As a result of comparing the particle sizes of each, the dehydrated QDs were synthesized with slightly smaller sizes. This means that the ligand is better attached because the perovskite surface defects caused by HO are passivated. And, by removing H_2O through the molecular sieve, the quantum yield (QY) increased by about 14%. Additionally, the photoluminescence (PL) intensity stability of the perovskite QD solution and the stability of the surface on which the solution was coated to the film were confirmed. As a result, the PL intensity of the dehydrated QD solution was maintained at 83.7% after 50 days, but the pristine QD solution decreased by about 50%. In addition, cracks were observed only on the surface of the glass/pristine QD thin film after 30 days, which is caused by ligand separation of the QDs coated on the surface. Also, as a result of observing each surface through FE-SEM, it was confirmed that aggregation was significantly suppressed in the thin film coated with dehydrated QD. Thus, we provide that the efficiency and stability of QDs were able to greatly improved by a facile method.

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5:00 PM EL11.11.10
Silicone-Integrated Organic Light-Emitting Semiconductor for Ultrahigh-Density OLEDs Hyukmin Kweon[1], Keun-Yeong Choi[2], Ryungyu Lee[2], Ukjin Jeong[1], Min Jung Kim[3], Hyunmin Hong[3], Borina Ha[1], Jiyeon Ha[1], Hayoung Oh[1], Bokyung Kim[1], Sein Lee[4], Jang-Yeon Kwon[4], Kwun-bum Chung[3], Moon Sung Kang[5], Hojin Lee[2] and Do Hwan Kim[1]; [1]Hanyang University, Korea (the Republic of); [2]Soongsil University, Korea (the Republic of); [3]Dongguk University, Korea (the Republic of); [4]Yonsei University, Korea (the Republic of); [5]Sogang University, Korea (the Republic of)

Due to unprecedented color purity, thin form-factor, near-instant response time, and expanded color-gamut, organic light-emitting diodes (OLEDs) have a wide spectrum of application from commercialized displays to frontier displays like microdisplays. To successfully realize the broad range of the OLEDs technologies, a precise pixelation technique that can implement fine red/green/blue (RGB) pixels with high production and reliability regardless of the dimensional form factor of the display is strongly required. To this end, various patterning methodologies for OLEDs have been developed, such as fine metal masks, inkjet printing, orthogonal photolithography, template-directed growth, and photoresist-type organic semiconductors. However, these approaches suffer from restricted resolution (limited to below 1,000 pixel per inch, ppi), pattern reliability, and productivity issue. Alternatively, photolithography with reactive ion etching (RIE) can be the promising solution for well-defined high-resolution of OLEDs. This is because the RIE-coupled photolithography (RCP) process induce anisotropic etching profiles, so that well-defined patterns down to sub-micron scales are effortlessly obtained. However, organic light-emitting semiconductor (OLES) has low compatibility to the RCP process because it is intrinsically vulnerable to chemical and physical damages which are inevitably encountered during the photolithography and RIE processes, so that distortion of patterns and degradation of its luminance property are obtained. This indicates that it is a big challenging task in the OLEs to develop fine RGB pixels with photolithographic patterning process.
Here, to facilitate high-resolution OLEDs with the RCP process, inspired by etching nature of silicon, we demonstrate silicone-integrated OLES (SI-OLES) in which OLES is molecularly entangled with a ladder-like organosilica network. The SI-OLES showed high chemical and physical endurance, as well as, anisotropic etching behavior toward RCP process. The developed precise anisotropic etching profile of the SI-OLES is originated from in-situ formation of non-volatile etch-blocking layer during the RIE, which is analogous to RIE etching chemistry of silicon materials. On the basis of unique features of the SI-OLES, we demonstrated ultrahigh-density RGB OLES anisotropic patterns corresponding to 4,216 ppi (4,938,271 patterns/cm^2). Furthermore, the electroluminescence characteristics of SI-OLES-based OLEDs (SI-OLEDs) exhibited non-destructive even after pixilation by the RCP process. Consequently, full-color SI-OLEDs (949 ppi) was realized by the application of three cycles of consecutive RCP processes, indicating that our material design of the SI-OLES can contribute toward practical realization of well-defined micro-OLEDs.

5:00 PM EL11.11.12
Opto-Electronic Device Signatures and Sensing with Organic Molecule Exciton States Emily G. Bittle[1], Chad Cruz[1], Sebastian Engmann[2,1], Katelyn P. Goetz[1], David Gundlach[1], John Stephenson[1] and Jared Wahlstrand[1]; [1]National Institute of Standards and Technology, United States; [2]Theiss Research, United States

Many new molecular materials being developed to increase efficiency in organic light emitting diodes and photovoltaics (OLEDs and OPV) rely on exciton interconversion between singlet and triplet states. These high binding energy excitons, with tunable spin character, are also under investigation for applications in quantum information science and spin- based computation. While detailed information about interconversion processes is accessible to ultra-fast optical measurements, within opto-electronic (OE) devices a multitude of processes can overwhelm reliable signal related to exciton dynamics. Certain signature measurements, such has half bandgap turn on in OLEDs as an indicator of triplet fusion, have proved to be unreliable indicators of interconversion processes. In our projects, we work to connect the photophysics to OE device physics to uncover the relationship between exciton dynamics and device output. We demonstrate measurements and modelling of the spin dependent singlet fission process in magnetic field-dependent OE device measurements and corresponding ultra-fast photophysical measurements that show simple EO devices can be used to estimate the zero field splitting spin parameters and sense magnetic fields using exciton states in molecules. Recent results that connect the impact of varying the molecular packing on singlet fission dynamics and related changes to OE device output will be shown.

5:00 PM EL11.11.13
Integrated Substrate for Enhanced Outcoupling Efficiency in Organic Light-Emitting Diodes Mohammad Mehdi Zarei and Paul Leu; University of Pittsburgh, United States

Organic light-emitting diodes (OLEDs) exhibit advantages of wide viewing angle, high contrast ratio, low weight, and power consumption as well as flexibility for applications such as displays and solid state lighting. However, their low light extraction efficiency hampers their overall external quantum efficiency (EQE). OLEDs are also utilize ITO for a transparent electrode where ITO is costly and brittle. In this work, we demonstrate high transparency, high haze glass that may be fabricated via a simple, one-step reactive etching process to improve quantum efficiency. The glass provides for graded refractive index at the substrate/air interface and reduces substrate mode losses. Furthermore, we demonstrate a metal microgrid that may be utilized to replace indium tin oxide (ITO), which is a costly transparent electrode material. The metal microgrid has low index of refraction and may reduce waveguide mode losses. The transmission, haze, and sheet resistance properties of integrated substrates are correlated with OLED performance as characterized by EQE, current density-voltage, radiance-voltage, and EQE-current density. The results demonstrate a pathway to improving the performance of OLEDs as well as lowering their manufacturing costs.

5:00 PM EL11.11.14
Growth Control of II-VI Epilayer on III-V Nanocrystals Doyoon Shin, Hakjune Lee, Jaemin Lim, Dongju Jung, Seongbin Im and Wan Ki Bae; Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of)

III-V/II-VI core/shell heterostructured nanocrystals (*h*-NCs) are promising photonic materials for various light-emitting applications. The photophysical properties and stability of III-V/II-VI *h*-NCs and the performance of photonic applications are governed by the morphology that determine their optoelectronic properties and photochemical stability. However, unlike conventional *h*-NC synthesis system, III-V/II-V core/shell *h*-NCs has been relatively difficult because of hetrerovalent surface polarity.
Herein, we unveil the growth rate of each facet to make anisotropic growth. Specifically, we design III-V/II-V core/shell *h*-NCs that control the surface dependent growth. We conduct a comprehensive study across synthesis, spectroscopic analysis, and calculation to identify the growth mechanism and photophysical properties according to the shape. Following the guidelines for structure engineering, we discuss the impact of engineered structure and reveal optical and optoelectronic properties across III-V/II-V core/shell *h*-NCs.

5:00 PM EL11.11.16
Solution Processed ZnO-based Electron Injection Layer for Stable OLEDs Tianxin Li[1], Jian Li[1] and Lin Song Li[2]; [1]Arizona State University, United States; [2]Henan University, China

With the introduction of zinc oxide nanoparticles as the most preferred electron transport layer (ETL), solution-based light-emitting diodes (LEDs) technology was significantly improved because of high transparency, high electron mobility, and low production cost in ZnO and a favorable alignment of its energy bands. Using ZnO as the ETL, we have developed highly efficient and stable Pd(II) 7-(3-(pyridine-2-yl-κN)phenoxy-κC)(benzo-κC)([c]benzo[4,5]imidazo-κN)[1,2-a][1,5]naphthyridine (named Pd3O8-Py5) inverted inorganic-organic hybrid OLEDs. By applying ZnO in various device architectures, we carefully examined the electrical properties and explored how to optimize device performance. According to our studies, a Pd3O8-Py5-based OLED achieved a peak EQE of 23.9%, retained high EQEs of 23.5%, and 18.7% at 1,000 and 10, 000 cd m^{-2}. As a result of optical outcoupling enhancement, its peak EQE reached 48.6%. Furthermore, the device demonstrated outstanding operational stability with a measured LT_{90} of 207 h at 10,435 cd m^{-2}, which corresponds to an estimated LT_{90} of 11,180 h at 1,000 cd m^{-2}. It is expected that such hybrid inorganic-organic OLEDs will emerge as a potential competitor to conventional OLEDs, since they have intrinsically stable electrodes and can be partially solution-processed, resulting in low-cost, large-area, and shadow mark-free OLEDs for future display and lighting applications.

5:00 PM EL11.11.17
Photo-Crosslinking Hole Transport Layer for Solution Processed Quantum Dot Light-Emitting Diodes Seongjae Lee[1] and Moon Sung Kang[2]; [1]Seoul National University, Korea (the Republic of); [2]Sogang University, Korea (the Republic of)

Quantum dots (QDs) have recently attracted many researchers' interest as promising materials for lighting. Despite much progress in QD light-emitting diodes (QD-LEDs), the performance of environmental-friendly QD-LEDs still lags behind that of heavy metal-based devices. In addition, since QD-LEDs are multilayer devices, an effective method of minimizing the underlying layer erosion by subsequent solution process is required for solution-processed QD-LEDs, which is significant for the cost-effective manufacture of large-area QD displays. Here, we demonstrate high-performance solution-processed Indium phosphide (InP) QD-LEDs via photo-crosslinking of the hole transport layer (HTL) with an efficient photo-crosslinker. Photo-crosslinking of hole transport materials (TFB and PVK) using an azide-based crosslinker allows a robust HTL minimizing the damage that may occur when the QD emissive layer is deposited onto the HTL in the solution process. The solvent resistance of photo-crosslinked HTL enables fabricating high-performance green InP QD-LED through the solution process. Optimizing the photo-crosslinked TFB layer, the maximum current efficiency of crosslinked TFB-based QD-LEDs is improved by about five times compared to pristine TFB-based ones. Also to investigate the effect of photo-crosslinking on the electrical properties of HTL, we analyze pristine and crosslinked TFB based hole-only devices by using an orthogonal solvent. Furthermore, double HTLs in the conventional QD-LEDs are implemented through photo-crosslinking to reduce the hole injection barrier, resulting in efficient hole injection.

5:00 PM EL11.11.19
Performance Improvement of Quantum-Dot Light-Emitting Diodes Using Double-Layered Electron Transport Layer Yisu Kim and Jeonghun Kwak; Seoul National University, Korea (the Republic of)

Quantum-dot light-emitting diodes (QLEDs) are emerging as a next-generation display due to the excellent light-emitting properties of quantum dots (QDs). In QLEDs, ZnO or ZnMgO nanoparticles (NPs) are widely used as the materials for an electron transport layer (ETL) due to their high electron mobility and similar conduction band minimum (CBM) level with that of QD emissive layer (EML). However, these characteristics of ZnO ETL induce the spontaneous injection of excess electrons to the EML, causing a charge imbalance with holes. To solve this issue, in this study, ZnS/ZnMgO double-layered ETL is introduced into the inverted InP-based red QLEDs. Compared to previously reported organic interlayers to block excess electrons, ZnS ETL has chemical robustness and good processability. The synthesized ZnS NPs have a wider bandgap, with their CBM upshifted by 0.7 eV compared with that of ZnMgO NPs. This high CBM becomes an effective energy barrier, which can suppress the injection of excess electrons and improve the charge balance. Consequently, our red-emitting InP QLEDs with ZnS/ZnMgO double-layered ETL exhibit 1. 30-fold higher external quantum efficiency (EQE) and 1. 37-fold higher current efficiency (CE) compared to those of pristine devices. We believe that ZnS/ZnMgO double-layered ETL structure is a promising alternative to improve device efficiencies by controlling the charge balance.

5:00 PM EL11.11.20
Direct Photolithography of Perovskite Nanocrytstals via *i*-Line Ligand Crosslinking Yong Hyun Jo and Moon Sung Kang; Sogang University, Korea (the Republic of)

Perovskite nanocrystals (PeNCs) are promising materials for electroluminescence (EL) applications in display due to their high quantum yield, narrow emission line as well as low-cost, simple synthesis method. In fabricating EL devices, patterning of PeNCs is a crucial step that determines the resolution and color purity. While conventional photolithography using photoresist is the seemingly adequate patterning process to meet the industrial requirement, the polar solvents commonly used for processing the photoresist is detrimental to PeNCs with strong ionic characteristics. Herein, we demonstrate photoresist-free, direct photolithography of $CsPbX_3$ PeNCs using an *i*-line (365 nm) UV source. This is specifically achieved with aids of light-induced ligand crosslinker (LiXer) that forms chemical bonding with the ligands of neighboring PeNCs to interlock them. Because *i*-line UV was exploited, the photoluminescence (PL) characteristics of PeNCs could be fully preserved upon irradiation, which was not the case when using 254 nm-DUV source. The use of benign *i*-line UV source is critical not only that it permits patterning PeNCs non-destructively but also because the apparatus is most widely available in display industry.

5:00 PM EL11.11.21

Universal Low-Temperature Thermal Crosslinker for Photolithographic Lift-Off Ptterning of Solution-Processed Electronic Materials Chang Hyeok Lim[1], Myeongjae Lee[2], BongSoo Kim[3] and Moon Sung Kang[1]; [1]Sogang University, Korea (the Republic of); [2]Korea University, Korea (the Republic of); [3]Ulsan National Institute of Science and Technology, Korea (the Republic of)

Electronic materials containing moieties with good solubility to organic solvents (such as alkyl pendent groups in organic semiconductors or organic ligands on nanoparticles/nanocrystals) can exploited through cost-effective solution process in device manufacturing. However, the capability to solution-process these materials yields technical challenges in making patterns through photolithographic process available in industry, as the materials are likely to degrade during the process exposed to solvent (the solvent in photoresist or in developer). In this work, we propose photolithographic lift-off patterning applicable to various solution-processible materials (including light-emitting quantum dots, light-emitting polymer semiconductors, metallic nanoparticles) using a low-temperature crosslinker universally applicable to the materials without degrading the intrinsic electronic/optoelectronic properties. The crosslinker is designed to undergo direct crosslinking reaction with neighboring alkyl chains (included in the ligands on inorganic nanoparticles or the pendent chains in polymers) at an annealing temperature low enough not to degrade the chemical/structural properties of photoresist. Exploiting the chemical robustness of the resulting crosslinked film, we demonstrate that films of colloidal InP quantum dots, light-emitting Super Yellow polymers, or Au nanoparticles can be patterned at a few micro-meter scale through conventional photolithographic lift-off process. We believe that this approach paves a novel route to form micro-meter scale patterns of solution-processible materials without compromising electronic/optoelectronic properties.

SESSION EL11.12: Virtual Session
Session Chairs: Jian Li and Lin Song Li
Thursday Morning, April 27, 2023
EL11-virtual

8:15 AM EL11.12.02
Theoretical Characterization of Excited States in Organic Light-Emitting Diodes Based on Thermally Activated Delayed Fluorescence Copper(I) Complexes Ajith Ashokan[1], Veaceslav Coropceanu[2] and Seyhan Salman[1]; [1]Clark Atlanta University, United States; [2]The University of Arizona, United States

Thermally activated delayed fluorescence (TADF) represents currently one of the most promising ways to realize highly efficient organic light-emitting diodes (OLEDs) without the use of heavy transition metals and offers flexibility to fine-tune the electronic and optical properties of purely organic molecules or complexes of affordable metals. Within the TADF materials, Cu(I) complexes received a great attention due to their cost-effectiveness and fine color tunability in addition to their large spin-orbit coupling which leads to at least 2-3 orders of magnitude larger rates of intersystem crossing between singlet and triplet states. As of now, however, a thorough description of the excited state and microscopic parameters of these systems is missing. A fundamental understanding of electron-vibrational couplings, spin-orbit couplings and other factors that define the radiative and non-radiative rates in metal-TADF complexes is also necessary for improving the device performance. The main goal of this project is to elucidate the excited-state dynamics of the electronic processes that take place in TADF OLEDs incorporating Cu(I) complexes. Here, we will present the results of Screened Density Functional Theory methods to describe the electroluminescence properties two-coordinate Cu(I) complexes featuring N-heterocyclic carbene ligands. We will also include spin-orbit coupling effects in the modelling scheme to describe the intersystem crossing, radiative and non-radiative transitions in these materials.

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SESSION EL12.01: Molecular Junctions, Properties and Functionalities I
Session Chairs: Lei Fang and Farnaz Niroui

Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3003

10:30 AM *EL12.01.01
The Complexity of Charge Transport in Molecular Break Junctions Herre S. van der Zant; TU Delft, Netherlands

Break junctions are a popular method to characterize the electrical properties of single moleucles [1]. However, the behaviour of a molecule in a junction is complicated and therefore difficult to assess experimentally. For example, the end to end single-molecule (fully stretched) configuration may not be the most probable one, while this is the benchmark in the comparison with theoretical calculations. So, the questions "What are the pathways for charge transport through a molecule and what is the conductance of the fully stretched molecule" can still not be answered in all cases. In this talk, I will discuss possible causes for the observed dispersion in the conductance histograms and show that by using unsupervised clustering methods, [2] preferably in combination with clever chemical engineering of molecule families, conduction pathways can be identified and the end-to-end single-molecule conduction can be established [3-6].

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11:00 AM EL12.01.02
Increased Molecular Conductance in Oligophenylene Wires by Thermally Enhanced Dihedral Planarization Woojung Lee, Shayan Louie, Austin Evans, Nicholas M. Orchanian, Ilana B. Stone, Boyuan Zhang, Yujing Wei, Xavier Roy, Colin Nuckolls and Latha Venkataraman; Columbia University, United States

Understanding and manipulating the electron transport within single-molecule wires are key for the development of molecular-scale devices. Significant efforts have been made to control electron transport properties with a variety of parameters including chemical designs of molecular three-dimensional conformations. As electron transport occurs much faster than intramolecular rotations, the average conductance of single-molecule wire is assumed to relate to its energy-minimum molecular conformation. Moreover, in a coherent tunneling regime, electron transport through a single-molecule wire has been theoretically established as a temperature-independent process. As such, the influence of temperature-driven dynamic molecular conformation on electron transport has not been widely investigated. Here, we demonstrate how the dynamic molecular conformation influences the electron transport through oligophenylene wires within a coherent tunneling regime. Using a custom-built variable-temperature scanning tunneling microscopy break-junction (STM-BJ) instrument, we find that the conductance of oligophenylene wires can be manipulated via subtle temperature control (296-328 K). Our DFT-based calculations disclose that thermally accelerated intramolecular rotations allow the oligophenylene wires to have a higher probability of being in a planar conformation compared to lower temperatures. The thermally enhanced planarization substantially increases the time-averaged electron tunneling probability, as the tunneling occurs primarily through π-orbitals. These calculations are consistent with the observation that more rotational pivot points in longer oligophenylene molecular wires lead to larger temperature dependence on conductance. These findings show that molecular conductance within coherent and off-resonant electron transport regimes can be controlled by manipulating dynamic molecular structures.

11:15 AM EL12.01.03
Radical-Enhanced Charge Transport in Non-Conjugated TEMPO Molecules Jialing Li[1], Ying Tan[2], Songsong Li[1], Hao Yang[1], Teng Chi[2], Brett M. Savoie[2], Bryan W. Boudouris[2] and Charles M. Schroeder[1]; [1]University of Illinois at Urbana Champaign, United States; [2]Purdue University, United States

Air and thermally stable organic radical molecules are ideal candidates for molecular spintronic devices. Although prior work has considered a wide variety of chemical structures for spintronics applications, key challenges remain in understanding the structure-property relationships in organic radical molecules at the molecular level. In this work, we study the charge transport properties of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) radical containing non-conjugated molecules using single molecule conductance experiments and semi-empirical quantum chemical simulations. Our results show that the TEMPO pendant groups promote the molecular charge transport compared to the quenched TEMPOH and neutral benzyl pendant groups. Furthermore, the molecular conductance of TEMPO-containing molecules decays with increasing length of molecular backbones similar to non-conjugated alkane chains, but the molecular conductance remains at larger values compared to alkane chains. Temperature-dependent single molecule experiments show that tunneling is the dominant charge transport mechanism in TEMPO-containing molecules. Experimental results are complemented by molecular simulations, which reveal the importance of molecular conformation on charge transport. Results from molecular simulations further show that TEMPO radicals interact with gold metal electrodes near the interface to facilitate a stabilized high-conductance configuration. Overall, our work directly reveals enhanced charge transport in non-conjugated molecules by incorporating open-shell radicals, which will help to inform the design of new materials for molecular electronic devices.

11:30 AM *EL12.01.04
Assembly and Transport Characteristics of Paramagnetic and Charged Single Molecule Circuits Masha Kamenetska; Boston University, United States

Incorporation of paramagnetic and charged molecules into single molecule circuits can increase the scope of observable phenomena due to new degrees of freedom in such molecules. Here I discuss my group's recent advances in establishing chemical design rules for forming stable junctions with coordination complexes containing transition metal atoms, charged linkers and organic paramagnetic compounds. We use Scanning Tunneling Microscope Break Junction (STMBJ), density functional theory (DFT) and non-equilibrium Green's Function methods to determine conductance, geometry and evolution of molecular junctions. We successfully form and measure the conductance of organic diradicaloid compounds with installed thioanisole linkers. In contrast, the formation of junctions with *ex situ* synthesized paramagnetic coordination complexes containing transition metal atoms is complicated due to disassembly of these complexes on gold. Instead, we find that transition metal centers can be reliably wired into single molecule junctions by coordinating *in situ* to anionic linkers during junction elongation. Through environmental control, we can tune the charge on anionic molecules to affect formation and transport properties, including quantum interference effects. *In situ* control and assembly of molecular junctions using charged moieties presents a new approach for creating molecular circuits with non-trivial electronic and spin functionality.

SESSION EL12.02: Molecular Junctions, Properties and Functionalities II
Session Chairs: Masha Kamenetska and Farnaz Niroui
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3003

1:45 PM *EL12.02.01
Single-Molecule Measurements Probe Nanoscale Physics and Chemistry Latha Venkataraman; Columbia University, United States

Over the past decade, there has been tremendous progress in the measurement, modeling and understanding of structure-function relationships in single molecule circuits. Experimental techniques for reliable and reproducible single molecule junction measurements have led, in part, to this progress. In particular, the scanning tunneling microscope-based break-junction technique has enabled rapid, sequential measurement of large numbers of nanoscale junctions allowing a statistical analysis to readily distinguish reproducible characteristics. Although the break-junction technique is mostly used to measure electronic properties of single-molecule circuits, in this talk, I will demonstrate its versatile uses to understand both physical and chemical phenomena with single-molecule precision. In this talk, I will present results from a recent work where we demonstrate that molecular wires can behave as one-dimensional topological insulators. We focus on a family of oligophenylene-bridged bis(triarylamines) with tunable and stable (mono-/di-)radicaloid character. These wires can undergo one- and two-electron chemical oxidations to the corresponding monocation and dication, respectively. The oxidized wires exhibit high reversed conductance decay with increasing length, consistent with the expectation for the Su-Schrieffer-Heeger-type one-dimensional (1D) topological insulators. Importantly, we show that for one length, the dication displays a significantly high conductance greater reaching beyond 0.1 G_0 ($2e^2/h$, the conductance quantum).

2:15 PM EL12.02.03
Formation and Evolution of Molecular Junctions Containing Metal Ions and Organic Radicals Brent Lawson[1], Efrain Vidal[2], Michael Haley[2] and Masha Kamenetska[1]; [1]Boston University, United States; [2]University of Oregon, United States

Creating single molecule-metal junctions containing metal ions or organic radicals is a promising route to achieving functional molecular devices. Here I discuss our recent advances in understanding formation and evolution of molecular junctions formed with organometallic molecules and organic radicals. Our work indicates that the atomic structure of the electrodes can influence charge transfer at the metal-molecule interface and affect junction evolution characteristics. With organic radicals, controlling charge transfer is critical to preserving radical properties. We measure the conductance of indenoindenodibenzothiophene (IIDBT) diradicaloid, an organic molecule with a stable singlet diradical-like character in its ground state, using Scanning Tunneling Microscope Break Junction technique. We incorporate thioanisole linkers into the molecule to decouple the electronic state from the electrode and to anchor it in place. We find reproducible conductance signatures using these molecules in ambient conditions in organic solvents. A combination of experimental and theoretical work using DFT suggests this family of stable diradicaloid organic molecules is a promising choice for studying and understanding electron transport through diradicaloid molecule-metal junctions.

2:30 PM EL12.02.04
Probing the Out-of-Plane Charge Transport in Organic Semiconductors Using Atomic Force Microscopy Mindaugas Gicevičius[1], Haoxin Gong[1], Nicholas Turetta[2], Martina Volpi[3], Yves Geerts[3], Paolo Samori[2] and Henning Sirringhaus[1]; [1]University of Cambridge, United Kingdom; [2]Université de Strasbourg, France; [3]Université libre de Bruxelles, Belgium

Recent years have seen a remarkable progress in the field of organic electronics with the in-plane charge carrier mobility routinely surpassing 10 cm^2/Vs in the best-performing materials. However, the miniaturization of organic semiconductor devices to achieve sub-micrometer active channel lengths and high switching frequencies is still limited by the contact resistance between metal electrodes and the organic semiconductor material. Efficiently controlling the contact and access resistance is, therefore, of crucial importance in pursuit of developing efficient electronic devices based on organic materials. Conventional approaches for achieving low contact resistance usually focus on interface engineering to achieve better alignment of energy levels. However, another significant contributor to high contact resistance is the out-of-plane mobility. Despite its importance, the out-of-plane mobility remains an often-overlooked parameter mainly due to the lack of available measurement techniques.

Herein, we report a novel method for evaluating the out-of-plane mobility and contact resistance based on conductive-probe atomic force microscopy (C-AFM). In this study, we prepared multi-layered single crystal films of the molecular semiconductor C8-DNTT-C8 by a solution shearing technique on electrically conducting substrates and investigated them using C-AFM. By using scanning probe microscopy to map the local changes in the out-of-plane electrical current we gain a close-up view of the out-of-plane conductivity and access resistance at an unprecedented molecular length scale. This study opens a new pathway for gaining a better understanding of structure-property relationships and enabling a more accurate engineering of materials and interfaces in organic semiconductor devices.

2:45 PM BREAK

3:15 PM *EL12.02.05
A Ladder-Type Conjugated Molecule as Highly Robust Multi-State Single-Molecule Switch Lei Fang[1], Jialing Li[2], Bo-Ji Peng[1], Charles M. Schroeder[2] and Daniel Tabor[1]; [1]Texas A&M University, United States; [2]University of Illinois at Urbana-Champaign, United States

Ladder-type constitution strongly enhances the chemical stability and yields well-defined physical properties that enables the fundamental studies of charge transport in multi-state, reversibly switchable aniline derivatives. Herein, we report the change in charge transport properties of a conjugated ladder-type cyclohexadiene-1,4-diimine directive at various protonation, lithiation and oxidation states. Our results demonstrate a 10-fold conductance increase from the reduced benzenoid structure to the oxidized quinonoid structure. Furthermore, acid/lithium salt addition renders two-step protonation/lithiation of the quinonoid molecule to a dicationic form in resonance with an air-stable open-shell diradical state. The fully protonated/lithiated state displays a conductance level 15 times higher than the neutral quinonoid state. Surprisingly, the charged quinonoid state also exhibits the possibility of interchain charge transport, which is not observed in the neutral state. A core-anchor group type and anchor group-anchor group type of dimerization are found to contribute to the intermolecular charge transport via DFT simulations(consider to remove such detail in abstract). Beside the chemically induced conductance changes, a stable and reversible conductance switch of over two orders of magnitude is achieved *in-situ* by electrochemical gating. Overall, this work highlights a highly robust, multi-state, single molecule switch, in which fully fused ladder-type constitution is incorporated to advance the stability, programmability, and efficiency of the single-molecule devices.

3:45 PM EL12.02.07
Self-Assembly in Supercritical Fluids—Connecting Top-Down and Bottom-Up Approaches to Nanoengineering Loren G. Kaake; Simon Fraser University, Canada

The development of devices based on single-molecule junctions requires not only robust control over molecular self-assembly but integration into structures that can interface with the macroscopic world. Accomplishing this task requires a manufacturing technique that simultaneously offers the reproducibility and accuracy of photolithography as well as the nanoscale control offered by solution phase self-assembly. In order to unify top-down and bottom-up approaches to nanoengineering, we are developing physical supercritical fluid deposition. This technique leverages the unique solubility properties of supercritical fluids to deposit molecules without the need for in-situ chemical reactions. The process relies on a peak in the isobaric saturation solubility with respect to temperature allowing thin films to be formed via precipitation onto heated substrates. The location of material deposition can be accomplished by controlling the local temperature on the substrate via simple joule heating. The resistive traces used for joule heating can be created via photolithography, allowing us to direct the solution phase self assembly with the accuracy of photolithography. Progress towards improving the resolution limit of the technique will be discussed as will the mechanisms of self-assembly and their effect on the nanoscale morphology of polymeric materials.

4:00 PM EL12.02.06
Combining Automated Synthesis with Single Molecule Electronics—Understanding the Role of Side Chains on Molecular Charge Transport
Jialing Li, Songsong Li, Edward Jira, Nicholas Angello, Martin Burke and Charles M. Schroeder; University of Illinois at Urbana-Champaign, United States

The development of next-generation organic electronic materials critically relies on understanding structure-function relationships in conjugated polymers. However, a major challenge lies in accessing the vast chemical space encompassed by synthetic organics while efficiently managing the large synthetic workload to survey new materials. Here, we use automated synthesis to overcome synthetic bottlenecks hindering access to the large chemical space for organic electronics. A library of terphenyl derivatives with different side chain compositions and anchors was prepared using a custom synthesis instrument for automated iterative Suzuki coupling. The role of side chain chemistry on the charge transport properties of conjugated oligomers was then systematically studied using single-molecule charge transport experiments. Our results show an unexpected concentration-dependent bimodal conductance in terphenyl molecular junctions with long alkyl side chains. We found that high conductance states arise due to surface adsorption and backbone planarization induced by the long side chains, which is confirmed by density functional theory simulations and a series of control experiments with asymmetric, planarized, and sterically hindered oligomers. Molecular junctions with oxygen-containing side chains are also investigated, showing high levels of conductance and reduced molecular adsorption behavior compared to alkyl side chains. Overall, our work highlights the role of side chain chemistry on charge transport and opens new avenues in combining automated synthesis with single molecule characterization to develop new materials for organic electronics.

4:15 PM *EL12.02.08
On the Origin of the Chirality-Induced Spin Selectivity in Molecular Junctions and Beyond Yonatan Dubi; Ben-Gurion University, Israel

When electrons are injected through a chiral molecule, the resulting current may become spin polarized. This effect, known as the chirality-induced spin-selectivity (CISS) effect, has been suggested to emerge due to the interplay between spin–orbit interactions and the chirality within the molecule. However, such explanations require unrealistically large values for the molecular spin–orbit interaction without any physical justification. Put simply, to date, the physical origin of the CISS effect is unknown.Here, we present the “spinterface mechanism” for the CISS effect, based on the interplay between spin–orbit interactions in the electrode, the chirality of the molecule (which induces a solenoid field), and spin-transfer torque at the molecule–electrode interface. The spinterface mechanism has already been shown to allow remarkable fit between theory and data for numerous experiment. We will provide new examples for such fits, further corroborating the mechanism. We will describe a set of experiments which can be used as a “smoking gun” for differentiating this mechanisms from other theoretical explanations. Finally, we will describe a spinterface mechanism for the CISS effect in photo-excited electrons scattered off a layer of chiral molecules.

SESSION EL12.03: Poster Session: From Molecules to Emerging Molecular Devices
Session Chairs: Masha Kamenetska and Farnaz Niroui
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL12.03.01
Charge Transport across Biomolecular Electronic Junctions. Ultraviolet and X-ray Photoemission Spectroscopy Studies Tatyana Bendikov[1], Jerry A. Fereiro[1,2], Cunlan Guo[1,3], Israel Pecht[1], Mordechai Sheves[1] and David Cahen[1,4]; [1]Weizmann Institute of Science, Israel; [2]Indian Institute of Science Education & Research, India; [3]Wuhan University, China; [4]Bar-Ilan University, Israel

Biomolecules such as proteins and peptides are potential candidates for building diverse functional electronic devices. Measuring and controlling electron transport (*ETp*) through these molecules, especially, as assemblies on solid substrates, i.e., part of an electronic device structure with solid electrodes, is a major goal of bio-molecular electronics. The electronic structure of the peptide/protein monolayer and/or its orientation in contact with an electrode can be directly related to the energy barrier and electrode/molecule coupling in the resulting junction.
Ultraviolet and X-ray Photoelectron Spectroscopies (UPS, XPS) with their high surface sensitivity have been used extensively to study the electronic and chemical structure of *molecular* thin films or monolayers on solid surfaces. Here we show how UPS and XPS measurements can provide a crucial information for understanding the mechanism(s) of *ETp* through biomolecule/Au electrode-containing junctions.
In the first example we show how the spatial position of a singe tryptophan “dopant” in a linear oligo-alanine chain may significantly influence *ETp* across

a self-assembled monolayer of these peptides between gold contacts.[1] In the second example we explore the effect of the side-chain of the peptide (*2Ala* vs *2Trp*) on its electronic properties.[2]
In the two next examples, the bacterial electron transfer protein Azurin (*Az*) [3] and a mutant (*N42C Az*)[4] are studied on Au substrates. We find that the *ETp* mechanism can be changed by changing just a linker (binding)[3] or the orientation[4] of the protein with respect to the Au substrate.
Finally, we demonstrate that the direction of current rectification and the conductance-voltage characteristics of the Photosystem 1 complex (*PS1*) can be controlled by its orientation on Au substrates.[5]

1. C. Guo et al, *PNAS*, 113, **2016**, 10785-10790.
2. C. Guo et al, *PCCP*, 20, **2018**, 6860-6867.
3. J. A. Fereiro et al, *JACS*, 140, **2018**, 13317-13326.
4. J. A. Fereiro et al, *JACS*, 142, **2020**, 19217-19225.
5. J. A. Fereiro et al, *Small*, **2022**, submitted.

5:00 PM EL12.03.03
Defining Qubit Properties in High-Valent Actinide Complexes Megan E. Hoover, Stephanie Gamble and Lindsay Roy; Savannah River National Laboratory, United States

Quantum computing is a rapidly emerging technology that has the potential to revolutionize computations unattainable with classical computers, and *f*-element systems have shown exceptional promise in quantum information processing. While progressing through the actinide series, the relativistic effects change the energetics of the 5*f* and 6*d* orbitals wherein control of a quantum bit (qubit) could be possible. For example, protactinium contains interesting characteristics and adopts the behavior of transition metals because of its near degeneracy of the 6*d* and 5*f* orbitals. This presentation outlines the potential for high-valent $5f^1$ early actinide complexes to act as qubits by evaluating the atomic properties, including spin-orbit coupling, crystal electric field, and nuclear spin. This research is set to establish basic understanding of the interplay between the *d* and *f* orbitals thereby generating a set of features to enhance quantum coherence in actinide complexes.

5:00 PM EL12.03.04
Single Molecule Detection of Metal-Biomolecule Binding Conformations Using Conductance Signatures Xiaoyun Pan[1], Cheng Qian[2,2], Lu Wang[2,2] and Masha Kamenetska[1,1,1]; [1]Boston University, United States; [2]Rutgers University, United States

Developing a fundamental understanding of the interactions between biogenic molecules and noble metal surfaces is important for guiding and advancing the development of biotic-abiotic interfaces, conductance measurements of biomolecule conductivity, and biosensing. Here, we use the Scanning Tunneling Microscope-based Break Junction (STMBJ) technique to measure the conductance and binding orientation of a single nucleobase, Adenine (Ade), and its derivatives on gold. We systematically study the conductance features of Ade and other structurally similar molecules that lack one or more of the candidate binding sites of Ade to assign individual molecular conductance features to specific metal-Ade binding configurations. Our results allow us to determine the binding orientations of Ade on gold unambiguously. To demonstrate the biosensing potential of these measurements, we show that we can sense and distinguish Ade from its biologically relevant variants, 6-methyladenine and 2'-deoxyadenosine. Finally, we apply these methods to determine the molecular conductance and binding configurations of other biologically functional molecules on gold, such as histidine and histamine. Our work establishes STMBJ as a powerful tool for characterizing the atomic structure of metal-organic interfaces and lays the foundation for biosensing on gold using single molecule conductance readout.

5:00 PM EL12.03.05
Vertical Organic Permeable Base Transistors with the Passivated Pinholes in Permeable Base Electrode In-Hye Lee and Kyung-Geun Lim; Korea Research Institute of Standards and Science, Korea (the Republic of)

Vertical organic transistors (VOTs) are emerging electronic devices that can overcome the limitations of conventional organic thin film transistors (OTFTs) based on lateral architecture. Here, organic permeable base transistors (OPBTs) were formed with an oxide layer on the base electrode as a dielectric layer by using an electrochemical oxidation called anodization, and passivated by self-assembled monolayer (SAM) treatment after forming AlO_x on the aluminum base electrode. The VOTs with the electrochemical oxidation and molecular passivation are simply manufactured and the charge carrier transport is significantly improved. SAM treatment is a regularly ordered organic monolayer that is spontaneously formed on a solid surface. Since the properties of the surface can be controlled, it is used on the surface of a base insulator to improve the carrier transmission performance of organic transistors. In this study, the oxidation and passivation of permeable base electrode were systematically controlled. The SAM treatment can reduce the leakage current of the base electrode and improve the current transmittance between the emitter and the collector. In addition, we observed the specific behaviors of vertical OPBT depending on the applied potential correlations between the middle base electrode and the bottom collector electrode.

5:00 PM EL12.03.06
Manipulating Quantum Interference in Single Molecule Junctions via Chemical Substitution and Environmental Control Hannah Skipper, Brent Lawson and Masha Kamenetska; Boston University, United States

Understanding and manipulating quantum interference (QI) effects through chemical design and external control is important for the development of molecular-scale devices. QI results from electrons tunneling through multiple molecular orbitals (MOs) each with a distinct phase with respect to the electrode attachment points on the molecule. In this work, we use Scanning Tunneling Microscope Break Junction (STMBJ) single molecule conductance measurements and electronic transport calculations to explore the effects of chemical composition and substitution in pyrazine-based molecular junctions. We find that QI effects dominate observed transport characteristics of these molecules, resulting in distinct conductance peaks through the meta but not the para pathway. Critically, destructive interference through the para position of the pyrazine ring can be manipulated via substitution at the meta position. By varying the environment surrounding the junction, we can control the charge of the chemical substituents and manipulate the alignment of individual MOs with the Fermi energy to tune QI through the para channel in pyrazine-based junctions from destructive to constructive. This work demonstrates environmental control of molecular QI, opening the door to *in situ* tuning of QI effects in single molecule junctions.

5:00 PM EL12.03.07
Ladder-Type Polyaniline Derivatives as a Highly Robust Multi-State Switch in Single-Molecule Junction Bo-Ji Peng[1], Jialing Li[2], Daniel Tabor[1], Lei Fang[1] and Charles M. Schroeder[2]; [1]Texas A&M University, United States; [2]University of Illinois at Urbana-Champaign, United States

Polyaniline (PANI) is of considerable interest due to its versatile chemical and electrochemical doping states. However, they suffer from chemical instabilities at acidic and oxidative conditions, which limits their applications in higher oxidative and protonated states. Herein, we reported a series of ladder-type PANI derivatives flanked with methylthiol groups on both ends as the model molecule for single-molecule conductance studies. The implementation of the ladder-type constitution prevents undesired hydrolysis and isomerization, rendering high stability of these molecules at different protonation and oxidation states. We studied the single-molecule charge transport properties of ladder-type PANI derivatives using the scanning tunneling microscope-break junction (STM-BJ) method. Our results demonstrate a 10-fold conductance increase from the reduced benzenoid structure to the oxidized quinonoid structure. Furthermore, leveraging the chemical stability that ladder-type constitution provides, acid/lithium salt addition renders two-stage protonation/lithiation of the quinonoid molecule to a dicationic form which shows open-shell diradical character in ambient conditions. The fully protonated/lithiated state displays a conductance level 15 times higher than the neutral quinonoid state. Surprisingly, intermolecular charge transport is also observed via the formation of stacked dimers assisted by pi-pi interaction. The experimental results are complemented by DFT calculations, which reveal smaller energy gaps and extended molecular conformations for higher protonated and lithiated states. Overall, this work highlights a highly robust, multi-state, single-molecule switch where a ladder-type constitution is incorporated into the PANI system to advance the stability, programmability, and efficiency of the single-molecule devices.

5:00 PM EL12.03.08
Performance of High-Mobility in BDT Trimers—Visualization of Electron-Phonon Coupling by ElPh Workflow Farahnaz Maleki[1], Makena Dettmann[1], Daniel Vong[1], Luke L. Daemen[2], John Anthony[3] and Adam J. Moule[1]; [1]University of California, Davis, United States; [2]Oak Ridge National Laboratory, United States; [3]University of Kentucky, United States

Phonons limit charge mobility in organic semiconductors by dynamically localizing charge carriers to a few molecules. The main synthetic strategy to overcome dynamic localization has been to use side chains to “damp out” phonon modes that limit charge mobility. Here we examine a different strategy, to introduce “large” small molecules that form extended crystals and reduce molecular motion. Tri(n-hexyl)silylethynyl benzodithiophene (BDT) trimer, has demonstrated one of the highest mobilities recorded (1.6 cm^2/Vs). To understand why the BDT trimer performs so well, the phonons spectra, are computed using our DFT based open source Davis computational spectroscopy (DCS) workflow and verified using inelastic neutron scattering (INS) measurements. We separately developed a workflow called ElPh to compute the atom specific contribution to electron-phonon coupling, which enables us to quantitatively map which parts of the molecule are actively engaged in charge mobility reduction. This process offers understanding for why this material performs so well. The simulation process is transferrable to design of other high-mobility organic electronic materials.

5:00 PM EL12.03.10
Probing the Rate of Singlet Fission in Tetracene Using Temperature and Magnetic Field-Dependent Transistor Measurements Katelyn P. Goetz, Chad Cruz, Sebastian Engmann, Curt A. Richter and Emily G. Bittle; National Institute of Standards and Technology, United States

Singlet fission results in the creation of a correlated pair of triplet excitons, making it an attractive phenomenon for devices that perform quantum computing tasks. While ultrafast optical techniques have proven insightful in understanding singlet fission and related processes, there is a need to experimentally probe them within a device context. Here, processes occurring on longer timescales, such as intersystem crossing, can become relevant and overlap with signals of singlet fission.

We access the spin dynamics of triplet excitons in organic field-effect transistors (OFETs) using magnetic field-modulated photoconductivity (MPC) measurements. We chose to use tetracene as the active layer because singlet fission in it has an energetically uphill component, as well as to enable comparison with a vast body of spectroscopic literature. Tetracene was grown as single crystals by the physical vapor transport technique to limit the effects of defects and microstructure. Measuring MPC as a function of temperature allows us to modulate the singlet fission rate, and applying a simple model gives insight into changes observed. Over the range of 350-170 K, the MPC signal, measured from -200 mT-200 mT, takes an M-shape with peaks at 8-10 mT and shoulders at 41-50 mT. These features are thermally activated, showing an MPC of 0% or slightly above at room temperature and decreasing until about 220 K. Our model suggests that this change is attributed to the thermal activation of singlet fission in tetracene. At the end points (+/- 200 mT), the much stronger decrease in MPC (as much as 11% at 220 K, with the exact value depending on the orientation of the triplet dipole with respect to the magnetic field) may be an indication that intersystem crossing is becoming a dominant spin-dependent process. Below 220 K, the MPC starts increasing again, which we attribute to a subtle phase transition. This work indicates that intersystem crossing should be considered when understanding photophysical processes in singlet fission devices.

5:00 PM EL12.03.12
Strain-Enabled Exciton Delocalization in Crystalline Phthalocyanine—A Pathway Towards Room-Temperature Macroscopic Coherence in Organic Semiconductors Libin Liang[1], Tabassum Joyee[2], Varun Mapara[2] and Madalina I. Furis[2]; [1]Intel Corporation, United States; [2]University of Oklahoma, United States

Rapid exciton (energy) transport is critical for the realization of efficient organic semiconductor devices that surpass current efficiency limitations. Solution -based fabrication techniques for crystalline molecular thin films with macroscopic ordering show potential for overcoming the limitations of the molecular Frenkel exciton hopping transport. Once static/ structural disorder is removed from these films, spectroscopy experiments reveal the superluminescent signature of exciton delocalization in an entire class of small molecules where the packing motifs favor stronger intermolecular coupling.[1]
In small molecule crystals the formation of delocalized and coherent excitons is the result of a complex balance between the long-range Coulomb interactions, short range π- stacking coupling and electron phonon coupling. The delocalization takes place when the latter is of the same order of magnitude as the nearest neighbor intermolecular coupling. Small energy phonon modes assist in the formation of coherent states while high energy molecular vibrations (dynamic disorder) introduce decoherence and localize the exciton.[2] The delocalization will favor ballistic energy transport through the system.
Here we report on how uniaxial strain induces a more robust coherent delocalized exciton state. The molecular thin films under study are deposited from solutions of metal-free octabutoxy Phthalocyanine (H_2OBPc) using a capillary pen - writing technique that results in macroscopic crystalline grains sizes, with molecules stacked in a J-like configuration along the [110] crystal axis.[3] It was shown theoretically and experimentally that exciton delocalization only occurs along this molecular stack making the films a 1D excitonic system.[4]
Temperature, strain-dependent luminescence, absorption and linear dichroism microscopy indicate applying uniaxial strain along the stacking axis has a similar effect lowering the temperature by 100K, in terms of the prevalence of the coherent exciton state. The coherence length is estimate from the ratio between the delocalized exciton photoluminescence intensity and its first phonon replica. Increasing strain to 4.2 % initially shortens the coherence length at low temperatures, however, further increase in the strain results in a surprising recovering of the initial value of 22 molecular units (approx. 10 nm). This can be explained by the trend observed in the ratio between the intermolecular coupling and the electron-phonon interaction, also estimated from the temperature dependence of photoluminescence and the associated radiative lifetime. The applied strain results in stronger intermolecular interactions that maintain the delocalization up to a temperature of 200K.[5]
Finally, the mechanism of delocalized exciton formation is confirmed through strain -dependent transient absorption measurements and confocal photoluminescence microscopy that reveal the excited Frenkel excitons delocalize in less than 500fs. The dynamic disorder induces the formation of a more localized exciton-polaron state 5ps later. This process suffers significant changes in the presence of strain.

[1]Rawat et al, *J. Phys. Chem. Lett.* **2015**, 6, 1834–1840
[2]Fornari et al, J. *Phys. Chem. C* **2016**, 120, 7987–7996
[3]Pan et al, *Nat. Commun.* **2015**, 6, 8201
[4]Liang et al, *J. Phys. Chem. C* **2021**, 125, 27966–27974
[5]Liang et al, *J. Phys. Chem. C* **2022**, 126, 8889–8896

SESSION EL12.04: Molecules in Quantum, Optical and Spintronic Devices
Session Chairs: Lei Fang and Farnaz Niroui
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3003

8:30 AM *EL12.04.01
Molecular Design of Color Centers Danna E. Freedman; Massachusetts Institute of Technology, United States

Physical structure creates electronic structure. By precise positioning of atoms through molecular chemistry we can design electronic structures for applications in quantum information science. We use ability to design both coarse and fine electronic structure through synthetic chemistry to create materials for quantum information science. Results on creating molecular color centers will be described.

9:00 AM EL12.04.02
High-Multiplicity States in Luminescent Organic Radicals Sebastian Gorgon[1,2], Jeannine Gruene[3], William Myers[2], Feng Li[4], Emrys Evans[5] and Richard Friend[1]; [1]University of Cambridge, United Kingdom; [2]University of Oxford, United Kingdom; [3]University of Wurzburg, Germany; [4]Jilin University, China; [5]Swansea University, United Kingdom

Organic luminescent radicals present a new and exciting platform for exploring molecular functionalities at the interface of their unique optical and spin properties.[1] Near-unity internal quantum efficiency for red emission was demonstrated for donor-acceptor structures based on the tris(2,4,6-trichlorophenyl)methyl (TTM) radical.[2] This opens these materials towards applications in technologies ranging from organic light-emitting diodes and photovoltaics with eliminated triplet losses, to photomagnetic devices and molecular-scale information transfer.

Here we present a new family of molecules based on the TTM radical motif which contain high-multiplicity states in their emission mechanism. By combining light-induced EPR with ultrafast transient absorption and temperature-dependent transient luminescence spectroscopy we find a mechanism that uniquely supports both a high emission yield and a high yield of generation of the high-spin species. This is enabled by very low activation barriers between excited states, which arises from energy level matching in our molecular design. Pulsed EPR spectroscopy allows us to characterize the potential of our system for future quantum information science applications.

References
[1] Teki, Y., Chem. Eur. J. 26, 980 (2020)
[2] Ai, X., Evans, E.W., Dong, S. et al., Nature 563, 536–540 (2018)

9:15 AM EL12.04.03
Investigating the Emergent Properties of Organized Spin Ensembles and Their Behavior at Interfaces Daphne Lubert-Perquel and Justin Johnson; NREL, United States

Quantum information science (QIS) remains an important field of research due to its far-reaching implications in computing, communication and advanced sensing applications. Molecular systems are the most recent candidates for QIS, with several recent perspectives and reviews discussing the valuable properties unique to such systems. Coordination compounds provide precise tailoring of specific magnetic properties through structural tuning, and phthalocyanines have been established as a versatile system. Vanadyl phthalocyanine (VOPc) is considered here, a spin ½ system with long (μs) coherence times. It is easily and predictably deposited on a range of substrates and so has been directly implemented in resonant cavities to promote spin-photon coupling, placed on functionalized surfaces, or incorporated into hybrid architectures for sensing applications.

Read-out of the stored quantum information is a key requirement of all spin qubits and much work is being done on molecular compounds to achieve optical readout. Here, we investigate the possibility of a digital state readout by combining a molecular spin system to a valleytronic material. Films consisting of a few layers of transition metal dichalcogenides (TMDC) have demonstrated circular polarized photoluminescence (PL) from the transition to a direct band gap semiconductor. Chiral emission is relevant to spin-selective optoelectronics and combining the molecular spin qubit with a TMDC substrate could lead to interesting opportunities in QIS. However, at this stage little is known of the electronic and spin interactions at such an interface and the extent of spin-valley cooperativity. We therefore present a comparative magneto-optical study of the VOPc thermally evaporated on MoS_2, $MoSe_2$ and WSe_2 as a function of polarization. This provides critical information to design new architectures for quantum devices.

9:30 AM *EL12.04.04
Quantum Control and Coherence of Spins from Semiconductor Devices to Synthetic Qubits Pratiti Deb[1], Sam Bayliss[1,2], Leah Weiss[1], Nikita Onizhuk[1], Daniel Laorenza[3], Giulia Galli[1], Danna Freedman[3] and David Awschalom[1]; [1]University of Chicago, United States; [2]University of Glasgow, United Kingdom; [3]Massachusetts Institute of Technology, United States

Quantum technologies benefit from atom-scale control of both the quantum bit and its local environment. In semiconductor materials, defects and dopants house localized electrons where the spin degree of freedom can be initialized and coherently controlled with a combination of optical and microwave signals. These semiconductor spin-qubits can be embedded in devices where their optical and spin properties can be enhanced by controlling both their electronic and nuclear-spin environment. Organometallic molecules provide an analogous platform for localized, coherent quantum states where both the qubit and its environment can be further modified via chemical synthesis. We have demonstrated optical addressability and coherent microwave control of the electron-spin ground-state of organometallic molecules containing a central chromium ion [1]. We have shown that the spin-optical interface of these molecular qubits can be tuned by modifying the structure and symmetry of the ligand field [1,2]. Atomistic modification of not only the qubit itself, but also its host environment can further be used to protect the qubit from magnetic field noise, for example due to the fluctuating electron or nuclear spin bath, yielding a five-fold improvement in spin coherence times by inducing noise-insensitive clock transitions [3]. This scalable approach to engineering quantum systems from the bottom up opens new avenues for tailoring synthetic qubits toward device-scale integration.

[1] S.L. Bayliss*, D.W. Laorenza* *et al,* Science **370**, 1309 (2020)
[2] D. W. Laorenza *et al,* JACS **143**, 50 (2021)
[3] S.L. Bayliss*, P. Deb*, D.W. Laorenza* *et al,* PRX **12**, 031028 (2022)

10:00 AM BREAK

10:30 AM *EL12.04.05
Quantum Optics with Organic Molecules Vahid Sadoghdar; Max Planck Institute for the Science of Light, Germany

Laboratory manipulation of single quantum emitters and single photons has matured to a routine procedure over the past two decades. Nevertheless, each solid-state emitter system (quantum dots, color centers, ions, etc) is still confronted with a range of material constraints that pose challenges for scaling and reliable use in devices. Our group has explored organic molecules in the class of polycyclic aromatic hydrocarbons (PAH) for about 25 years. In this presentation, I discuss our efforts of the last decade in coupling molecules to high-finesse Fabry-Perot open cavities, plasmonic nano-antennas and chip-based photonic circuits. We demonstrate dipole-induced transparency, strong coupling, single-photon nonlinearities as well as the cooperativity of two molecules via a common mode of a micro-resonator. Moreover, I present data on high-resolution spectroscopy of the vibronic transitions in single molecules as well as a theoretical proposal for a hybrid optomechanical platform that can lead to long coherence and storage times.

11:00 AM EL12.04.06
Electrical Initialization and Readout of Triplet Exciton Spins Taylor Wagner[1,2] and Obadiah Reid[2,3]; [1]Colorado School of Mines, United States; [2]National Renewable Energy Laboratory, United States; [3]University of Colorado Boulder, United States

Molecular electronics offer several important advantages for spintronic, quantum sensing, and quantum computing fields. The ease of synthesis and fabrication combined with tunable spin physics makes some of these organic systems promising initial candidates for use in quantum information, however a key challenge is the ability to address individual molecular spins. Promising gate operations and coherence times have already been demonstrated with triplet exciton spin transfer using optical techniques, but electrical readout of these states would move these systems closer towards functional microelectronic circuits. Here we present a pathway towards electrical initialization and readout of triplet spins using the phenomenon of organic magnetoresistance (OMAR) with polycrystalline pentacene.

Pentacene and many of its derivatives and dimers, including 6,13-Bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene), are studied for their ability to undergo a process known as singlet fission. Under illumination, these molecules readily excite to the first excited singlet state and efficiently and rapidly fission into two first excited triplet states onto neighboring molecules. This phenomenon has been fairly well explored for use in photovoltaics, and because of this, the process is well known to generate triplets of relative polarized spin due to their initial entanglement upon formation. Interactions of these polarized triplet spins with charge carriers creates a mixed state that holds information of both triplet spins. This triplet-charge spin-spin interaction is electrically detectable and forms the basis for singlet fission molecules to be explored for quantum information science. Polycrystalline pentacene is therefore a great model system for manipulation of these spin-spin interactions due to its large carrier mobility and ability to generate a high density of long-lived triplet excitations.

As the detection mechanism of these spin states, we look to theory of OMAR, where it has been shown that the interaction between triplets and mobile charges fundamentally changes the resistance through a thin film organic layer based on the applied magnetic field. We have fabricated polycrystalline pentacene devices that minimize the other commonly observed OMAR effects to isolate the response seen from these triplet-polaron encounters. Development of a quantum kinetic model through the application of the Stochastic Liouville equation of the triplet-charge mixed states reveals predictions that agree well with experiment. The model also provides predictions of the magnetoresistance when spin selective contacts are introduced, which would allow only anti-aligned triplet spins to quench, eventually purifying the triplet spins aligned with the applied field.

This triplet spin purification acts as an initialization process and can be achieved through a secondary thin film using a phenomenon known as chirality induced spin selectivity (CISS). This relatively newly discovered effect uses spiral-like chiral constituents to polarize either light or polaron spin of a specific orientation under an applied magnetic field. We show the effect of using the (S) and (R) chiral versions of $(PEA)_2PbI_4$ perovskite as a polarizing hole injection layer into polycrystalline pentacene. These results combined with detection via magnetoresistance provide promising first steps in the room temperature initialization and readout of molecular triplet spins.

11:15 AM *EL12.04.07
Creating Mass-Scale Precision Plasmonic Nanocavities and Their Functionalities Jeremy J. Baumberg; University of Cambridge, United Kingdom

Light can be confined through plasmonics to the nanoscale using coinage metals, particularly tightly within nm-wide dielectric gaps between metal facets. I will present recent advances in the nanoparticle-on-mirror concept [1] which creates robust and atomic-scale precision nanocavities that finally open up systematic exploration of many light-matter coupled phenomena. I will demonstrate how the size and shape of the nanoparticle facets play a key role, and can be controlled to modify in-/out-coupling of light. Enhanced structures can show hundred-fold increases in SERS emission (exceeding a million counts/mW/s) which enables high speed real-time interrogation of the dynamics of individual atoms and molecules in the nanocavities.
I will show a variety of phenomena from single de/protonation events [2], single molecule catalytic chemistry, and electrochromic functionalities [3], to the ability to create low-cost uncooled detectors of mid-IR light through upconversion in such plasmonic nanocavities [4]. I will also show that these structures can be simply wired up for a variety of molecular electronics and photoconductive devices [5,6]. I will introduce how optical forces are hundred-fold enhanced in such nanocavities [7-9]. I will finally discuss the prospects for such nanoscale building blocks across a variety of fields.

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11:45 AM EL12.04.08
Mechanically-Reconfigurable Molecular Junctions with Sub-Nanometer Tunability Weikun Zhu, Peter Satterthwaite and Farnaz Niroui; Massachusetts Institute of Technology, United States

Diverse and unique functionalities of molecules have extended their applications beyond electronics to fields including optics, plasmonics, mechanics, spintronics, and quantum technologies. Molecular devices with structurally-tunable, nanometer-thin critical dimensions are highly desirable for their extended sensitivity, energy efficiency and speed. Building such molecular platforms reliably, however, has been a challenge due to the fabrication limitations posed by top-down techniques.

Here, we present nanoparticle contact printing as a technique for scalable fabrication of molecular junctions in the form of mechanically active plasmonic resonators where the molecules serve as nanoscale reconfigurable springs with sub-nm control. The plasmonic resonator is configured as a nanoparticle-on-mirror structure, where a compressible dielectric molecular spacer is sandwiched between a metallic nanoparticle and a metallic film. To achieve scalable patterning of these active resonators, we developed nanoparticle contact printing, where >2000 colloidal plasmonic gold nanoparticles are deterministically patterned onto template-stripped gold with sub-50 nm control over positional accuracy. The resulting nanoparticle-on-mirror constructs are highly sensitive to sub-nm structural changes in the molecular junction. We demonstrate the dynamic mechanical tunability of the molecular junction and its limits by testing the resonators under thermal cycling, where the molecular layer undergoes thermal expansion and recovery. The ~1.2 nm spectral tunability observed upon heating reflects a mere ~30 pm change in the molecular gap, highlighting the sensitivity and precision of this platform. Such tunable structures, whose response can be modified through choice of the molecular layer, can form building blocks for mechanically active molecular devices, enabling high-throughput statistical and correlative characterization of the molecular mechanics, and integration into emerging nanoscale sensors, actuators, reconfigurable optical devices, and tunable metasurfaces.

SESSION EL12.05: Molecules in Electronic and Spintronic Devices
Session Chairs: Yuxuan Cosmi Lin and Farnaz Niroui
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3003

1:30 PM *EL12.05.01
Integrating Single-Molecule Electronic Devices Josh Hihath; Arizona State University, United States

In recent years incredible strides have been made in the development of molecular electronic systems that possess unique functionality. By combining chemical design with physical modeling and electrical characterization techniques it has become clear that molecules are capable of a wide range of impressive electronic functions that extend far beyond the development of standard devices such as transistors and diodes. An array of electromechanical, electrochemical, thermoelectric, and quantum devices now provide promise for memory devices, sensors, and multi-state logic units which could yield new paradigms for in-memory computing, various post von Neumann architectures, or for chemical and biological sensing systems. But, despite these possibilities, one of the major issues that arose in the nascent days of molecular electronics still lingers and limits its ultimate utility. That issue is integration. Despite a wide range of unique devices, and novel chemical and physical properties, it has remained difficult to integrate these materials into a larger-scale system in a way that is reliable, reproducible, and eventually manufacturable. In this talk we will discuss emerging approaches aimed at moving molecular-scale electronic systems from the lab and into applications. To integrate top-down lithographic approaches with bottom-up self-assembly methods we utilize novel micro-electromechanical systems (MEMS) that allow robust single-molecule electrical measurements at the chip-level; the programmability imparted by DNA nanotechnology to create novel nanoscale electrical and lithographic systems; and finally the utility of carbon nanotubes for making secure and robust contact to a single-molecule to allow facile integration with traditional photolithographic processes.

2:00 PM EL12.05.02
Template Stripping of Diverse and Heterogeneous Surfaces for Scalable Molecular Electronics Peter Satterthwaite, Sarah Spector and Farnaz Niroui; Massachusetts Institute of Technology, United States

Reliable molecular junctions require high-quality self-assembled molecular monolayers. To form such monolayers, clean, ultra-smooth (< 1 nm root-mean-square roughness) growth surfaces are required. One approach to such surfaces is template stripping, where the material of interest is deposited on a template, such as a silicon wafer, then delaminated from the underlying substrate, revealing a clean, ultra-smooth surface suitable for molecular assembly. Conventionally, this template stripping approach has been limited to large-area surfaces of metals such as Au, Ag, Pd and Pt, which naturally have low adhesion to the underlying silicon surface, allowing for delamination. Though suitable for fundamental studies, these large-area surfaces of low-adhesion noble metals have limited prospects for integration into molecular devices and systems.

Here, we demonstrate template stripping of diverse materials (Au, Pt, Al, SiO_2, Al_2O_3) including and beyond those achievable through conventional template stripping approaches. We overcome the requirement for a low-adhesion material by functionalizing the underlying silicon substrate with molecular release layers that enable reliable stripping regardless of material adhesion, while maintaining the surfaces ultrasmooth (< 1 nm). This expands the use of template stripped surfaces to the assembly of diverse molecular monolayers beyond those readily compatible with assembly on conventional, noble metal surfaces. This approach further opens the possibility of integrating molecules with materials, beyond noble metals, that display functionalities, such as spintronic or semiconducting, critical for the emerging molecular devices. We further demonstrate lithographic patterning of template stripped surfaces to realize ultra-flat, ultra-smooth surfaces composed of multiple materials. These planarized heterogenous surfaces allow for orthogonal assembly chemistries to be run on the same substrate, opening possibilities for fabrication of more complicated molecular device architectures. Because our template stripping approach mirrors conventional wafer bonding, we discuss its prospects for scalable fabrication of substrates suitable for molecular electronic devices on an industry-compatible toolset.

2:15 PM EL12.05.03
Manipulation of Spin-States in All-Organic Di-Radicals Molecular Junctions Thomas Baum[1], Saleta Fernández[2], Diego Peña[2] and Herre S. van der Zant[1]; [1]TU Delft, Netherlands; [2]Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS) , Universidade de Santiago de Compostela, Santiago de Compostela, Spain

Graphene is believed to be an optimal material for a promising new generation of nanoscale devices using spin as information carrier, storage and

processing [**1**]. During the last years, atomically precise synthesis of poly-aromatic hydrocarbons (PAH) has been developed [**2**-**3**] allowing new possibilities to engineer their transport properties and controll the separations between the spins. The intrinsic pi-paramagnetism emerging spontaneously as radical states in open-shell graphene structures give rise to a more delocalized, mobile and isotropic magnetism than electrons in *d*-orbitals. Nonetheless, graphene-based nanomaterials also emerge as an ideal solution to combine excellent spin transport properties with large diffusion length and long coherence time needed for quantum spintronic applications with energy scales compatible with room-temperature operations.
We report on manipulation of spin-spin interactions for PAH di-radical molecules [**4**] in a mechanically controlled break junction (MCBJ) and in 3-terminal device (electro-migration break junction EMBJ) at low temperature. Magnetic fingerprints of the molecules manifest themselves by zero-bias peaks in the differential conductance spectra attributed to a Kondo resonance arising from hybridization of one of the radical electrons with the metallic electrodes and spin-flip inelastic electron tunnelling spectroscopy (IETS) steps originating from the singlet-triplet gap of the free electrons [**5**]. Varying the distance between the electrodes in the MCBJ affects the coupling strength and varying the gate voltage in the EMBJ affects the energy level alignment with the Fermi level of the electrodes. Thus, by mechanical manipulation and electrostatic gating the spin signature of the molecule can be adjusted and controlled. This study provides new insight on the interplay between magnetic fingerprints of all-organic molecules embedded in solid-state devices.

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This project received funding from the European Union Horizon 2020 research and innovation program under grant agreement N°863098 – SPRING. The molecules used were synthesized by the group of Diego Peña from Universidade de Santiago de Compostella.

2:30 PM *EL12.05.04
The Promise and Challenge of Bottom-Up Synthesized Carbon Electronics Yuxuan Cosmi Lin; Taiwan Semiconductor Manufacturing Company, Taiwan

Graphene nanoribbons (GNRs) synthesized from the bottom up with molecular precursors have enabled the capability of engineering the electronic, optical, magnetic and quantum physical properties with atomics scale precision, which promises novel functionalities and next-generation computing devices. This talk presents recent progress and remaining challenges of the technology integration of bottom-up synthesized GNRs into field-effect transistors (FETs). Several key technology components for GNR FETs are covered, include band-gap engineering, synthesis and alignment of long-length GNRs, achieving low-resistance electric contacts, and high-k gate stack integration. A statistical approach that combines theoretical modeling and experimental characterization is developed to evaluate and benchmark the device performance. Remaining challenges and future research directions are discussed for the further improvement of device performance of GNR FETs.

3:00 PM BREAK

4:00 PM EL12.05.06
Detection and Identification of SARS-CoV-2 Variants Using Single-Molecule Conductance Measurements Zahra Aminiranjbar[1], Mashari Alangari[2], Caglanaz Akin[3], Yiren Wang[4], M.P. Anantram[4], Ersin Emre Oren[3] and Josh Hihath[5]; [1]University of California, Davis, United States; [2]Hail University, Saudi Arabia; [3]TOBB University of Economics and Technology, Turkey; [4]University of Washington, United States; [5]Arizona State University, United States

Since the start of the 2019 pandemic (COVID-19), the development of rapid and cost-effective testing has been an ongoing effort to help combat this highly transmittable and infectious disease. Over the past two years, the virus has continued to mutate and evolve, and several variants of SARS-CoV-2 have emerged which have reduced the vaccines' effectiveness. Therefore, there is a significant need for surveillance of the SARS-CoV-2 variants of concern to track the spread of the disease and help to confine the virus. Currently, the standard identification method for the subvariants utilizes reverse-transcription polymerase chain reaction (RT-PCR). However, this method is not suitable for rapid, high throughput testing of large populations, it is costly, time-consuming, and requires expert staff. Here we present an alternative to RT-PCR based on single-molecule conductance measurements which open new avenues for sensitive and cost-effective detection of the SARS-CoV-2 variants of concern.
Previous studies using the single-molecule break junction (SMBJ) approach have demonstrated that this technique is capable of detecting and identifying RNA: DNA hybrids via their conductance values. This work focuses on identifying SARS-CoV-2 variants of concern based on the codon sequences that represent mutations in the spike protein. Our hypothesis is that using a specific DNA probe that is complementary to the RNA for every mutation would result in a specific conductance value that represents the presence of the variant in the sample. Therefore, we can detect and identify each variant in a mixed sample based on their unique electronic fingerprints.
We focus on the alpha, beta, and delta variants which according to the World Health Organization (WHO) are classified as SARS-CoV-2 variants of concern. We design a series of 12 base-pair DNA probes that contain the mutation and would bind to the corresponding RNA section of the alpha and beta variant genome block. Our experimental results indicate that in the presence of the mutation, the conductance value of the hybrid RNA: DNA sequence is significantly different from when there is no mutation present. We further utilize the XGBoost machine learning classifier to aid in the rapid detection of the SARS-CoV-2 variants. This work demonstrates the utility of the SMBJ technique for the accurate detection and identification of SARS-CoV-2 variants with the potential for real-time application.

4:15 PM DISCUSSION TIME

4:30 PM *EL12.05.08
Materializing Cognition - Information Processing with Cognitive Matter Wilfred G. van der Wiel[1,2]; [1]University of Twente, Netherlands; [2]University of Münster, Germany

Throughout history, man has exploited matter to carry out tasks well beyond his biological constraints. Starting from primitive tools with functionality solely derived from shape and structure, we have moved on to responsive matter that can change its properties upon external stimulus and even further to adaptive matter that can change its response depending on the environment. One of the grand scientific and intellectual challenges is to make matter that can actually *learn*. Such matter's behavior would not only depend on the here and now, but also on its past. It would have memory, autonomously interact with its environment and self-regulate its action. We may call such matter 'intelligent'.
Here we introduce the concept of "intelligent matter"[1] and discuss a number of experiments on disordered nanomaterial systems, where we make sure of "material learning" to realize functionality. We have shown that a 'designless' network of gold nanoparticles can be configured into Boolean logic gates

using artificial evolution[2]. We further demonstrated that this principle is generic and can be transferred to other material systems. By exploiting the nonlinearity of a nanoscale network of boron dopants in silicon, referred to as a dopant network processing unit (DNPU), we can significantly facilitate classification. Using a convolutional neural network approach, it becomes possible to use our device for handwritten digit recognition[3]. An alternative material-learning approach is followed by first mapping our DNPU on a deep-neural-network model, which allows for applying standard machine-learning techniques in finding functionality[4]. We also show that the widely applied machine-learning technique of gradient descent can be directly applied *in materia*, opening up the pathway for autonomously learning hardware systems[5]. Finally, we show that kinetic Monte Carlo simulations of electron transport in DNPUs can be used to reproduce the main characteristics and to depict the charge trajectories[6].

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SESSION EL12.06: Virtual Session I: From Molecules to Emerging Molecular Devices

Session Chairs: Maiken Mikkelsen and Farnaz Niroui
Tuesday Morning, April 25, 2023
EL12-virtual

8:00 AM *EL12.06.01
Opportunities and Challenges in Single-Molecule Sciences Xuefeng Guo; Peking University, United States

This talk will exemplify our on-going interest and great effort in developing efficient lithographic methodologies capable of creating molecular electronic devices through the combination of top-down micro/nanofabrication with bottom-up molecular assembly. These devices use nanogapped nanomaterials (such as silicon nanowire (SiNW) and graphene) as leads or probes formed by electron beam lithography and precise oxygen plasma etching. Through robust chemical linkages, functional molecular bridges terminated with active moieties are covalently wired into the functionalized graphene/SiNW nanogaps to form stable single-molecule junctions with desired functionalities. We have used these approaches to reveal the dependence of the charge transport of individual metallo-DNA duplexes on p-stacking integrity, and fabricate molecular devices capable of realizing label-free, real-time electrical detection of biological interactions at the single-event level, or switching their molecular conductance upon exposure to external stimuli, such as ion, pH and light.

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8:30 AM EL12.06.02
Tetrathiafulvalenes as Anchors for Building Highly Conductive and Mechanically Tunable Molecular Junctions Qi Zhou, Kai Song, Guanxin Zhang, Xuwei Song, Junfeng Lin, Yaping Zang, Deqing Zhang and Daoben Zhu; Institute of Chemistry, Chinese Academy of Sciences, China

In our work, we demonstrate that tetrathiafulvalene (TTF), which is an important building unit for functional materials, can act as a new anchor for molecular devices. We show that, in TTF-fused naphthalene diimide molecular wires, the sulfur atoms in TTF directly bind to gold electrodes and form single Au-molecule-Au junctions. The unique TTF-Au contacts created via Au-S bonding enable highly efficient hybridization of Au orbitals and molecular conducting π-channels, yielding strong electrode-molecule coupling and remarkably high conductance. Moreover, we introduce additional thiohexyl (SHe) anchors to the TTF unit and show that the multiple Au-S binding sites in these molecular wires offer mechanically switchable binding modes through either TTF-Au or SHe-Au interaction. This leads to mechanically tunable metal-molecule electronic coupling and conductivity in single molecule devices. These findings provide a new strategy for building highly tunable molecule-metal interfaces for molecular devices.

8:45 AM *EL12.06.03
Carbon Nanorings and Nanobelts for Molecular Devices Yaping Zang; Institute of Chemistry, Chinese Academy of Sciences, China

Carbon nanorings cycloparaphenylenes (CPPs) and carbon nanobelts (CNBs) are typical hoop-shaped nanocarbons that have unique radially oriented π-systems. This talk will summarize our recent work on incorporating these unique nanocarbons into molecular electronic devices using the scanning tunneling microscope-break junction technique. We show that, compared with traditional linear molecular devices, the hoop-shaped CPP and CNB based devices have significantly higher conductance. DFT-based calculations elucidate that the high performance of these devices arises from the distorted, radially π-conjugated molecular structures. These findings demonstrate the potential of using hoop-shaped conjugated nanocarbons to achieve unprecedented electronic performance, and may stimulate future design of nanoscale devices based on unconventional molecular geometries.

9:15 AM EL12.06.04
Electric Field Catalysis of Electrophilic Aromatic Substitution of Cycloparaphenylenes Junfeng Lin and Yaping Zang; Institute of Chemistry, Chinese Academy of Sciences, China

Electrophilic aromatic substitution (EAS), which involves the formation of charge-transfer complex between electrophiles and the electron-rich aromatic rings, is one of the most fundamental reactions in organic chemistry. Due to the relatively large energy barrier for the charge transfer activation, EAS reactions are often limited to systems containing highly activated (nucleophilic) nuclei or very strong Lewis acid catalysts. Here, instead of traditional chemical reagents, we demonstrate the utilization of an oriented external electric field (OEEF) to catalyze the EAS reactions based on the scanning tunneling microscope break junction technique. Using cycloparaphenylenes with unique radially π-conjugated structures as the aromatic substrates, we can apply the OEEF perpendicular to the aromatic ring, which is crucial for harnessing the field effect. Under a very mild condition (a voltage of <1 V), the applied OEEF can significantly accelerate the EAS by the otherwise unreactive Au electrophile, cleaving the inherently inert $C(sp^2)$-$C(sp^2)$ bond and leading to high-yield (~97%) formation of linear oligophenylenes terminated with covalent Au-C bonds. These results not only demonstrate the feasibility of OEEF catalysis of EAS, but also offer a way of exploring new mechanistic principles of classic organic reactions aided by OEEF.

SESSION EL12.07: Virtual Session II
Session Chairs: Pascal Gehring and Farnaz Niroui
Tuesday Morning, April 25, 2023
EL12-virtual

10:30 AM *EL12.07.01
Chemical Control Of Heat Transport And Vibrational Energy Redistribution In Molecules Gemma C. Solomon; University of Copenhagen, Denmark

Controlling heat flow is an important goal for materials, for example, to thermally insulate components or, conversely, to allow heat to rapidly dissipate. One area where this is technologically relevant is the microelectronics industry where computer chips are limited both by the challenges of miniaturization but also thermal management. At the same time, chemical control of heat transport is not part of traditional chemistry, where there has been much more focus on the electronic processes involved in making and breaking chemical bonds, so we cannot rely on established chemical knowledge to design new thermal management materials. Today, we need new methods and understanding to broaden our chemical intuition for thermal transport properties of molecules.
In this talk I will outline our efforts to develop chemical intuition for how we can control heat transport in molecules. While our understanding is far from complete, we can outline some general principles. Structural disorder in flexible systems, perhaps unsurprisingly, results in vibrational mode localization and reduced heat transport. While one might expect that breaking chemical bonds to yield non-bonded, self-assembled systems, would reduce heat transport it can also increase heat transport in certain cases. Finally, mass-disorder, for example from by changing to an inorganic complex instead of an organic molecule can be very effective at suppressing heat transport. Less clear are the effects of changing the structure of an organic molecule, for example between conjugated and saturated systems, leaving open a broad area of uncertainty as to ideal systems.

11:00 AM EL12.07.02
Thermocurrent Spectroscopy of Yu-Shiba-Rusinov States in Single-Molecule Junctions Serhii Volosheniuk[1], David Vogel[2], Christina Wegeberg[2], Marcel Mayor[2,3,4], Herre S. van der Zant[1] and Pascal Gehring[5]; [1]Delft University of Technology, Netherlands; [2]University of Basel, Switzerland; [3]Karlsruhe Institute of Technology (KIT), Germany; [4]Sun Yat-Sen University (SYSU), China; [5]Université Catholique de Louvain, Belgium

The interaction between magnetic impurities and superconductors leads to fascinating physical phenomena resulting from the competition between Kondo screening and Cooper pair formation [1]. To this end, individual magnetic impurities can form states within the superconducting gap, called Yu-Shiba-Rusinov (YSR) states [1,2]. YSR states are of great interest because they have the potential to realise topological superconductivity. Here we show that such YSR states form in a neutral and stable all-organic radical molecule coupled to proximity induced superconducting break-junction electrodes. We experimentally study the thermoelectric response [3] of the system at mK temperatures, both in the YSR regime and – by applying magnetic fields – in the Kondo regime [4]. Ultimately, we observe a two-fold increase of the thermoelectric efficiency which is induced by the YSR states. This study highlights the power of thermocurrent measurements as a new spectroscopic tool to study nanoscale devices, and reveals new strategies for engineering highly efficient thermoelectric energy conversion at cryogenic temperatures.

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11:15 AM EL12.07.03
Controlling Quantum Interference for Molecular Electronics Hatef Sadeghi and Sara Sangtarash; University of Warwick, United Kingdom

Thanks to their sub-10 nanometre size, molecules offer a fantastic platform for exploiting quantum effects at room temperature. Recently, it was shown that molecular wires can mediate long-range, phase-coherent tunnelling with remarkably low attenuation beyond a few nanometres, even at room temperature [1]. This opens up the possibility of using quantum interference (QI) to control the transport of electrons, spins and phonons through molecular junctions consisting of a single or a few molecules between electrodes.

In this talk I will present evidence for room-temperature QI in molecular junctions and discuss the agreement and disagreement between experiments and predictions based on phase-coherent quantum transport theory [2]. Then, I will discuss strategies to control QI in molecular junctions [3] including chemical and structural modifications of molecules, and the application of electric field or light. I will then discuss how these strategies can be used to improve the efficiency of thermoelectric materials for energy harvesting and cooling, to improve spin filtering through molecules for quantum information applications, and to selectively sense biological species.

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11:30 AM *EL12.05.05
Robust Resistive and Mem-Devices for Neuromorphic Circuits T. Venky Venkatesan[1,2]; [1]University of Oklahoma, United States; [2]National Institute of Standards and Technology, United States

Artificial intelligence (AI) has been heralded as the flagbearer of the fourth industrial revolution but comes with a cost and that is computing power. It is projected that by 2040, we will need more computing energy than the total energy we can produce now. So, we need devices that can offer higher computing/ storage density with low energy consumption like neurons. We are addressing these challenges using oxide and molecular-electronic based memristors, which enable us to overcome the von Neuman bottleneck by co-locating the memory and computing functions on the same device, as in neuromorphic computing.
I will discuss a variety of strategies for forming oxide based memristors using different phenomena- band filling and creating a quasi-conduction band, using oxygen vacancies to create conductive percolation, using metal-insulator transitions, or using asymmetric tunneling at a ferroelectric barrier. The relative merits of the various approaches will be detailed.
In addition, I will touch upon memristive devices and circuits made from an azo-aromatic complex with extra-ordinary reproducibility, robustness, and scalability. These devices have been shown to switch with energies approaching atto-joules with measured switching times shorter than 5 ns. By using a simple cross bar array, we have shown that these devices perform with an energy-speed product 5000 times that of a state-of-the-art CMOS circuit.

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SYMPOSIUM

April 11 - April 26, 2023

Symposium Organizers
Ana Arias, University of California, Berkeley
Paschalis Gkoupidenis, Max Planck Institute
Francesca Santoro, Forschungszentrum Jülich/RWTH Aachen University
Yoeri van de Burgt, Technische Universiteit Eindhoven

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* Invited Paper
\+ Distinguished Invited

SESSION EL13.01: Neuromorphic Devices and Systems I
Session Chairs: Paschalis Gkoupidenis and Yoeri van de Burgt
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3005

10:30 AM *EL13.01.01
Thousands of Conductance Levels in Memristors Monolithically Integrated on CMOS J. Joshua Yang[1,2,3]; [1]University of Southern California, United States; [2]University of Massachusetts Amherst, United States; [3]TetraMem Inc., United States

Neural networks based on memristive devices have shown potential in substantially improving throughput and energy efficiency for machine learning and artificial intelligence, especially in edge applications. Because training a neural network model from scratch is very costly, it is impractical to do it individually on billions of memristive neural networks distributed at the edge. A practical approach would be to download the synaptic weights obtained from the cloud training and program them directly into memristors for the commercialization of edge applications. Some post-tuning in memristor conductance may follow afterward or during applications. Therefore, a critical requirement on memristors for neural network applications is a high-precision programming ability to guarantee uniform and accurate performance across a massive number of memristive networks. This translates into the requirement of many distinguishable conductance levels on each memristive device, not just lab-made devices but more importantly, devices fabricated in foundries. High precision memristors also benefit other neural network applications, such as training and scientific computing. Here we report over 2048 conductance levels, the largest number among all types of memories ever reported, achieved with memristors in fully integrated chips with 256x256 memristor arrays monolithically integrated on CMOS circuits in a standard foundry. We have unearthed the underlying physics that previously limited the number of achievable conductance levels in memristors and developed electrical operation protocols to circumvent such limitations. These results reveal insights into the fundamental understanding of the microscopic picture of memristive switching and provide approaches to enabling high-precision memristors for various applications.

11:00 AM *EL13.01.02
Materials and Device Concepts Based on Organic Electrochemical Transistors for Sensing and Signal Processing Jonathan Rivnay; Northwestern University, United States

Organic mixed ionic/electronic conductors (OMIECs) have gained considerable interest in bioelectronics, power electronics, circuits and neuromorphic computing. These organic, often polymer-based, semiconductors rely on a combination of ionic transport, electronic transport, and high volumetric charge storage capacity. Despite recent progress and a rapidly expanding library of new materials, the understanding of stability and transport/coupling of ionic and electronic carriers remain largely unexplored. We highlight recent synthetic and processing approaches used to tailor electrochemical device properties revealing new classes of OMIEC active materials, as well as new opportunities enabled by such advances. Control of ionic transport and trapping for example presents a promising avenue towards the development of non-volatile electrochemical transistors. We show that additives in prototypical conducting polymers can lead to neuromorphic function which can mimic basic neural function. In addition, the bulk transport properties of OMIECs enable device concepts that achieve co-localization of sensing with signal processing including amplification of electrophysiological and biochemical sensors, and devices with highly non-linear responses for spiking neurons.

11:30 AM EL13.01.03
Hysteresis and Temperature-Dependence of Organic Electrochemical Transistors Lukas M. Bongartz[1], Matteo Cucchi[2,1], Anton Weissbach[1], Tommy Meier[1], Hans Kleemann[1] and Karl Leo[1]; [1]Technische Universität Dresden, Germany; [2]Neuro-X Institute, EPFL, Switzerland

Due to their synaptic functionality of interacting electronic and ionic charge carriers, organic electrochemical transistors (OECTs) are highly attractive candidates for a new generation of organic neuromorphic devices. While such systems are regularly realized by a liquid electrolyte on an organic mixed ionic–electronic conductor, this very feature of a liquid operation represents a severe challenge for employing OECTs in dense integrated circuits. By using a solid-state electrolyte composed of an ionic liquid in a photopatternable polymer matrix, we realize devices of outstanding performance in terms of high on-off-ratio ($\sim 10^5$), low threshold voltage (<200 mV) and a subthreshold swing close to the thermodynamic limit of 61 $\mathrm{mVdec^{-1}}$. The devices are further characterized by a pronounced hysteresis in their transfer curves, for which we define an empirical parameter that allows for straightforward and well-fitting description of its strength. Investigating it as a function of various parameters, we find a significant dependence on the scan rate, in which two regimes can be identified: for descending scan rates, we first see the hysteresis to increase until a certain limit, after which it gradually decreases again to a minimal, non-zero degree. We show that the paths of the hysteretic transfer curve remain separate even after hours, and thus present themselves as two separate states that give the OECT an inherent memory functionality.

Given the remanent nature of this share of hysteresis, we use the solid OECT system for the first systematic, temperature-dependent characterizations of this device class. These reveal several special insights into the thermodynamics of the system, two results of which are particularly impressive. First, we find a non-linear decreasing hysteresis with temperature. Second, we observe that the subthreshold swing decreases in a certain range with increasing temperature. This behavior is contrary to what is expected from MOSFET theory and thus represents a reverse Boltzmann dependence. To study this finding, we delve into the thermodynamics of the system and describe the underlying Gibbs free energy via the interaction of neutral and polaronic species. We identify the relative strengths of these interactions as the cause of a bistable Gibbs function and show that the model can well explain the dependencies of both the hysteresis and the subthreshold swing.

Considering the importance of stable hysteresis as a memory functionality in neuromorphic devices, the explanation of such via suitable models is of considerable significance. Using the presented framework, we can derive statements about device optimizations from the Gibbs free energy function and thus point out directions to realize *e.g.*, transistors of certain hysteresis and switching behavior in a targeted way. As such, we also show ways to specifically realize hysteresis-free solid OECTs by introducing external components to the system.

We consider the results of these investigations to greatly enhance the understanding of OECTs and finally accelerate their usage in advanced applications.

11:45 AM EL13.01.04
Stabilizing Neural Networks on Forgetful Organic Neuromorphic Devices Daniel Felder[1,2], Katerina Muche[2], John Linkhorst[2] and Matthias Wessling[2,1]; [1]DWI–Leibniz Institute for Interactive Materials, Germany; [2]RWTH Aachen University, Germany

Organic neuromorphic device networks can accelerate neural network algorithms and directly integrate with microfluidic systems or living tissues. Proposed devices based on the bio-compatible conductive polymer PEDOT:PSS have shown high switching speeds and low energy demand. However, as electrochemical systems, they are prone to self-discharge through parasitic electrochemical reactions. Therefore, a neural network's synapses forget their trained conductance states over time. In this work, we integrate single-device high-resolution charge transport models to simulate entire neuromorphic device networks and analyze the impact of self-discharge on network performance. Furthermore, we search for robust algorithms for artificial and spiking neural networks through model-based hardware-algorithm co-design. The simulations reveal that artificial neural networks are affected differently by self-discharge-induced weight drift depending on their structure. For example, a single-layer nine-pixel image classification network commonly used in experimental demonstrations shows no significant impact of self-discharge during the first 10 hours. On the other hand, a multi-layer network for the approximation of the circle function is shown to degrade significantly over twenty minutes with a final mean-squared-error loss of 0.4. For artificial neural networks, we propose to counter the effect by periodically reminding the network based on a map between a synapse's current state, the time since the last reminder, and the weight drift. With a map obtained through validated simulations, this method can reduce the effective mean-squared-error loss to below 0.1, even with worst-case assumptions. On the other hand, spiking neural networks are shown to stabilize their weights within a narrow range through spike-timing-dependent plasticity and have the potential to compensate for the effects of self-discharge with optimized algorithms fully. Electrochemical organic neuromorphic devices have yet to be integrated into larger device networks. This work predicts their behavior under nonideal conditions, proposes two strategies to mitigate the worst-case effects of parasitic self-discharge, and opens pathways toward implementing fast and efficient neural networks on organic neuromorphic hardware.

SESSION EL13.02: Materials for Neuromorphic Devices I
Session Chairs: Paschalis Gkoupidenis and Yoeri van de Burgt
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3005

1:30 PM *EL13.02.01
Thermodynamic Engineering of Oxygen Transport in Materials for Nonvolatile Resistive and Electrochemical Memory Yiyang Li; University of Michigan, United States

In-memory computing using analog resistive memory promise substantial improvements in the energy efficiency of deep neural networks. Valence-change memory (VCM) and electrochemical random-access memory (ECRAM) are two promising analog resistive memories that stores information through the migration of oxygen vacancies. In this work, we show how materials thermodynamic engineering and especially phase separation can be used to control oxygen transport and create nonvolatile memory devices. We first investigate two-terminal filamentary VCM, and show that the widely used transport model based on Fickian diffusion does not accurately describe oxygen migration during retention. Instead, oxygen transport is governed by phase separation and spinodal decomposition, which enables certain resistance states to be indefinitely nonvolatile. Next, we apply these thermodynamic principles to design three-terminal ECRAM cells and achieve the first nonvolatile ECRAM cell that operate under short circuit configurations without a switch.

2:00 PM EL13.02.02
Tunable Intervalence Charge Transfer in Ruthenium Prussian Blue Analogue Enables Stable and Efficient Biocompatible Artificial Synapses
Donald A. Robinson, Michael Foster, Raga Krishnakumar, Mark D. Allendorf and A. A. Talin; Sandia National Laboratories, United States

Reversible electrochemical doping of ruthenium hexacyanoruthenate, a type of Prussian blue analogue (PBA), enables the on-demand tuning of electronic conductivity by more than four orders of magnitude. Inkjet-printed electrochemical random access memory (ECRAM) devices based on Ru-PBA and lithium- or proton-conducting ionogel electrolytes exhibit excellent switching efficiency and long-term memory retention, important characteristics for analog artificial synapses in neuromorphic circuits. We also demonstrate excellent biocompatibility with live neurons and the use of Ru-PBA ECRAM devices to detect dopamine, promising first steps toward connecting artificial and biological neural networks. In-situ probing of metal-metal charge transfer by UV/Vis/NIR absorption spectroscopy reveals a switching mechanism whereby electrochemically tunable valence mixing between N-coordinated Ru sites controls the carrier concentration and mobility, as independently supported by both Marcus-Hush electron transfer theory and more conventional band structure predictions from DFT. The experimental agreement achieved by both theoretical approaches supports a general mechanistic picture that intramolecular charge transfer reactions, more commonly studied in polynuclear mixed valence small molecules, are central to electronic conductivity in extended coordination frameworks.

2:15 PM EL13.02.03
Brain-Inspired Biomolecular Networks for Reservoir Computing Joshua Maraj and Stephen A. Sarles; The University of Tennessee, Knoxville, United States

Biomolecular structures assembled using the droplet interface bilayer (DIB) technique of lipid coated aqueous droplets in a hydrophobic medium allow construction of modular aqueous compartments separated by artificial lipid membranes. These membranes can be functionalized with active biomolecules to enable sensing and information processing, including but not limited to transmembrane proteins. When doped with alamethicin (Alm) or monazomycin (Mz), DIBs become volatile memristors that exhibit voltage-dependent short-term synaptic plasticity (STP). This property has led to their use as artificial synapses for neuromorphic hardware implementations of artificial intelligence algorithms, such as reservoir computing (RC).
RC is an algorithm that uses specific device properties such as nonlinearity and fading STP to simplify classification of dynamic signals. We have previously demonstrated that individual Mz-doped DIB biomolecular synapses (BS) are suitable for use in RC classification and dynamic function learning, but little research has been done into forming BS networks for use in RC. An advantage of this approach is the ability to combine sensing and information processing into elements of the same network. Due to the customizability of individual compartment contents, sensing functions can be assigned to specific network locations by including thermoreceptors, mechanoreceptors, etc. into those droplets, but not others. In this work we present methods for rapid assembly and characterization of BS networks and schema for use in an RC framework, as well as hypothetical architectures for multimodal sensing.
For assembly of BS networks, we develop a multi-welled “egg crate” style structure to hold droplets stationary to both maintain contact with neighboring droplets and electrodes in the bottom of each well. These electrodes are controlled and measured by multichannel NI-DAQs. Tested network structures will include linear networks, multilayer perceptrons of linear layers, and hexagonally packed clusters. To test the RC capability of each network, we use the UCI Epileptic Seizure Recognition Data Set to stimulate the reservoir. Additionally, using real world sensor data from a morphing airfoil in a wind tunnel, we input these signals as voltages into the droplet network and measure the conductance states of each node to classify and predict gusting behavior. For a visual task, we classify a custom set of 5x5 digits. We hypothesize that using a combination of Alm and Mz will yield higher accuracy than either alone in most cases.
The above cases represent an electrical task, a mechanosensitive task, and a light sensitive task. In the future, these signals can be directly processed and classified by including the relevant transmembrane sensing channels used in organisms. Ongoing work seeks to stabilize these networks into devices that may be used in-device.

2:30 PM *EL13.03.01
Organic Nervetronics for Next-Generation Computing and Nerveprosthetics Tae-Woo Lee; Seoul National University, Korea (the Republic of)

Real-time information processing is an important feature of biological nerves. To implement such properties (event-driven, parallel operation, etc.) artificially, organic nervetronics have been upsurged. Furthermore, artificial synapses can be combined with sensors and actuators to emulate the functions of biological sensory and motor neurons with a simple circuit structure. In addition, it consumes 10^{-6} times less energy in operation than a CMOS-based von Neumann computing system. This organic neural electron can become a new strategy for soft robotics, next-generation computing, and neuroprosthetics by imitating biological neuroplastic events which can replace the damaged nerves.
First, we controlled the microstructure of various organic semiconductors, and blended two diketopyrrolopyrrole (DPP) based semiconductor with different side chain to achieve long-term plasticity. Also, by producing trapping site for ions, ion-gel gated artificial synapses showed extremely long-term retention time.
Furthermore, we developed an artificial nerve that emulates biological afferent and efferent nerve. The connection of biological organs and artificial afferent nerves shows a hybrid reflex arc that shows future applicability for neural prostheses. The movement of the detached cockroach leg can be controlled by external sensory information. Also, an artificial auditory system was developed by integrating a triboelectric nanogenerator an artificial

synapse. The optoelectronic artificial sensorimotor nerve emulates optogenetically engineered neurons and synapses. The contraction of artificial muscles well imitates biological muscle contraction. The stretchable nervetronics reproduced coordinated bipedal movement and practical motions such as 'kicking a ball' and 'walking/running' in living animals. Neuroplasticity-based artificial nerves can be not only used for next-generation computing systems but also restore the biological afferent and efferent nerve response which can pave a new way to future neuromorphic computing.

3:00 PM BREAK

SESSION EL13.03: Adaptive Sensing and Biointerfacing I
Session Chairs: Ana Arias and Francesca Santoro
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3005

3:45 PM EL13.03.02
An Artificial Sensory Neuron System Based on Pieozo-Ionic Synaptic Transistors with Suspended Porous Ion Gel Yun Goo Ro, Dahun Lim, Cheolhong Park, Youngoh Lee, Youngsu Lee and Hyunhyub Ko; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Electronic skin (e-skin) composed of sensors mimicking human mechanoreceptors became an indispensable technology in wearable electronic systems, robots, and human-machine interfaces (HMIs). To embody humanoid robots that have human-level perception and cognition, recent endeavors are devoted to the development of intelligent e-skin. Humans are capable of remembering and learning from external information by brain neurons that communicate with each other through synapses. In response to external stimuli, synapses are strengthened or weakened and the connections between neurons are controlled. Through this synaptic process, humans have persistently evolved cognition and intelligence by adapting to different environments. Artificial synaptic device that mimics a biological synapse is an emerging electronic platform that can realize human-like robots when integrated with e-skin.
We report an artificial sensory neuron system composed of an artificial synapse and a mechanoreceptor that allows tactile perception and learning based on a pressure sensitive organic electrochemical transistor (OECT). The OECT is composed of an organic semiconductor poly(3-hexylthiophene-2,5-diyl) (P3HT) as a channel and a piezo-ionic gel of ferroelectric polymer poly(vinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) and ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide) as both a gate dielectric layer and a pressure sensing layer. To increase the pressure sensitivity, the piezo-ionic gel with the porous structure is utilized for the effective structural deformation and localized stress concentration in response to pressure. In addition, a suspended gate dielectric structure, where the piezo-ionic gel is floating above the channel with the help of spacers having an air gap in between, is adopted. When the piezo-ionic gel contacts the semiconductor channel under external pressure, spontaneous piezopotential is created inside the polymer matrix, which induces movements of ions and formation of electric double layers (EDLs) at each gate electrode/ion gel and ion gel/channel interfaces, and consequent modulation of the drain current of the channel. The suspended gate dielectric structure induces the abrupt generation of EDLs under application of pressure, enhancing the pressure sensitivity. In contrast to the conventional synaptic transistors that require external gate bias for the transistor operation, in our device, piezopotential created by pieozo-ionic gel from external stimuli replaces the external gate bias, enabling low energy consumption of the device. Moreover, monolithic integration of the tactile sensing component and the synaptic transistor, where they are stacked vertically, enables high density integration of pressure sensitive synaptic transistor per unit area. In particular, the precise control of ion migration and trapping in the channel enables an artificial sensory neuron system exhibiting not only highly-sensitive detection of external pressure with different pulse frequencies, but also excellent synaptic learning behaviors such as excitatory postsynaptic current (EPSC), paired-pulse facilitation (PPF) and transition of short-term plasticity (STP) to long-term plasticity (LTP). For the potential application in humanoid robots, we integrate our OECT device on a robotic hand and demonstrate that the robotic hand can respond and adapt to different types of external pressure.

4:00 PM *EL13.03.03
2D+ and 3D Electrodes Provide Tight Connections with Neurons Andreas Offenhaeusser, Pegah Shokoohimehr, Bogdana Cepkenovic and Jamal Shihada; Forschungszentrum Julich, Germany

Our understanding of the brain and general neural systems is based on models of increasing complexity, from 2D cell culture to organoids and organotypic slices to animal models. These models provide significant insight into neuronal information processing in the brain, but require advanced electrophysiological measurement technologies to achieve long-term stable recordings with single-cell and millisecond space-time resolution. Thus, challenges remain to study information processing between neurons with high spatiotemporal resolution and high signal-to-noise ratio (SNR). These challenges are overcome by well-established planar multichannel devices, but at the expense of signal-to-noise ratio. Without sufficient electrode-cell coupling, planar microelectrode arrays (MEAs) provide low-amplitude signals that are difficult to correctly assign by spike sorting algorithms. Furthermore, the unresolved subthreshold signals lose valuable information that is essential for direct estimation of synaptic weights and correct generation of connectivity matrices in neural networks.

To yield better cell-electrode coupling, numerous vertical nanostructures and nanoelectrodes have been developed by several groups. Here we present the concept of nanocavity (NC) MEAs with vertical nanostraws. High aspect ratio nanostraws (NS) were engineered to initiate tight cell-structure coupling, while the nanocavity reduces the electrode impedance. This combination yields a spontaneous tight mechanical coupling and results in long-term recordings with increased signal amplitude, with no poration-inducing external forces or surface functionalization. Moreover, simultaneous patch-clamp and MEA recordings of the coupled neuron directly demonstrated the capability of our device to record post-synaptic potentials. Here we show that PSP resolution persisted throughout the measurements, indicating a stable and long-term subthreshold amplitude sensitivity.

Simultaneous electrical recordings with good spatial and temporal resolution from 3D neuronal structures (organoids or organotypical slices) is also technological limited. Here we present our recent developments to overcome this limitations by 3D MEA which allow the recording from inside the neuronal tissue.

4:30 PM *EL13.03.04
Optical Detection of Neuroelectric Signals Using Electrochromic PEDOT Bianxiao Cui; Stanford University, United States

Neurons encode input and output information through electrical signals. Optical detection and imaging of electric activities provide unprecedented spatial flexibility and parallelization. In the last decade, the advancement of voltage-sensitive fluorescent proteins, and small potentiometric dyes, has drastically enhanced the capability of optical recording of electrical activity in cells. However, the use of fluorophores requires membrane insertion and suffers from photobleaching, phototoxicity, and limited time resolution. We exploit the unique physical properties of electrochromic PEDOT material, whose optical properties can be modulated by the applied electric potential. Combined with sensitive optical detection, we developed an electrochromic optical recording (ECORE) technique that achieves label-free and non-perturbative detection of action potentials in neurons, cardiomyocytes, and brain slices.

SESSION EL13.04: Poster Session
Session Chairs: Paschalis Gkoupidenis and Yoeri van de Burgt
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL13.04.01
Optically Stimulated Synaptic Transistor using Polyimide and Indium-Gallium-Zinc Oxide Co-Sputtered Layer for Flexible Neuromorphic Device Jong Hyuk Ahn, Min Seong Kim, Jong Bin An, Kunho Moon, Sujin Jung and Hyun Jae Kim; Yonsei University, Korea (the Republic of)

Recently, light stimulation-based synaptic devices are attracting attention as artificial neuromorphic systems due to their capability to mimic the functions of visual neurons, such as light recognition and image processing. These devices have advantages, such as wide bandwidth, low crosstalk, and high processing speed, compared to electrical stimulation-based synaptic devices. So far, various kinds of materials including carbon nanotubes, quantum dots, organics, oxide semiconductors, and halide perovskites have been researched for the realization of optoelectronic synaptic devices. Among them, oxide semiconductors are considered as one of the promising materials, due to their superior characteristics of simple, large area manufacturing capability coupled with excellent electrical properties. However, most oxide semiconductors cannot absorb long wavelength visible light because of their large optical bandgap (> 3.0 eV), so additional light absorbing layer is essential for detecting full range of visible light. In this paper, we proposed a facile method for fabricating optoelectronic synaptic transistor in which polyimide (PI) and indium-gallium-zinc oxide (IGZO) co-sputtered layer (PICL) was introduced for visible light absorption. PI is an organic material that can reduce the brittle nature of oxides, which can open up the potential of applicability to flexible devices, and also has the advantage of being applicable to vacuum sputtering process.

We compared the persistent photoconductivity (PPC) of the IGZO thin-film transistor (TFT) and the PICL optoelectronic synaptic transistor after illumination of red-light pulses of 1 mW/mm^2 intensity, 0.2 Hz frequency. In the case of the IGZO TFT, the drain current (I_{DS}) was maintained at 4.48×10^{-13} A for 400 s. In the case of the PICL optoelectronic synaptic transistor, the I_{DS} continued to increase during the cycle of 400 s, from 5.86×10^{-10} A to 2.71×10^{-7} A. Unlike the IGZO TFT, the PICL optoelectronic synaptic transistor showed PPC characteristics. PPC is due to the slow recombination speed of carriers, generated by light, when the light is turned off. PI and IGZO co-sputtering process formed sub-gap states, such as uncoordinated oxygen species, metal hydroxides, hydrogen anions, and organic components inside the IGZO bandgap, and these sub-gap states attributed to the PPC in the PICL optoelectronic synaptic transistor.

Synaptic functions including excitatory postsynaptic current (EPSC), paired pulse facilitation (PPF), and short/long term memory (STM/LTM) behaviors of the PICL optoelectronic synaptic transistor were demonstrated. EPSC of the PICL optoelectronic synaptic transistor was measured under illumination of a single red-light pulse of 5 mW/mm^2 intensity, 0.2 Hz frequency. After applying the light pulse, the I_{DS} sharply increased from 0.50×10^{-10} A to 0.57×10^{-8} A. After turning off the light, the I_{DS} gradually decreased and converged to 4.41×10^{-9} A. When the light is turned off, electrons excited by light into the conduction band of the IGZO channel layer start recombination with holes in the valence band. PPF index of the PICL optoelectronic synaptic transistor was 192.6% under illumination of red-light pulses of 5 mW/mm^2 intensity, 0.8 Hz frequency. The I_{DS} of the 1st EPSC and 2nd EPSC was 2.69×10^{-9} A and 5.18×10^{-9} A, respectively. The I_{DS} decayed right after the light was turned off and converged to 2.78×10^{-9} A. Both STM/LTM behaviors were measured under illumination of red-light pulses of 10 mW/mm^2, 0.05 Hz frequency, and 5/20 (STM/LTM) pulse numbers. The I_{DS} of the 1st EPSC, 5th EPSC, and 20th EPSC were 1.10×10^{-11} A, 8.88×10^{-9} A, and 1.21×10^{-7} A, respectively. From the STM result, the I_{DS} decayed sharply right after turning off the light, whereas the LTM result showed much slower decay of the I_{DS}. These results showed the strong potential of the PICL optoelectronic synaptic transistor in the field of photonic neuromorphic systems.

5:00 PM EL13.04.02
Quantum Dot Embedded Photonic Synapse-Based Biomimetic Autonomous Light Modulation System Seongchan Kim[1,2], Hong Chul Moon[3], Sohee Jeong[4] and Jeong Ho Cho[5]; [1]Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of); [2]The Pennsylvania State University, United States; [3]University of Seoul, Korea (the Republic of); [4]Sungkyunkwan University, Korea (the Republic of); [5]Yonsei University, Korea (the Republic of)

In order to perceive objects clearly, humans receive an appropriate amount of light through the light modulation response. In this study, we fabricated a biomimetic autonomous light modulation system that mimics the pupil and corneal reflections. For the fabrication, the photonic synapse was designed by embedding quantum dots in a metal oxide semiconductor layer. Here unlike other quantum dot based photonic synapses, the introduction of quantum dots can improve the inhibitory properties of photonics synapse. Subsequently, we emulate the pupillary light reflex through the incorporation of the quantum dot embedded photonic synapse, electrochromic device, and CMOS components. Moreover, corneal reflex was stimulated through the connection between a solenoid-based eyelid and the pupillary light reflex system. The system capable of perceiving an appropriate amount of light through autonomous light modulation presents a platform for biomimetic prosthesis.

5:00 PM EL13.04.03
Electrochemically Driven One-Body Torsional Artificial Muscles from Polymer-Coated Carbon Nanotube Yarn Seongjun Kim, Jae Sang Hyeon and Seon Jeong Kim; Hanyang University, Korea (the Republic of)

Torsional artificial muscles are being developed to replace electric motors in the field which needs miniaturization. Among the various types of torsional muscles, electrochemical torsional muscles have many advantages including fast reaction, easy control, high energy efficiency, and a natural latching state. For the electrochemical artificial muscle, carbon nanotubes (CNTs) are one of the best materials due to their remarkable mechanical strength and high capacitance. Previously reported electrochemical torsional CNT muscle used a CNT yarn made by twist insertion into the sheets. These CNT muscles showed great rotating performance. However, these muscles could only use a half of the available voltage range for actuation, which means that only one of the positive and negative voltage ranges could be used, so their rotation performance is limited. In addition, counter and reference electrodes made it difficult to make a compact muscle system. To solve these problems, we demonstrate a torsional muscles which rotate in one direction throughout the whole available voltage range. By coating the CNT yarn with an ion-exchange polymer, poly(sodium 4-styrenesulfonate) (PSS), the potential of zero charge of CNT yarn shifts to the outside to the electrochemical stability window of aqueous electrolytes. It means that only cations participate to a muscle rotation for the whole voltage range, resulting the rotation in the one direction from -1 to +1 V. The rotation degree and speed of the PSS-coated CNT muscles are higher than the neat CNT muscles, since the voltage range is doubled. Moreover, the PSS-coated CNT muscles are easy to make a compact one-body structure which consists of upper and lower muscles. The upper muscle and the lower muscle of the pedal rotates in the opposite direction when a voltage is applied to the one-body muscle system. One muscle works as electrochemical and mechanical counter for the other muscle, so the rotation of the pedal is maximized and its rotation also has high reversibility. This high-performance and one-body torsional muscle is useful for various applications, such as microbotics and microfluidics.

5:00 PM EL13.04.04
Gel Mechanoreceptor Sensor Inspired by Merkel Disk Kyoung-Yong Chun, Seunghwan Seo and Chang-Soo Han; Korea University, Korea (the Republic of)

The tactile sensor existing in human skin is a complex and efficient biosensor. Many researchers have been inspired by skin sensors and have manufactured advanced tactile sensors through the development of various materials and structures. In this study, the signal types of slow adapting (SA) and rapid adapting (RA), which are one of the characteristics of the skin sensor, were analyzed according to the material and structure of sensors. Also, the optimization process was described. For the experiments poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFe) gel was used to manufacture the self-powered sensor, and copper and Ag wire were used as electrodes. For pressure sensing, PVC gel electrolyte adding ionic liquid was prepared and used. Basically, PVDF-TrFe gel and PVC gel were applied to obtain RA and SA signals, respectively. We tried to optimize the sensor sensitivity through the optimization of PVC ion gel electrolyte.

5:00 PM EL13.04.05
Temporal Information Decoding with Organic Electrochemical Memory Transistors Yuyang Yin, Shaocong Wang, Zhongrui Wang and Paddy K. L. Chan; The University of Hong Kong, Hong Kong

In the big-data era, information processing heavily relies on advances in computing methods and hardware. Being a promising contender for new-generation computing hardware, neuromorphic devices manifest better energy efficiency compared to traditional CMOS-based digital systems by collocating the memory and processing units in a bio-inspired manner. Organic electrochemical transistors (OECTs) possess rich nonlinear dynamics, such as short-term plasticity, which enables integrating of temporal inputs with a fading memory. This property favors time-domain signal processing using reservoir computing, which allows classification or prediction at a substantially low training cost. In this talk, we will demonstrate how to use the OECT memory to classify human electrophysiological signals. PEDOT:Tos/PTHF based OECT devices are employed as reservoir computing hardware to encode images or biological signals by tailoring the dynamics of the devices. Devices with different channel dimensions can discriminate different temporal inputs encoded in the form of voltage pulse trains and can further recognize binary digit patterns and decode electromyography (EMG) signals at decent successful rate. Such reservoirs, featuring multiple memristive devices with different dynamics, would provide better adaptability and generality in handling complex temporal data.

5:00 PM EL13.04.06
Neuromorphic Device Based on Glycoprotein Extracted from Epithelial Mucus for Skin-Attachable Electronics Kunho Moon, Sung Min Rho, Sujin Jung, Jong Hyuk Ahn, Youjin Seo and Hyun Jae Kim; Yonsei University, Korea (the Republic of)

As technological advances are heading toward hyper-connectivity between entities, an unprecedented amount of data is being processed. Thus, conventional von Neumann architecture is gradually reaching its intrinsic limit called the 'von Neumann bottleneck' where the system's throughput is degraded due to the physical separation between processing and memory units. Inspired by human brains consisting of neurons and parallelly connected synapses, neuromorphic devices capable of multilevel storage and data processing at a single device level with low power consumption are expected to resolve the bottleneck issue. While several attempts are being made to integrate neuromorphic devices in various applications, it is also the case for skin-attachable healthcare monitoring devices for remote diagnostics. For such devices to be realized, several requirements including biocompatibility and flexibility should be met, which can hardly be achieved using inorganic materials like silicon.
In this work, organic material called mucin, a type of glycoprotein prevalent in the epithelial mucus of most animals was introduced as an active layer of a two-terminal neuromorphic device or a neuromorphic memristor. The fabricated device has an Mg/mucin/p^+-Si structure of metal-insulator-metal configuration while the mucin layer was deposited by a simple spin-coating technique. The utilization of two-terminal devices as neuromorphic memristors has been extensively studied due to their structural resemblance with biological synapses. The top and bottom electrodes each correspond to pre- and post-synapses, and the modulation of neural connectivity is emulated by conductivity adjustment of an active layer with an input voltage pulse. Several synaptic functions including excitatory post-synaptic current (EPSC), paired-pulse facilitation (PPF), long-term potentiation (LTP), and long-term depression (LTD) were successfully emulated with the mucin-based neuromorphic memristor.
Applying a 1.5 V, 10 ms voltage pulse to the top electrode has generated a 55.0 µA EPSC, characterized as a sudden increase in current level and immediate return close to the initial level but with a slight increment. While EPSC corresponds to the short-term memory (STM) behavior of the human brain, PPF property was further tested to demonstrate STM to long-term memory (LTM) transition. 1.5 V, 10 ms voltage pulses were consecutively applied with 10 ms intervals between them, resulting in increased EPSC from 55.0 to 67.1 µA and thereby achieving the PPF index of 122% (PPF index = $A_2/A_1 \times 100(\%)$, A_n: Peak current of the n^{th} EPSC). LTP and LTD properties were finally examined using 10 consecutive 1.5 V positive voltage pulses and -1.0 V negative voltage pulses. The current level gradually increased and decreased with repetitive positive and negative voltage pulses, and this tunability of the current level well resembles the memory behavior of biological synapses.
An X-ray photoelectron spectroscopy (XPS) depth analysis was conducted to figure out the mechanism of the synaptic behavior of the device. The Mg *2p* spectrum was deconvoluted to the Mg-Mg peak centered at 49.6 ± 0.2 eV and the Mg-O peak centered at 50.7 ± 0.2 eV. The area percentage of the Mg-O peak was larger as 57.5% for the Mg/mucin interfacial site, indicating the formation of the Mg oxide layer. As the diffusion coefficient of Mg (24.9×10^{-6} m^2/s) is known to be larger than that of O (4.3×10^{-9} m^2/s) in an Mg oxide system, migration of Mg ions rather than oxygen vacancies is thought to contribute to the formation and rupture of Mg ion-based conductive filament (CF) depending on the polarity of applied voltage pulses. In this regard, the gradual formation and rupture of CF are assumed to be visualized as potentiation and depression of mucin-based neuromorphic memristor. Based on these results, it is strongly believed that mucin-based neuromorphic memristors can be applied to future skin-attachable healthcare monitoring devices.

5:00 PM EL13.04.07
Midinfrared (MIR) Triggered Photoacoustic Film for Neuromodulation Zhiyi Du, Mingsheng Li, Guo Chen, Maijie Xiang, Nan Zheng, Chen Yang and Jixin Cheng; Boston University, United States

Photoacoustic has been shown as an emerging method for imaging and cellular modulation in biomedical applications. Up to this date generation of photoacoustic signals in photoacoustic agents and materials relies on absorption based on the electronic transitions in visible range such as gold nanoparticles or NIR range such as carbon based materials. However, operation in these wavelengthes will also interfere with other imaging modality using the same range. For example, successfully photoacoustic modulation has been achieved using carbon materials that broadly absorb while quality of Ca imaging when recording neuron responses upon modulation can be affected. Here, we show for the first time the intrinsic vibrational transition of C-H bond upon absorption of MIR can lead to efficient photoacoustic conversion. Specifically, owing to the high concentration of C-H bond in it, PDMS film was shown to generate 3 MPa photoacoustic pressure at 10 μm away from acoustic source under 2960 cm^{-1} laser illumination, corresponding to 190 N/J PA conversion efficiency. Such a high PA conversion is comparable to the widely developed CNT/PDMS PA device. Successful photoacoustic neurostimulation of GCaMP6f labeled cortical neurons cultured on PDMS film has been demonstrated and validated using Ca imaging. Taking the advantage of high transparency of PDMS film in visible and NIR range, especially at the GCaMP6f fluorescence excitation and emission wavelengths (i.e., 497 and 512 nm), Ca imaging can be performed in both epi and trans modes with substantially improved imaging quality. By focusing the illumination area, neuromodulation with high spatial resolution of 5-10 microns can be achieved to enable single neuron and subcellular stimulation. Given the fact that C-H bond is commonly existed in most of the organic materials and has the absorption far away from visible range, we herein provide a universal method to fabricate transparent photoacoustic film highly compatible with fluorescence imaging.

5:00 PM EL13.04.08
Vertical Organic Artificial Synaptic Devices with Electric Field Permeable Pinhole Electrode Nahyun Jeong[1,2] and Kyung-Geun Lim[1,2]; [1]Korea Research Institute of Standards and Science, Korea (the Republic of); [2]University of science and technology, Korea (the Republic of)

Key Words: Artificial synapse, Vertical organic transistor, Neuromorphic electronics , pinhole metal electrode, permeable source electrode

Vertical organic field effect transistors (VOFETs) with the electric field permeable source electrode have great advantages such as low voltage operation and energy consumption due to a nano scale channel length. However, conventional electric field permeable source electrodes like silver nanowires and carbon nano tubes have a network structure which is formed by random self-assembly, hence it's difficult to control network density and position. Here, we introduced a metal thin film formed by thermal evaporation in the vacuum chamber which has a number of nanoscale pinholes that allow the electric field to pass through from gate dielectric. Also, we controlled the pinhole morphologies, such as density or size, to facilitate the electric field permeability. As a result, VOFETs with the electric field permeable pinhole metal source show high current density at low operating voltage. Moreover, the biological synapse characteristics including short term plasticity (STP), long term plasticity (LTP) and Spike-timing dependent plasticity (STDP) are stimulated by light pulse to trigger charge trapping of the active layer and the light absorbing material. Due to the novel and advanced results, the photonic synapse based on VOFETs are expected to be used as image sensing or optical communication devices.

5:00 PM EL13.04.09
Multifunctional Organic Neuromorphic Transistors by Controlling the Ferroelectricity of P(VDF-TrFE) via Photocrosslinking Young-Seok Song[1], Seungyeon Kim[1], Myeongjae Lee[2], BongSoo Kim[2] and Tae-Wook Kim[1]; [1]Jeonbuk national Univeristy, Qatar; [2]Ulsan National Institute of Science and Technology, Korea (the Republic of)

The beginning of the era of the big data, Internet of Things (IoT) and AI (Artificial Intelligence), it is necessary to process the massive amount of data. So far, many data processing method follows the classical Von Neumann's computer architecture. With this method as the data processes in series, as the amount of data increase, it is very inefficient way. So many researchers are trying to realize the neuron networking by mimicking the human brain for the parallel data processing method and it calls neuromorphic transistors. Additionally, the advantages of using organic materials like mechanical properties that match with human tissue and the working mechanisms of those devices are compatible with human physiology. [1,2]
So, in the organic neuromorphic researchers are focused on mimicking the human brain, especially synaptic function. But these transistors cannot be regarded as unique multifunctional devices because all bult-in functions are mutually combined. To address this, we focus on the separation of electrical switching and data storage functions in organic ferroelectric memory transistors [3].

This study was conducted to create a multifunctional neuromorphic device by mixing P(VDF-TrFE) (poly(vinylideneflurodie-trifluoroethylene)), a ferroelectric polymer, and various photocrosslinker 2Bx, 4Bx and 6Bx. [4] High permittivity needed for electrical switching and the ferroelectricity needed for data storage become compatible by restricting the motion of P(VDF-TrFE) via photocrosslinking. When irradiating the UV light to the photocrosslinker, compared to the reference photocrosslinker, the 4Bx and 6Bx have 2 times and 3 times more azide groups. So, with the less amount of concentration of 4Bx and 6Bx, we observed almost the same results with using more concentration of 2Bx. Additionally depend on the difference of ferroelectricity, the neuromorphic electrical properties like Short-term potentiation (STP), Long-term potentiation (LTP) and Long-term depression (LTD) etc. showed totally different results.

As a result, we realized multifunctional organic neuromorphic thin film transistors which has both switching and data storage property with the photocrosslinking of the P(VDF-TrFE) films. Also, with the various photocrosslinker, we successfully observed the increased ferroelectricity modulation efficiency of P(VDF-TrFE) films.

5:00 PM EL13.04.10
Selective Control of Supported Lipid Bilayers in a Neuromorphic OECT Ugo Bruno[1,2], Chiara Ausilio[1,2], Claudia Lubrano[3,4] and Francesca Santoro[1,3,4]; [1]Istituto Italiano di Tecnologia, Italy; [2]Università degli Studi di Napoli Federico II, Italy; [3]Forschungszentrum Jülich GmbH, Germany; [4]RWTH Aachen University, Germany

Neuromorphic engineering was developed to build machines able to emulate key features of the brain that allows for the fulfilment of several complex tasks at the same time, with unmatched energy efficiency. To date, hardware implementation of spiking neurons has been successfully developed, in which complex silicon-based building blocks may be combined to mimic several aspects of biological neurons[1].
Conversely, neuron-inspired devices cannot be limited to communicate through spikes, but they may require additional features like synaptic plasticity[2]. In light of this, organic neuromorphic devices and in particular PEDOT:PSS-based organic electrochemical transistors (OECTs) are emerging as ideal candidates, as their biocompatibility and soft-nature allows for the integration with living tissue[3].
In this scenario, in order to promote the seamless integration between artificial and biological neurons, the integration of neuromorphic OECTs with a supported lipid bilayer (SLB), was successfully demonstrated[4], enhancing neuromorphic features, such as short-term plasticity (STP).
While proving the possibility of integrating a biomembrane with an organic transistor, such artificial device is still far from recapitulating an actual post-synaptic neuron, hampering a proper interface with living cells. In fact, the composition of the SLB used is still far from the complex architecture of a neuronal membrane. In addition, the positioning of the bilayer between the gate and the channel of the OECT hinders the passage of ions. Furthermore, long-term plasticity (LTP) was not demonstrated.
In light of this, the present work proposes to go further, by exploiting a microfluidic module coupled to a solvent-assisted lipid bilayer[5] (SALB) technique that allows to form and confine a neuron-inspired phospholipidic membrane on the polymeric channel of a planar-gated PEDOT:PSS-based OECT, *de facto* engineering a post-synaptic artificial neurons. The correct formation and the morphological properties of the bilayer are investigated and the effect of the SLB on the electrical properties of the artificial neuron are assessed. Here, such unprecedented integration allows for the enhancement of the biomimetic potential of the transistor, while not hindering the free passage of ions. In addition, neurotransmitter-mediated LTP is demonstrated. This work ultimately paves the way towards the building of new biomimetic platforms that can be used to interface with living neurons in their native environment.

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5:00 PM EL13.04.11

Artificial Polymer Tactile Memory Triggered by Mechanosensitive Ion Dynamics Hayoung Oh[1], Hyukmin Kweon[1], Joo Sung Kim[1], Seongchan Kim[2], Haisu Kang[3], Dong Jun Kim[1], Hanbin Choi[1], Seung Geol Lee[3,3], Jeong Ho Cho[2] and Do Hwan Kim[1]; [1]Hanyang university, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of); [3]Pusan National University, Korea (the Republic of)

Tactile memory is a crucial sensory modality allowing human skin to perceive and interpret surroundings, which is vital role in practical daily activities of human. On the basis of the tactile encoding functionality, humans are able to not only identify familiar objects via touch, but also reliably and repeatedly address (e.g., gripping and lifting) them in non-destructive manners by retrieving prior acquired tactile information. This tactile recognition and memory abilities, in sensory system of human skin, are achieved by ion dynamics-based tactile signal transmission through somatosensory nerves consist of numerous synapses. Synaptic memory functions such as short- and long-term plasticity (STP, LTP) can be realized through ion-driven neural signal transfer, so that the perception and memory of tactile information proceed with extremely low energy consumption and real-time processing. To mimic the ion-based biological tactile memory processing, methodologies have been studied to integrate pressure sensors, signal converters, and ion gel-gated transistors in parallel or to make dual gated-ion gel transistors. However, these suffer from a lack of LTP capability, which is a major property to implement tactile memory. This is because without a series of voltage spikes, ion accumulation near semiconductor layer is effortlessly dissipated to achieve an ionic equilibrium state, so that programmed conductance (i.e., tactile memory level) is rapidly disappeared. Applying additional voltage pulses to the ion gel could be a plausible solution to maintain the conductance state. However, in this case, voltage input cannot be decoupled with tactile stimuli. This strongly implies that utilization of conventional ionic material design and ion dynamics is insufficient to realize ideal tactile memory in iontronic artificial tactile nerves.
Herein, we describe mechano-modulated ion dynamics, in which free ion density and migration are independently controlled by tactile stimuli and electric-field (E-field). Before applying tactile stimuli, the electrochemical property of ions is not dominated by external E-field, which is not observed behavior in conventional ion gel. Interestingly, after pressure is applied, free ion density can be increased, so that ionic conductivity and charge relaxation time are simultaneously changed. From that moment, ion transport property is dominated by external E-field. This suggests that generated free ions by tactile stimuli can render synaptic memory signals (reflecting tactile information), and the external E-field can independently control the tactile memory level. Utilizing the proposed ion behavior, we demonstrated monolithic tactile memory synaptic transistors (TMSTs), capable of perceiving tactility and augmenting the memory in a single device simultaneously. The TMSTs showed highly sensitive tactile recognition and effective tactile memory (retention time > 30 min) which can be precisely modulated by voltage pulse and tactile stimuli. We believe that the novel concept of ion dynamics will provide new insight into developing synaptic electronics for neural prosthetics and soft robotics.

5:00 PM EL13.04.12

Probing The Working Mechanism of Organic Nanowire Memristors Based On a Series of Oxocarbon Derivatives Aaron A. Cookson and James Ryan; Swansea University, United Kingdom

Neuromorphic computation is a promising way to overcome the limits of the von Neumann chip architecture in modern computing. The current problems computation faces are due to the bottlenecks in the current Von Neumann architecture. These include storage, resolution and speed in which data can be processed. Memristors (memory + resistance) have been explored as an option to replace current computing chips due to their memory storage capabilities and their ability to dynamically change their physical properties when applying a bias. [1] The memristor was mathematically derived by L. Chua in 1971 and has been demonstrated in the lab since. [2] Organic memristors have been an area of interest because of the ability to tune the structure and functional groups of a molecule to enhance the electrical performance of a device, including memory and volatility performance. [3][4]

Recently our group demonstrated a working analog memristor based on 2,4-bis[4-(diethylamino)-2-hydroxyphenyl]squaraine (SQ) nanowires on gold interdigitated electrodes. [5] The device showed exceptional analog switching behaviour with large hysteresis loops and increased conductivity with successive sweeps. The device showed non-volatile memory behaviour which can be compared and is on par with benchmark transition metal oxide devices. The working mechanism of the device, however, was seen to differ from transition metal oxide (TMO) memristors. The concentration of oxygen vacancies in TMOs is responsible for the memristive behaviour in TMO memristors. Initially we proposed that protons in SQ could be responsible for the memristive behaviour, especially as squaric acid and another oxocarbon, croconic acid, undergo inter-intra-molecular proton tautomerism. [6] To test this hypothesis, we performed a series of experiments using impedance spectroscopy and current-voltage measurements under a variety of environmental conditions. Hydration studies were employed to determine whether proton conduction occurred in SQ nanowires, which would be analogous to oxygen vacancies in TMOs. [7] Hydration studies, while ruling out intermolecular proton transport in these devices, reveal interesting observations on what controls the magnitude of hysteresis in these devices. We have since began to test alternative oxocarbon derivatives and salts in order to both develop deeper insights into the working mechanism of these devices as well as realise enhanced performance. Indeed, there are certainly a number of exciting routes to take in order to fully explore, and exploit, the potential of squaraine and related small molecule mixed conductors in the fields of bioelectronics, organic electrochemical transistors, organic batteries and neuromorphic computing.

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5:00 PM EL13.04.13
Hydration of a Side-Chain-Free N-Type Semiconducting Ladder Polymer Driven by Electrochemical Doping Jiajie Guo[1], Lucas Flagg[2], Duyen Tran[1], Shinya E. Chen[1], Ruipeng Li[3], Nagesh Kolhe[1], Rajiv Giridharagopal[1], Samson Jenekhe[1], Lee Richter[2] and David S. Ginger[1]; [1]University of Washington, United States; [2]National Institute of Standards and Technology, United States; [3]Brookhaven National Laboratory, United States

We study the organic electrochemical transistors (OECTs) performance of the ladder polymer, poly(benzimidazobenzophenanthroline) (BBL) in an attempt to better understand how an apparently hydrophobic side-chain free polymer is able to operate as an OECT with favorable redox kinetics in an aqueous environment. We examine two BBLs of different molecular masses from different sources. Regardless of molecular mass, both BBLs show significant film swelling during the initial reduction step. By combining electrochemical quartz crystal microbalance (eQCM) gravimetry, *in-operando* atomic force microscopy (AFM), and both *ex-situ* and *in-operando* grazing incidence wide-angle x-ray scattering (GIWAXS), we provide a detailed structural picture of the electrochemical charge injection process in BBL in the absence of any hydrophilic side-chains. Compared with *ex-situ* measurements, *in-operando* GIWAXS shows both more swelling upon electrochemical doping than has previously been recognized, and less contraction upon dedoping. The data show that BBL films undergo an irreversible hydration driven by the initial electrochemical doping cycle with significant water retention and lamellar expansion that persists across subsequent oxidation/reduction cycles. This swelling creates a hydrophilic environment that facilitates the subsequent fast hydrated ion transport in the absence of the hydrophilic side-chains used in many other polymer systems. Due to its rigid ladder backbone and absence of hydrophilic side-chains, the primary BBL water uptake does not significantly degrade the crystalline order, and the original dehydrated, unswelled state can be recovered after drying. The combination of doping induced hydrophilicity and robust crystalline order leads to efficient ionic transport and good stability.

SESSION EL13.05: Adaptive Sensing and Biointerfacing II
Session Chairs: Ana Arias and Francesca Santoro
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3005

8:30 AM EL13.05.02
Diode Connected Organic Electrochemical Transistors—Enhanced Stability Two-Terminal High Transconductance Bioelectronic Devices and Mixed Conductor Testbeds Bryan D. Paulsen[1], Wonil Sohn[2], Emily Schafer[1], Reem Rashid[1], Dilara Meli[1] and Jonathan Rivnay[1,1]; [1]Northwestern University, United States; [2]Rice University, United States

Organic Electrochemical Transistors (OECTs) leverage the volumetric ionic-electronic coupling inherent to Organic Mixed Ionic Electronic Conductors (OMIECs) to produce low-voltage high-gain devices that can directly interface with ionic and biological media. As such OECTs are a crucial building blocks in bioelectronic and neuromorphic circuits. As said circuits advance there is a desire to simplify the implementation of OECTs while retaining their unique functionality. While normally employed as three terminal devices (3T-OECTs), here we investigate two terminal diode-connected OECTs (DC-OECTs). We show that DC-OECTs are an effective two terminal testbeds for characterizing OMIECs materials. We establish that DC-OECTs reproduce both the steady-state and frequency domain J-V behavior of saturation regime 3T-OECTs across a series of accumulation mode p-type OMIEC channel materials, from which can be extracted accurate OECT and OMIEC figures of merit: cut-off frequency, threshold voltage (V_t), device transconductance (g_m), electronic carrier mobility (μ), and μC^* (the product of mobility and volumetric capacitance). Leveraging the fact that the g_m of DC-OECTs is equally high as 3T-OECTs, we employ DC-OECTs as current amplifiers in electrocardiogram (ECG) measurements, demonstrating their effective transduction and amplification of bioelectronic signals. DC-OECTs open new opportunities for simplified cross-bar integration of OECTs in sensing arrays, and simultaneous sensing-stimulation device functionality. Beyond these application opportunities, DC-OECTs provide enhanced device stability. Voltage cycling reveals that the drain current and g_m stability of DC-OECTs is greatly enhanced compared to 3T-OECTs by avoiding deleterious drain potentials in the OFF state, and this enhancement was found to be general across all OMIECs investigated. Finally, we investigated the applicability of two terminal diode connected OECTs to neuromorphic circuits, where simple crossbar arrays are attractive.

8:45 AM *EL13.05.03
Artificial Sense Technology Xiaodong Chen; Nanyang Technological University, Singapore

Artificial senses refer to the emulation of human's basic senses and assimilate them to functional devices and systems to help us understand and perceive the world around us. This research topic of artificial senses is transdisciplinary and lies at the confluence of materials science, bioengineering, medical sciences, electrical engineering, and computer science. Some use cases, including enhanced sensory capabilities to overcome physical human limitations, improved robotic capabilities and diagnostics with smart information processing, and prosthetics and health-monitoring devices to improve quality of life, are drawing much attention. In this talk, I will present some latest progress in artificial tactile and olfaction with the viewpoint from materials development, sensor fabrication, information processing, and system integration. Artificial senses would be a new enabling technology to construct next-generation intelligent devices and systems, paving the way for advanced soft robotic applications, rehabilitation, prosthetics, and so on.

9:15 AM *EL13.05.04
Thiophene-Based Trimers for Evolvable and *In-Vivo*-Manufactured Electrodes and Electronics Magnus Berggren; Linkoping University, Sweden

An ensemble of different thiophene-based trimers, substituted with desired biomolecular entities, have been synthesized for neuronal and neuromorphic applications. While dissolved in aqueous and/or physiological media, the trimers aggregate and adhere to (cell and tissue) surfaces followed by enzymatic or electrochemical polymerization. Those interactions allow us to build up electrodes and electronic systems for evolvable signal processing and *in vivo*-manufactured bio-interfacing. The fundamentals of the trimer-based bioelectronics will be reported along with applications in neuromorphic and neuronal applications.

9:45 AM BREAK

SESSION EL13.06: Adaptive Sensing and Biointerfacing III
Session Chairs: Xiaodong Chen and Francesca Santoro

Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3005

10:30 AM *EL13.06.01
Interrogation of Brain and Peripheral Organ Neurophysiology with Multifunctional Fibers Polina Anikeeva; Massachusetts Institute of Technology, United States

Over the past decade multifunctional fibers have been applied to recording and modulation of neuronal signaling in the central nervous system in behaving rodents. In this talk, I will first touch upon translational challenges associated with applying powerful fiber neurotechnology in large animal models as a steppingstone to applications in human patients. I will then discuss our recent efforts to create fiber-based probes suitable for interrogation of neuronal signaling in peripheral organs. For instance, applications of fiber-based probes to studies of enteric (gut) circuits will be discussed along with the materials challenges posed by the anatomy and physiology of the gastro-intestinal tract. I will further describe the translational efforts in applying peripheral fiber neurotechnology in large animal models and the potential therapeutic benefits that can be delivered by these biologically informed multifunctional tools in conditions with disrupted peripheral innervation. Together, this talk will highlight the promise and challenges of preclinical implementation of fiber-based neurotechnologies.

11:00 AM *EL13.06.02
Stretchable Bioelectronic Devices for Epidermal, Retinal, and Neural Prostheses Donghee Son; Sungkyunkwan University, Korea (the Republic of)

Soft wearable/implantable bioelectronic systems capable of monitoring electrophysiological signals evoked by external mechanical/optical/electrical stimuli and delivering the feedback information have been considered essential functional components in realizing the future closed-loop prostheses. Despite such significant progress, materials fatigue and the corresponding electrical malfunction issues still remain challenging due to the lack of optimal materials/fabrication/integration/system strategies that simultaneously meet tissue-device modulus matching, electrical/mechanical durability, biocompatibility, uniformity, reproducibility, and even strain-induced error correction.
Herein, we describe optimal materials design strategies and device fabrication/integration technologies for the three different kinds of intrinsically stretchable prosthetic bioelectronics. Using various stretchable conducting/semiconducting composites, we developed damage-durable prostheses consisting of mechanical/electrophysiological/optoelectronic sensors, non-volatile resistive random access memory, and quantum dot display modules for the shape-tunable prosthetic skin, retina, and even peripheral nerve. Further, to improve the sensing accuracy of soft bioelectronic devices, electrical malfunctions originating from either repetitive stretching-induced materials relaxation or fatigue were precisely corrected by using machine learning techniques, leading to realization of the high-performance strain-insensitive soft bioelectronics.

11:30 AM EL13.06.03
Comprehensive Study on the Ion-gel Gated Organic Transistor for Next-Generation Point-of-Care Testing Dae-Gyo Seo[1], Jayoung Kim[2,3], Sunghyun Park[2], Zhenan Bao[3] and Tae-Woo Lee[1]; [1]Seoul National University, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of); [3]Stanford University, United States

With the growing demand for rapid clinical diagnosis and health monitoring, point-of-care (PoC) devices with high sensitivity, low-cost, high-energy efficiency, and wearable are gaining tremendous attraction.
We present the biosensor system based on ion-gel gated organic transistors (IGOTs). By tuning the gate capacitance of the IGOTs, we could modulate the device properties such as transconductance, threshold voltage, and hysteresis. Furthermore, high and commensurate capacitance made the IGOTs possible to read out the capacitance changes which cannot be detected by the MOSFET due to the relatively small capacitance as to affinity-based biosensors. Also, we revealed the relationship between the device property and the sensing ability. This resulted in outstanding biomolecule sensing performance of IGOTs. We projected a new possibility for PoC healthcare monitoring and diagnosis with high sensitivity, low-cost, high-energy efficiency, and wearable devices based on IGOTs.

11:45 AM EL13.06.04
Small Molecule Memristors for Neuromorphic Computing James Ryan and Aaron A. Cookson; Swansea University, United Kingdom

Neuromorphic computation is a promising way to overcome the limits of the von Neumann chip architecture in modern computing. Memristors can play a key role in the realization of neuromorphic devices due to their inherent memory storage and ability to dynamically alter physical properties such as resistance in response to an incoming stimulus.[1] Organic memristive devices have the potential to generate new paradigms in the memristor device field due to the inherent ability to tune the electronic properties of organic molecules for greater electrical or memory/volatility performance, which is currently a bottleneck for solid-state transition metal oxide (TMO) memristors.[2],[3] In this talk, I will highlight a new approach to fabricate high performance memristive devices based on small molecules. First, I will highlight our recent demonstration of an organic nanowire memristor based on 2,4-bis[4-(diethylamino)-2-hydroxyphenyl]squaraine (SQ) and then proceed to discuss some very recent developments in our lab.[4]

In our initial study, SQ nanowire memristors were fabricated using a very simple but effective approach whereby we deposit SQ NWs on an interdigitated gold electrode to form a lateral Au/SQ/Au architecture. These prototype devices demonstrate the hallmarks of memristor operation such as current hysteresis loops and dynamic conductivity in response to multiple voltage sweeps. The volatility of the conductivity states written to the device is also shown to have long memory retention without voltage bias, demonstrating non-volatility. These results are on par with benchmark transition metal oxide devices (TMO). These results demonstrate a straightforward and very promising approach to fabricate robust and low-cost memristive devices. The fabrication method offers an excellent platform for device prototyping and high-throughput screening of potential memristive materials.

Following on from our initial study, we are looking into the working mechanism of SQ NW memristors via a suite of electronic and electrochemical techniques applied under varying temperature and environmental conditions, exploring alternative molecules and developing a more scalable approach to fabricate organic memristors based on small molecule semiconductors. All of these topics will be highlighted and an up-to-date summary of the progress we are making will be provided.

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SESSION EL13.07: Materials for Neuromorphic Devices II
Session Chairs: Simone Fabiano and Yoeri van de Burgt
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3005

1:30 PM *EL13.07.01
Electronic and Photonic Neuromorphic Device Concepts Based on Organic and Hybrid Materials Systems Emil J. List-Kratochvil[1,2]; [1]Humboldt-Universität zu Berlin, Germany; [2]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany

Artificial neural networks (ANN), inspired by biological nervous systems, enable signal processing beyond the capabilities of von Neumann computer architectures. Through dynamically adapting the connectivity (synaptic weights) in individual devices and by applying learning algorithms ANNs can offer in memory and tensor computing capabilities. Yet, to fully unleash the potential of hardware ANNs there is still a need for neuromorphic device concepts, which properly emulate all necessary synaptic functions adequately and allow for an easy integration into large scale hardware ANNs. In this contribution we will demonstrate organic ionic/electronic [1] as well as plasmonic/photonic [2] neuromorphic device concepts using different types of hybrid material systems. We will show that all presented devices concepts can be used to mimic fundamental functions of a synapse, such as long-term plasticity showing potentiation and depression, spike-time or spike-rate dependent plasticity or may be trained to realize AND- or OR logic gate operations and well as small scale photonic ANNs.

This work was supported by the Deutsche Forschungsgemeinschaft through the CRC 951

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2:00 PM EL13.07.02
Neuromorphic Organic Electrochemical Transistors, Neurons and Robotics in Hybrid Self-Learning Platforms Ugo Bruno[1,2], Daniela Rana[3,4], Chiara Ausilio[1,2], Ottavia Bettucci[1], Claudia Lubrano[3,4] and Francesca Santoro[1,3,4]; [1]Istituto Italiano di Tecnologia, Italy; [2]Università degli Studi di Napoli Federico II, Italy; [3]Forschungszentrum Jülich GmbH, Germany; [4]RWTH Aachen University, Germany

Neuromorphic platforms are emerging as new computational paradigm[1], with the ultimate goal of building artificial neural system, by replicating the efficiency of the brain in terms of parallel computation.
Such technologies can mirror several aspects of the brain, by exploiting complex circuits[2] or by exploiting unique features of innovative materials[3]. Among the plethora of the available materials and structures, organic electrochemical transistors (OECTs) have emerged as ideal candidates in the building of complex neuromorphic systems, able to interface with living organisms[4] and to learn autonomously[5].
Notably, PEDOT:PSS-based OECTs have been employed in the implementation of the first biohybrid synapse. Here, cells cultured *in vitro* could directly communicate with such artificial neurons by means of neurotransmitters, emulating a biological chemical synapse[6].
In this scenario, such devices may offer the possibility of merging electronic devices and biological neurons in an unprecedented way, addressing challenges that current technologies are not able to face, such as EMG-based prosthetics limbs failures[7] and treatment of symptoms in neurodegenerative diseases[8].
The present work demonstrates an artificial post-synaptic neuron that drives a prosthetic hand, coordinating its grasp with the activity of pre-synaptic biological cells cultured inside the microfluidic channel of the device itself.
The artificial neuron can communicate with its biological counterpart, by oxidizing neurotransmitters directly secreted by neuronal cells resulting in an update of its synaptic weight, as a stable conductive state of the polymeric channel that is then used to tune the movement of the artificial hand. In a physiological condition, such synaptic weight allows for the complete closure of the hand. Conversely, when a dysregulation of the neurotransmitter secreted by the pre-synaptic cells occurs, emulating a pathological condition, the post-synaptic neuron loses the control of the prosthetic limb. Here, a feedback controller is introduced, regulating its synaptic weight and allowing for the recovery of the physiological condition. Such result is achieved by introducing hydrogen peroxide inside the microfluidic chamber that can reverse the neurotransmitter mediated synaptic weight update. Furthermore, the neuromorphic core of such platform is exploited to achieve reinforcement learning, ultimately paving the way towards a novel generation of hybrid devices able to combine decades of development of silicon-based technologies with innovative features of organic neuromorphic devices.

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2:15 PM EL13.07.03
Neurorobotic Approaches to Emulate Human Motor Control with the Integration of Artificial Synapse Seonkwon Kim[1], Seongchan Kim[2], InCheol Kwak[1], Soo Young Cho[1], Dong Gue Roe[1], Yonghyun A. Kwon[1], Jung Woo Moon[1], Seonmi Eom[1] and Jeong Ho Cho[1]; [1]Yonsei University, Korea (the Republic of); [2]The Pennsylvania State University, United States

The advancement of electronic devices has enabled researchers to successfully emulate human synapses, thereby promoting the development of the novel research field of artificial-synapse-integrated soft robots. This paper proposes an artificial reciprocal inhibition system that can successfully emulate the human motor control mechanism through the integration of artificial synapses. The proposed system is composed of artificial synapses, load transistors, voltage/current amplifiers, and a soft actuator to demonstrate the muscle movement. The speed, range, and direction of the soft actuator movement can be precisely controlled via the preset input voltages with different amplitudes, numbers, and signs (positive or negative). The artificial reciprocal inhibition system can impart lifelike motion to soft robots and is a promising tool to enable the successful integration of soft robots or prostheses in a living body.

2:30 PM *EL13.08.02
Molecular-Scale Hardware that Mimic Synapses Christian A. Nijhuis; University of Twente, Singapore

Inspired by the energy efficiency of brains and the ever-increasing demand for miniaturised electronics, there is a drive to develop devices that mimic the dynamic character of neurons and synapses to realize, for instance, non-von Neumann neuromorphic computing. Mostly, such operations are realized with energy inefficient and complex silicon-based circuits or with mesoscale memristors, but molecular hardware for doing so is not available yet [1]. In this context, molecular switches are an interesting approach, but so far molecular switches lack the dynamical, time-dependent character inherent to synapses [2,3]. It has been notoriously difficult, however, to reversibly address molecular switches in solid-state tunnel junctions.[3,4,5]. Recently, we developed a new type of an electrically driven molecular switch that can toggle between two different functionalities.[5] By coupling fast electron transport to slow proton addition steps, we created dynamic molecular switches that show large hysteretic negative differential conductance [6]. These switches mimic basic spike-rate dependent plasticity, Pavlovian learning, and emulate all Boolean logic gates. These molecular switches are promising to develop spiking neural networks and open new ways to design molecular-electronic devices.

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SESSION EL13.09: Neuroprosthetics and Novel Spiking Concepts I
Session Chairs: Paschalis Gkoupidenis and Yoeri van de Burgt
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3005

8:30 AM *EL13.09.01
Biorealist Organic Electrochemical Neurons Simone Fabiano; Linkoping University, Sweden

Future brain-computer interfaces will require local and highly individualized signal processing of fully integrated electronic circuits within the nervous system and other living tissue. Due to their poor biocompatibility, circuit complexity, low energy efficiency, and operating principles fundamentally different from the ion signal modulation of biology, traditional neuromorphic implementations based on silicon have limited bio-integration potential. Organic mixed ionic-electronic conductors (OMIECs) are in a stage of rapid development as novel applications that use these versatile materials continue to emerge. In OMIECs, the strong coupling between ions and electrons enables efficient signal transduction, making these materials ideal for interfacing electronics with biological systems. Here, we will use OMIECs to develop organic electrochemical neurons and synapses with ion-modulated spiking. We will discuss their facile integration with biological nerves and demonstrate simple neurosynaptic circuits with neurotransmitter-/amino acid-/ion-based spiking modulation capabilities. These soft and flexible organic electrochemical neurons and synapses operate at low voltage and respond to multiple stimuli, defining a new era for bio-integrable artificial neuronal systems.

9:00 AM *EL13.09.02
Skin-Like Neuromorphic Devices for Intelligent and Personalized Wearable Technology Sihong Wang; University of Chicago, United States

For leveraging wearable technologies to advance precision medicine, personalized and learning-based analysis of continuously acquired health data is indispensable, for which neuromorphic computing could provide the most efficient implementation of artificial intelligence (AI) data processing. For realizing on-body neuromorphic computing, skin-like stretchability is required to be combined with the suite of desired neuromorphic metrics. In this talk, I will introduce our research in developing new electronic materials, device designs, and fabrication processes for imparting intrinsic stretchability onto neuromorphic devices that can provide state-of-the-art computing performance. I will also show the practical applicability of this device for implementing machine-learning computing and algorithms for health data analysis, when the computing hardware is under human-body-induced deformation.

9:30 AM EL13.09.03
Organic Neuromorphic Spiking Circuits—From Sensory Coding and Neurotransmitter-Mediated Plasticity to Retina-Inspired Computing Functions Giovanni Maria Matrone[1,2], Eveline van Doremaele[2], Sophie Griggs[3], Gang Ye[4], Iain McCulloch[3,5], Francesca Santoro[6,7] and Yoeri van de Burgt[2]; [1]Northwestern University, United States; [2]Technische Universiteit Eindhoven, Netherlands; [3]University of Oxford, United Kingdom; [4]Shenzhen University, China; [5]King Abdullah University of Science and Technology, Saudi Arabia; [6]Istituto Italiano di Tecnologia, Italy; [7]RWTH Aachen University, Germany

The fundamental mechanisms of signal communication within the human body rely on the spiking frequency of action potentials.[1] Through biological receptors and afferent neuronal cells, stimuli from the external world are encoded into a spiking pattern and transmitted to the central nervous systems where they are processed via interneurons. Indeed, the direct dependence of spikes frequency on the magnitude of the stimulus is generally referred to as “sensory coding”.
Neuromorphic electronics is currently experiencing a huge increase in research activity, aiming to mimic the architecture of the human brain to enable parallel computing with high energy efficiency[2] and local processing, thus advancing intelligent systems interfacing with the human body[3].
Replicating the interdependent functions of receptors, afferent neurons and interneurons with spiking circuits, sensors and biohybrid synapses is an

essential first step towards merging neuromorphic circuits and biological systems, crucial for computing at the biological interface.
Moreover, establishing an active interaction with biological tissues, especially with the central nervous system, requires adaptive computing systems that are not only able to receive biologically encoded inputs but also to process and communicate these.
Recently, organic materials have been employed to build electronic circuits that mimic the spiking behaviour of neurons[4,5]. Despite processing complex sensorial input, these systems still lack mechanisms to modulate the encoded signal[6].
However, a combination of bioelectronic devices may recreate a "neuronal pathway" that in nature relies on the cooperation of spiking (neurons and interneurons) and non-spiking elements such as mechano-chemical sensors (receptors), as well as neuromodulator junctions (chemical synapses).
Here it is presented a novel adaptive spiking circuit that replicates afferent neurons "sensory coding" from external physical stimuli. The neuromodulatory activity of interneurons is emulated by associating the spiking circuit with biohybrid synapses demonstrating an interdependent chemical synaptic connection. To establish a full neuronal pathway, these key biological functions are combined, showing the signal transduction from light stimulus to spiking frequency and to dopamine-mediated plasticity: a retinal pathway primitive.
This circuit constitutes a fundamental building block for programmable neural pathways that are able not only to perform "sensory coding", transducing both physical as well as physiological environmental information, but also to locally execute bio-inspired pre-processing functions: an essential step towards realizing processors dynamically communicating with the nervous system.

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9:45 AM EL13.09.04
Non–Von Neumann Multi-Input Spike Signal Processing Enabled by an Artificial Synaptic Multiplexer Dong Gue Roe, Dong Hae Ho, Soo Young Cho, Yonghyun A. Kwon, InCheol Kwak, Seonkwon Kim, Jung Woo Moon, Seonmi Eom and Jeong Ho Cho; Yonsei University, Korea (the Republic of)

Multiplexing is essential for technologies that require processing of a large amount of information in real time. Here, we present an artificial synaptic multiplexing unit capable of realizing parallel multi-input control system. Ion gel was used as a dielectric layer of the artificial synaptic multiplexing unit because of its ionic property, allowing multigating for parallel input. A closed-loop control system that enables multi-input–based feedback for actuator bending control was realized by incorporating an ion gel–based artificial synaptic multiplexing unit, an actuator, and a bending angle sensor. The proposed multi-input control system could simultaneously process input and feedback signals, offering a breakthrough in industries in which the processing of vast amounts of streaming data is essential.

10:00 AM BREAK

SESSION EL13.10: Neuroprosthetics and Novel Spiking Concepts II
Session Chairs: Paschalis Gkoupidenis and Yoeri van de Burgt
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3005

10:30 AM *EL13.10.02
Large-Scale Organic Electronics for Neural Signal Acquisition and Processing Jennifer Gelinas; Columbia University Irving Medical Center, United States

Analysis and modulation of neurophysiological signals are increasingly leveraged to understand brain functions and treat neuropsychiatric disorders. Deriving more usable information from neurophysiologic methods could accelerate progress toward these goals, but current approaches are hampered by a trade-off of resolution and invasiveness. Our approach is to design and develop organic electronics that permit large-scale acquisition and manipulation of brain activity patterns to the resolution of individual neurons. Leveraging the conformability and volumetric capacitance of these materials, we have created devices that permit high spatiotemporal resolution interaction with in vivo neural networks. Furthermore, we investigate the capacity of fully implantable integrated circuits based on internal ion-gated organic electrochemical transistors (IGTs) to process neural data in real-time and enable physiologically relevant manipulation of these signals.
These devices enabled us to identify novel network properties in epilepsy models that are amenable to targeted therapeutic interventions. We were able to effectively detect and modulate pathologic signals to prevent disease progression. Such studies have set the foundation for translation of these devices in human subjects, where we have characterized cortical microcircuits in patients undergoing neurosurgical procedures. Our results highlight the potential for organic electronics to safely enhance our ability to acquire, interpret, and modify neural signals, with the goal of facilitating discovery of biomarkers and therapies for patients with neuropsychiatric disorders.

11:00 AM EL13.10.03
Graphene-Edge Neuroelectronics for Ultrahigh-Density Subcellular Single-Unit Recording Yunxia Jin[1,1,1], Chne-Wuen Tsai[2,1], Sippanat Achavananthadith[2], Dat T. Nguyen[3], Jerald Yoo[2,1], Yuxin Liu[1,1,1] and John S. Ho[1,2,1]; [1]National University of Singapore, Singapore; [2]Department of Electrical and Computer Engineering, National University of Singapore, Singapore; [3]Integrative Sciences and Engineering Programme, National University of Singapore Graduate School, Singapore

Single-unit electrophysiological recording at electrode density comparable to neural density is critical to interrogate the function of the brain and the study of neurological diseases. In addition, three-dimensional triangulation of neuron location by spatially oversampled multiple single-unit recording requires closely-packed ultrahigh-density electrodes. However, the electrode spatial density is currently limited by high electrochemical impedance and availability of interfacing materials and fabrication method. Here, we propose and demonstrate a graphene-edge neuroelectronics with a density of more than 2000 electrodes/mm^2, exceeding the neural density in the brain. By exposing nanotextured graphene edges on the cross-section of the probe, each channel of dimensions less than 12 μm achieves an impedance of less than 1 MΩ and a charge injection capacity of more than 1 mC/cm^2. Notably, the probe records neural activity with high action potential amplitudes approaching 1 mV and allows reliable detection of multiple single-units in cortical areas. We further show that chronically implanted probes exhibited stable electrochemical impedance, high signal-to-noise ratio of more than 20 dB, and single-unit tracking capabilities over 3 months. This work paves the way for ultrahigh-density chronic neural recording for closely-packed neurons in the brain.

11:15 AM EL13.10.04
A Redox-Reversible Switch of DNA Bonding and Structure Jason D. Slinker[1] and Robert Kuchta[2]; [1]The University of Texas at Dallas, United States; [2]University of Colorado Boulder, United States

A controlled interface with nanotechnology is key to progressing interests in adhesion, photonics, electronics, energy harvesting and storage, sensing, and thermal management. Electrically reconfigurable biological materials open pathways for advancing these broad interests and enhancing current efforts to leverage biological self-organization to generate novel materials with designer medical, mechanical, optical, and electrical properties. We have identified DNA base surrogates with redox-reconfigurable hydrogen bonding behavior based on alloxazine, the redox-active moiety of the biological flavin cofactors. Alloxazine DNA base surrogates were synthesized and incorporated into DNA duplexes as surrogate bases that function as a redox-active switch of hydrogen bonding. Circular dichroism revealed that 24-mer DNA duplexes incorporating one or two alloxazines exhibited spectra and melting transitions like DNA with only canonical bases, indicating the constructs adopt a conventional B-form conformation. Thiolated DNA duplexes incorporating alloxazines were self-assembled onto multiplexed gold electrodes and probed electrochemically. Square wave voltammetry revealed a redox peak near −0.27 V versus a Ag/AgCl reference, consistent with the reduction of the alloxazine moiety. Furthermore, alternating between alloxazine oxidizing and reducing conditions modulated the redox peak consistent with the formation and loss of hydrogen bonding, which disrupts the base pair stacking and charge transport efficiency. These alternating signals support the assertion that alloxazine can function as a redox-active switch of hydrogen bonding, useful in controlling DNA and bioinspired assemblies.

11:30 AM EL13.08.03
Sensing Drug-Induced Blockage of Voltage-Gated Calcium-Ion Channel from Differentiated Neuronal Membrane Monitored via Organic Microelectrode Array Zixuan Lu[1], Chiara Barberio[1], Aimee Withers[1], Anna-Maria Pappa[1,2], Alexandra Wheeler[1], Konstantinos Kallitsis[1], Eleonora Martinelli[1], Achilleas Savva[1], Walther Traberg-Christensen[1] and Róisín Owens[1]; [1]University of Cambridge, United Kingdom; [2]Khalifa University of Science and Technology, United Arab Emirates

Neuronal ion-channel proteins are crucial membrane components directly related to neuron electrical activities. Disturbance of neuron signals and natural toxin effects caused by Ion-channel dysfunctional diseases still burden the global healthcare system. The study of native ion channels from cell membranes provides a simplified and direct model to study the drug and toxin effects on targeted ion-channels.[1] Microelectrode arrays were fabricated and coated with conducting polymer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) as the active interfacing layer.[2] SH-SY5Y neuroblastoma cells was chemically differentiated with a 10-day process, and significant increase of neuronal marker expression was detected by immunofluorescence imaging and Western blot. Differentiated cells show a drastic increase of neurite outgrowth, which is an important benchmark of mature neurons. Further, native-neuronal membrane vesicles (also called blebs) were chemically induced from SH-SY5Y. By vesicle-fusion process, the SH-SY5Y membranes were successfully integrated onto the organic microelectrode arrays (OMEAs) and characterized by electrical (electrochemical impedance spectroscopy (EIS)) and optical (fluorescent recovery after photobleaching (FRAP)) methods. Then, calcium-ion channel blocking-effects with an antiarrhythmic drug, verapamil, were detected and analyzed by EIS. The calcium ion-channel protein was more than 50% upregulated after differentiation, and this difference was proved by a dose-response of the ion-channel blocking assay via electrical monitoring. Our neuronal membrane-on-chip system provides a time-efficient, cell-free, and label-free platform for pharmacology study and drug discovery on native ion-channel activities.

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SESSION EL13.11: Materials for Neuromorphic Devices III

Session Chairs: Paschalis Gkoupidenis and Francesca Santoro
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3005

1:30 PM *EL13.11.01
Near-GHz Switching in Polymer-Based Artificial Synapses—Characterization and Switching Mechanisms Alberto Salleo; Stanford University, United States

In this talk I will describe an organic electrochemical neuromorphic device that switches at record-low energy (<0.1 fJ projected, <10 pJ measured) and voltage (< 1mV, measured), displays >500 distinct, non-volatile conductance states within a ~1 V operating range. Our organic neuromorphic device works by combining ionic (protonic) and electronic conduction and is essentially similar to a concentration battery. Our synapses display outstanding speed (<20 ns) and endurance achieving over 10^9 switching events with very little degradation all the way to high temperature (up to 120°C). These performance metrics are impressive yet very surprising for polymers that are usually perceived as slow and subject to degradation. In this talk I will describe the unique structural properties that lead to such fast switching and high endurance which we deduce from *operando* electrochemical characterization using synchrotron radiation.

2:00 PM *EL13.11.02
Two-Terminal Neuromorphic Devices Based on Organic Electrochemical Diodes Myung-Han Yoon; Gwangju Institute of Science and Technology, Korea (the Republic of)

Although various types of neuromorphic devices base on memristive, phase-change, and ferroelectric characteristics are proposed, there exist few examples of two-terminal neuromorphic behaviors driven by ion-intercalated modulation. Herein, we report the organic electrochemical diode (OECD)-based two-terminal neuromorphic device architecture. The proposed devices operate via key principles based on polarity-dependent current-rectification and activity-dependent electrochemically-floated potential shift of organic mixed ionic-electronic conductors with low oxidation potentials. The actual potential of a given active channel layer could be effectively modulated by repeated electrical stimulations through the input node so that the non-conductive channel became conductive under the forward bias below 0.8 V and vice versa. We also demonstrated that patterned devices in series/parallel could show the behaviors of programmable AND or OR logic gates as a proof-of-principle of integrated digital circuits.

2:30 PM EL13.11.03
Organic Electrochemical Transistor-Based Immunosensor for Sars-Cov-2 Spike Protein Detection Renan Colucci, Dimitrios Koutsouras, Paschalis Gkoupidenis, Paul W. Blom and Ulrike Kraft; Max Planck Institute for Polymer Research, Germany

With rapidly increasing transmissions of the severe respiratory syndrome coronavirus 2 (SARS-CoV-2), the World Health Organization (WHO) classified the SARS-CoV-2 outbreak as a global pandemic in March 2020.[1] Since then, SARS-CoV-2 has severely impacted society and health globally. To break the spread of such a virus, quick, reliable, easy to handle, point-of-care testing strategies with low detection limits are crucial. Currently, there are two standard tests, reverse transcription–quantitative polymerase chain reaction (RT–qPCR) and viral antigen test (rapid test). Both do not fulfill the demand completely: The first one provides high sensitivity but requires trained personal, high sample quality and specialized equipment. The second one provides a rapid result (~30 min) and is suited for point-of-care testing, but lacks sensitivity.[2] Hence, novel approaches and methodologies for low-cost and precocious-stage diagnosis are needed. Devices able to address these demands are electronic biosensor. A typical biosensor is composed of a bioreceptor that interacts with the analyte and a transducer that converts the resulting biological incident into a measurable signal.[3] Organic electrochemical transistors (OECT) are excellent transducers for the conversion to electronic signals, since they operate well in aqueous (biologic) environments at low potentials (usually < 1 V). Furthermore, they provide self-signal amplification.[4] Here, we present an organic electrochemical transistor (OECT)-based biosensor that allows the detection of SARS-CoV-2 spike protein down to concentration levels of 10^{-15} M (equivalent to 10^{-13} g*mL^{-1}). The OECTs are modified with SARS-CoV-2 immunoglobulin G (IgG) and the SARS-CoV-2 spike protein biorecognition results in a shift of the transfer curves. The proteins incubation time is 30 min, which is equivalent to the standard antigen tests. In summary, we have successfully developed a promising immunosensing platform based on OECTs with a highly sensitive diagnostic method for COVID-19, suitable for point-of-care testing.

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2:45 PM EL13.11.04
Photo-Enhanced Output in Highly Transparent Thin Film Transistors Based on Organic/Inorganic Hybrids for Neuromorphic Synapses Xiaojuan Fan; Marshall University, United States

We report that highly transparent thin film transistors were built on glass substrates based on amorphous metal oxide and polymer hybrid structures through solution processing at room temperature. UV-Vis-NIR microscopic spectroscopy measurements were conducted on organic/inorganic hybrid materials. Thin films on Si wafers show optical interference fringes, indicating that the as-prepared samples are of high quality, i.e., smooth and uniform, from which thin film thicknesses can be derived. The transistors consist of a layer of metal oxide/PEG mixture as the active semiconductor and a layer of PMMA as dielectric materials on transparent conductive ITO contacts. Source and drain electrodes were deposited by an e-beam evaporator of 4 nm thick Cu and 200 nm thick Au in various combinations of channel length and width. The 4-probe station *IV* characteristics display a depletion mode for *p*-type transistors. Such transistors can undergo an unusual conversion from depletion mode to enhancement mode by photo-stimulation without switching the polarity of gate voltage. The mechanism is attributed to dramatic photo-current generations in amorphous metal oxide-embedded polymer hybrids under light irradiation. The selected polymers are biocompatible, enabling the fabricated transistor devices applicable to the research of neuromorphic synapses.

SESSION EL13.12: Virtual Session
Session Chairs: Paschalis Gkoupidenis and Yoeri van de Burgt
Wednesday Morning, April 26, 2023
EL13-virtual

8:00 AM *EL13.12.02
Designing Bioelectronic Materials for Regenerative Medicine Molly Stevens; Imperial College London, United Kingdom

This talk will provide an overview of our work on chemical modification and functionalisation strate-gies to obtain designer polymers for bioelectronic applications in regenerative medicine and therapeutics. We introduce moieties to the polymer backbone to obtain tunable properties such as semi-conductivity [1], self-immolation [2] and light sensitivity [3]. Our bioconjugate capture probes allow for multiplexed high-dimensionality biosensing [4]. I will also discuss the opportunities presented by organic bioelectronics as tissue and cell interfacing materials for stimulating regeneration [5], with examples of our current research in cardiovascular and neurological therapies. Finally, I will discuss how we are actively engaging in efforts towards the democratisation of healthcare innovations [6].

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8:30 AM *EL13.10.01
Soft Self-Healable Actuatable Electro-Luminescent Materials Benjamin C. Tee; National University of Singapore, Singapore

Neuromorphic architectures can enable significant power efficiencies in machine learning tasks[1,2]. The use of soft, organic materials can allow for integration of sensing, actuation and data transmission onto neuromorphic platforms. In this talk, I will share our recent work on developing asynchronous data transmission systems2 for neuromorphic in combination with soft flexible electronic materials and devices3. Using such systems, we can generate unique datasets containing high speed sensory data, for e.g., a MNIST like tactile dataset[4] and apply them to use cases in robotics5.

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SYMPOSIUM

April 10 - April 25, 2023

Symposium Organizers
Udo Bach, Monash University
T. Jesper Jacobsson, Nankai University
Jonathan Scragg, Uppsala Univ
Eva Unger, Lund University

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* Invited Paper
\+ Distinguished Invited

SESSION EL14.01: High Throughput Synthesis
Session Chairs: T. Jesper Jacobsson and Jinzhao Li
Monday Morning, April 10, 2023
Moscone West, Level 3, Room 3014

8:15 AM *EL14.01.01
Rational Design and Investigation of Catalysts for Sustainable Resources Hannah N. Barad; Bar-Ilan University, Israel

As a major part of trying to mitigate global climate change and improve sustainable resources, discovery of new, stable, and highly active catalyst materials is a pressing issue. There are several reasons for this, first, currently the most efficient and stable catalysts for the chemical processes that we use to transform raw resources into products with the desired functions (chemicals or energy), *e.g.*, H_2 evolution and CO_2 reduction, contain expensive rare and precious elements such as Pt and Ir. This explains the efforts to find abundant, accessible, low-cost, stable alternatives that will yield process efficiencies comparable or better than those we have today. For example, for water splitting, many new materials with different compositions have shown promising results as catalysts. However, they are mostly prepared by wet chemical synthesis, which results in chemical waste and can be too slow for industrial use. Second, the morphology of the catalysts is important because it affects their catalytic properties as higher surface areas yield more catalytically active sites, surface energetics change, leading to improved reaction rates, etc. These reasons emphasize the motivation to accelerate the process of finding new materials with varying nanostructures and optimized functionality, by systematic exploration of several parameter spaces.
In recent years, artificial intelligence, namely by machine learning (ML) tools, has gained prominence in the field of materials science. The use of ML accelerates new material predictions and assists with finding unexpected correlations between the process-structure-function relations of materials, which leads to a better understanding and focus of the vast parameter spaces that exist in materials science. Rational design by ML in conjunction with combinatorial materials science promotes the rapid discovery and analysis of new materials, and enables breakthroughs in materials science, which would otherwise not have been possible.
Here we present the progress in the development of electrocatalysts using rational design with ML in conjunction with combinatorial synthesis and high-throughput characterization. We investigate changes in composition and nano-morphology on material libraries and their effects on the catalysis of reactions such as O_2 evolution, CO_2 reduction, and CH_3OH oxidation. The different nanostructures and compositions show high activity and stability as electrocatalysts. The insights gained, indicate a dependence of catalytic activity on composition and nanostructuring, which the standard experimental techniques cannot achieve or explore, thus illustrating the importance and impact that composition and structure have, and will have, on developing sustainable catalysts. This can only be done by high-throughput experimentation design, combined with machine learning tools, which will assist with appropriate path directions and ensure rational studies on catalysis in the future.

8:45 AM EL14.01.02
Harnessing Non-equilibrium Syntheses to Develop New High Throughput Approaches for Highly Efficient Oxide Thin-Film Semiconducting Photoelectrodes Ronen Gottesman[1,2]; [1]The Hebrew University of Jerusalem, Israel; [2]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany

A unique approach to exploring non-equilibrium synthesis parameter spaces of oxide thin film photoelectrodes will be presented, broadening the pathway toward discovering new chemical spaces inaccessible through conventional solid-state reactions.
There is an increasingly urgent need for disruptive and innovative materials that satisfy the chemical and physical requirements to reduce global warming through sustainable development. Fortunately, only a fraction of the possible combinations were studied, making it likely that the best materials are still awaiting discovery. However, designing controlled synthesis routes of single-phase oxides with low defects concentration will become more difficult as the number of elements increases;[1,2] and there are currently no robust and proven strategies for identifying promising multi-elemental systems.
These challenges demand an initial focus on synthesis parameters of novel non-equilibrium synthesis approaches rather than chemical composition parameters by high-throughput combinatorial investigations of synthesis-parameter spaces. This would open new avenues for stabilizing metastable materials, discovering new chemical spaces, and obtaining light-absorbers with enhanced properties to study their physical working mechanisms in photoelectrochemical energy conversion.
Using two non-equilibrium synthesis tools: pulsed laser deposition and flash photonic sintering can form gradients in synthesis parameters without modifying composition parameters, which enables reproducible, high-throughput combinatorial synthesis over large-area substrates and high-resolution observation and analysis. Even minor changes in synthesis significantly impact material properties, physical working mechanisms, and performances, demonstrated by the relationship between synthesis conditions, crystal structures of α-SnWO$_4$,[3] and properties over a range of thicknesses of CuBi2O$_4$,[1] both emerging light-absorbers for photoelectrochemical water-splitting used as model multinary oxides. Our approach addresses an immediate need by focusing on novel non-equilibrium synthesis approaches of disruptive and innovative materials that meet the chemical and physical requirements for reducing global warming through sustainable development.

1. Gottesman, R. *et al.* Overcoming Phase-purity Challenges in Complex Metal Oxide Photoelectrodes: A Case Study of CuBi2O$_4$. *Adv. Energy Mater.* 2003474 (2021) doi:10.1002/aenm.202003474.
2. Gottesman, R. *et al.* Pure CuBi2O4 Photoelectrodes with Increased Stability by Rapid Thermal Processing of Bi$_2$O$_3$/CuO Grown by Pulsed Laser Deposition. *Adv. Funct. Mater.* **28**, 1910832 (2020).
3. Gottesman, R. *et al.* Shining a Hot Light on Emerging Photoabsorber Materials : The Power of Rapid Radiative Heating in Developing Oxide Thin-film Photoelectrodes. *ACS Energy Lett.* **7**, 514–522 (2022).

9:00 AM EL14.01.03
High Throughput Discovery of Photoelectrode Assemblies for Solar Fuels Generation Joel Haber; California Institute of Technology, United States

The development of efficient, stable photoelectrodes remains a primary materials challenge in the establishment of a scalable technology for artificial photosynthesis. The typical photoelectrode architecture consists of a semiconductor light absorber coated with an auxiliary material that serves a combination of functions, including corrosion protection, electrocatalysis, light trapping, carrier transport, and elimination of deleterious surface recombination sites. We describe high throughput investigations of alloying of metal oxide light abosrbers and the variation in performance and photo-response of integrated photoelectrode libraries. Photoelectrode assemblies based on promising coating compositions and loadings were investigated in detail.

9:15 AM *EL14.01.04
Towards Self-Organizing Two-Dimensional Hybrid Perovskites—Machine Learning Driven Co-Navigation of Chemical and Compositional Spaces Jonghee Yang[1], Benjamin Lawrie[2], Amirhossein Rahimi[1], Sergei Kalinin[1] and Mahshid Ahmadi[1]; [1]University of Tennessee, Knoxville, United States; [2]Oak Ridge National Laboratory, United States

Two-dimensional (2D) hybrid perovskites combine the richness of physical functionalities of inorganic materials and complexity and stimulus responsiveness of organic molecules in a single bulk dynamic material. The unique aspect of these materials is the thermodynamic (meta) stability, allowing for self-organized formation of complex large-period structures. Combined with the ease of fabrication, these materials not only have extensively demonstrated state-of-the-art high-performance optoelectronics but also offer the pathway towards versatile applications including sensors, electronic and neuromorphic devices as well as their cost-effective mass production. However, discovery and optimization of these materials require joint optimization of the composition of the inorganic components and selection of the molecular moieties, to harness the phase formation and self-assembly processes on the material level, and extend it to the micro- and macro scale functional devices. In this talk, I will discuss the potential of machine learning driven high throughput automated experiments to accelerate the discovery of 2D and quasi 2D hybrid perovskites, optimize the processing pathways, and understand the kinetics of their formation. I will also discuss how the high throughput liquid and solution-based synthesis can be transitioned into the thin film formation for functional applications.

9:45 AM BREAK

10:15 AM *EL14.01.07
Combinatorically Inkjet-Printed Metal Halide Perovskite Optoelectronic Devices Emil J. List-Kratochvil[1,2]; [1]Humboldt-Universität zu Berlin, Germany; [2]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany

Beyond the use in home and office-based printers, inkjet printing has become a popular structuring and selective deposition technique. More recently great interest also exists in emerging industrial areas like in the manufacturing of printed circuit boards, solar cells, flexible organic electronic and medical products.
Metal halide perovskites (MHP) have received great attention in recent years, predominantly due to the high performance of perovskite solar cells. The versatility of the material has also allowed its use in light-emitting diodes and photo detectors, amongst other optoelectronic device applications. In these device applications the tunability of the energy bandgap is of particular importance. In contrast to other semiconducting material classes the energy bandgap in MHPs can be easily tuned by controlling the halide ratio in the compositions using pure and mixed halide gradients ranging from pure MAPbI3 via MAPbBr3 to MAPbCl3. Moreover, the drop-on-demand capabilities of inkjet printing enable the deposition of the MHP inks in a precise ratio to produce specific perovskite compositions with dedicated energy bandgaps in the printed thin film. By this means we can fabricate multiple perovskite compositions absorbing or emitting light at specific wavelengths in a single printing step. Using various mixed halide perovskites, we will show the fabrication of combinatoricallyprinted photodetector arrays [1,2] as well as large area multi color light emitting devices [3].

[1] Schröder, V. R. F. et al. Using Combinatorial Inkjet Printing for Synthesis and Deposition of Metal Halide Perovskites in Wavelength Selective Photodetectors. Advanced Engineering Materials (2021).
[2] Näsström, H. et al. Combinatorial inkjet printing for compositional tuning of metal-halide perovskite thin films. Journal of Materials Chemistry A (2022).

[3] Hermerschmidt, F. *et al.* Finally, inkjet-printed metal halide perovskite LEDs – utilizing seed crystal templating of salty PEDOT:PSS. *Materials Horizons* **7**, 1773-1781 (2020).

10:45 AM EL14.01.06

High-Throughput Analysis of Combinatorial Metal Halide Perovskite Libraries, a FAIR Dataset in NOMAD Hampus Näsström[1], Pascal Beblo[2], Fatima Akhundova[2], Oleksandra Shargaieva[2], José M. Prieto[1], Hannes Hempel[2], Claudia Draxl[1], Eva L. Unger[2,1,3] and Thomas Unold[2]; [1]Humboldt-Universität zu Berlin, Germany; [2]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; [3]Lund University, Sweden

Machine learning and artificial intelligence claims to offer a paradigm shift in how experimental materials research is performed. However, these methods often require uniformly labeled and very large datasets, something that is not traditionally available in experimental materials research. One way to begin obtaining the necessary data volumes is by applying high-throughput technologies.
In this work, we present a high-throughput investigation of metal halide perovskites for the use in optoelectronics. Combinatorial libraries of $Cs_yPb_{1-y}(Br_xI_{1-x})_{2-y}$ perovskites were fabricated by thermal co-evaporation and investigated using contact-less high-throughput characterization such as hyperspectral photoluminescence imaging, time-resolved photoluminescence mapping and grazing-incidence wide-angle X-ray scattering mapping. The high-dimensional datasets of each sample were reduced and combined to zero-dimensional descriptors using automated analysis. These descriptors were used to show how the theoretical photovoltaic power conversion efficiency depends on the Br to I and Cs to Pb ratios in a previously unexplored range of the $Cs_yPb_{1-y}(Br_xI_{1-x})_{2-y}$ solid solution. A generalized data schema for combinatorial thin films was developed in order to disseminate the dataset in a Findable, Accessible, Interoperable and Reusable (FAIR) way within the Novel Materials Discovery (NOMAD) repository. Through NOMAD, the labeled data of the 3456 individual samples of this dataset can be combined with others to provide the volume of experimental data needed for applications in machine learning and artificial intelligence.

11:00 AM EL14.01.08

High-Throughput Synthesis and Characterization of Ternary Nitride Perovskites Rebecca Smaha[1], Rachel Sherbondy[2], Kevin Talley[1], Sage Bauers[1], Geoffrey L. Brennecka[2] and Andriy Zakutayev[1]; [1]National Renewable Energy Laboratory, United States; [2]Colorado School of Mines, United States

Oxide perovskites are robust, stable, and display a wide range of functional properties, and halide perovskites have made a significant impact in photovoltaics and other optoelectronics. The greater covalency of nitrogen than oxygen and halogens makes nitrides attractive for semiconducting and other functional applications in renewable energy. Recent advances in experimental methods, particularly combinatorial methods, for synthesizing nitride materials have led to a rapid increase in the number of known ternary nitride phases. We recently experimentally realized $LaWN_3$ in thin film form as the first oxygen-free nitride perovskite, a goal that has long presented a synthetic challenge due to the difficulty of completely excluding oxygen during synthesis and the high oxidation states required for the *A* and/or *B*-site cations. $LaWN_3$ crystallizes in polar space group R3c and exhibits a large piezoelectric response,[1] opening a host of possible avenues to target novel compounds for functionalization, including as potential multiferroics for spintronic applications.

Here we present the high-throughput synthesis and detailed investigation of new *RE*-*M*-N (*RE* = La, Ce; *M* = W,Mo) ternary nitrides via RF sputtering. This phase space is nearly unexplored, and the combinatorial synthesis and high-throughput characterization methods used here allow rapid exploration, accelerating the discovery of novel materials and pinpointing which have promising properties for functional applications. We report on a detailed investigation of the structure, optoelectronic properties, and crystallization dynamics of thin film $LaWN_3$. The optoelectronic properties are found to be highly sensitive to stoichiometry. In addition, we discuss the recent discovery and characterization of two new Ce-based nitride perovskites, $CeMN_3$ (*M* = W, Mo), which display low-temperature magnetic frustration.[2] Recent work on new phases obtained with other *A*- and *B*-site cations is also discussed.

[1] Talley et al., Science 374, 1488–1491 (2021).
[2] Sherbondy et al., Chem. Mater. 34, 6883–6893 (2022).

11:15 AM EL14.01.09

Combinatorial Vacuum-Deposition of Metal Halide Perovskite Films and Solar Cells Isidora Susic[1], Adi Kama[2], Lidón Gil-Escrig[1], Chris Dreessen[1], Francisco Palazon[3], David Cahen[4,2], Michele Sessolo[1] and Henk J. Bolink[1]; [1]University of Valencia, Spain; [2]Bar-Ilan University, Israel; [3]Universidad Politécnica de Cartagena, Spain; [4]Weizmann Institute of Science, Israel

The development of vacuum deposited perovskite materials and devices is partially slowed down by the minor research effort in this direction (at least when compared with the field of solution-processed perovskites), but also from one of its intrinsic characteristics: long timeframe for the optimization of even a single perovskite composition since in one deposition run only a single set of parameters can be used (i.e. set of deposition rates for a certain set of precursors). Combinatorial materials science (CMS) is a method that can be used to accelerate the study of compositionally varying perovskites. When CMS is applied to thin-films, a compositional gradient is deposited on purpose on a single large area substrate, referred to as a library, forming many different compounds or materials in a single deposition run. Here we report the combinatorial vacuum-deposition of wide bandgap perovskites of the type $FA_{1-n}Cs_nPb(I_{1-x}Br_x)_3$, by using 4 sources and a non-rotating sample holder.[1] From initial deposition rates calculated based on stoichiometry and properties for each precursor, we run a combinatorial deposition and high throughput characterization. By using small pixel substrates, we are able to produce >100 solar cells with different perovskite absorbers in a single deposition run. The materials are thoroughly characterized by spatially resolved and/or high throughput techniques, including optical, morphological and structural techniques. By subsequent fine tuning of the deposition rates, we can alter the gradient and reproduce the best performing formulations in standard depositions with rotation. We extended the method for optimizing wide bandgap CsMAFA triple-cation perovskite solar cells, which are found to be efficient but not thermally stable. With the aim of stabilizing the perovskite phase, we add guanidinium (GA^+) to the material formulation, and obtained CsMAFAGA quadruple-cation perovskite films with improved thermal stability, as observed by X-ray diffraction and rationalized by microstructural analysis. The corresponding solar cells showed similar performance with a remarkable thermal stability, when compared to the triple-cation perovskite devices.[2] We believe this approach can encourage the discovery of materials, and serve as a basis to prototype other compositions (low bandgap, lead- free) overcoming the current limitations of vacuum deposition as a research tool for perovskite films.

[1] I. Susic, A. Kama, L. Gil Escrig*, C. Dreessen, F. Palazon, D. Cahen, M. Sessolo*, H. J. Bolink, Adv. Mater. Interf. 2022, Accepted for publication.

[2] I. Susic, L. Gil Escrig, F. Palazon, M. Sessolo*, and H. J. Bolink, ACS Energy Lett. 2022, 7, 4, 1355–1363

11:30 AM EL14.01.10

High Throughput Exploration of Novel Perovskite-Inspired Materials Using Combinatorial Inkjet Printing Allan Starkholm[1], Vincent Schröder[2], Hampus Näsström[2], Emil J. List-Kratochvil[2] and Eva L. Unger[1]; [1]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; [2]Humboldt-Universität zu Berlin, Germany

Perovskite solar cells (PSCs) have since 2012 attracted considerable attention, which can be attributed to the facile synthesis and thin film deposition, as well as to high power conversion efficiencies. However, there are two major challenges that currently hinder the commercialization of PSCs, and therefore need to be addressed; poor stability and the presence of toxic lead. Perovskites have a large structural and compositional space and research during the last decade has resulted in several new perovskite and perovskite-related materials with suitable properties for utilization as energy materials.[1] This, in turn, has further expanded the chemical and structural space of potentially interesting perovskite-inspired materials, which requires the use of suitable, scalable, high-throughput methods for the discovery of new candidate materials. This is crucial in order to swiftly identify new materials for energy applications to accelerate the transition towards a more sustainable economy. The time-consuming materials discovery process combined with the historically long implementation time of new photovoltaic technologies[2] is, as of today, limiting the possibility to speed up this important transition. Inkjet printing is a scalable fabrication technique that has been proven valuable for the deposition of perovskites as large area modules. Furthermore, inkjet printing has been demonstrated as a potentially interesting tool for combinatorial, high-throughput, deposition of numerous perovskite compositions with potential for solar cell application.[3] In this work, the use of combinatorial inkjet printing to screen a large compositional space of novel perovskite and perovskite-inspired materials for optoelectronic devices is presented. We developed direct and high-throughput analysis strategies to evaluate the performance potential of these materials in operando.

[1] A. Starkholm, L. Kloo, P. H. Svensson, *J. Am. Chem. Soc*. **2020**, *142*, 18437-18448.
[2] R. Grossa, R. Hannaa, A. Gambhirb, P. Heptonstalla, J. Speirs, *Energy Policy*, **2018**, *123*, 682–699.
[3] H. Näsström, O. Shargaieva, P. Becker, F. Mathies, I. Zizak, V. R. F. Schröder, E. J. W. List-Kratochvil, T. Unold, E. Unger, *J. Mater. Chem. A,* **2022**, *10*, 4906– 4914.

11:45 AM EL14.01.11
High-Throughput Energy Materials Discovery Udo Bach; Monash University, Australia

The effects of global warming are calling for a rapid transition from fossil to renewable energy sources. New materials for energy generation and storage are required to enable this transition. In this presentation we will introduce a new research tool which introduces elements of automation and artificial intelligence to the field of materials discovery. The new research platform will be hosted at the Melbourne Centre for Nanofabrication and is part of the Australian Centre for Advanced Photovoltaics. The main purpose of this installation is to accelerate the development of novel printable photovoltaic materials such as lead halide perovskites and their lead-free analogues, it is however also applicable towards the discovery of energy materials more broadly. It entails three integrated robotic sections. The first allows to formulate inks from liquid and solid chemical precursors, the second section allows to produce thin films from these inks via solution processing techniques and the third section hosts a number of characterization tools to determine the optical, electronic and structural properties of these films. The entire system operates under inert gas atmosphere with a clock speed of 5 minutes and the ability to operate autonomously for 24 hours.

SESSION EL14.02: Robots and Automated Experimentation
Session Chairs: Udo Bach, Emory Chan and Carolin Sutter-Fella
Monday Afternoon, April 10, 2023
Moscone West, Level 3, Room 3014

1:30 PM *EL14.02.01
Towards Stable Hybrid Perovskites: High-Throughput Characterization and a Machine-Learning-Assisted Analysis Marina S. Leite; University of California, Davis, United States

Hybrid organic-inorganic perovskites (HOIPs) represent a promising class of material for next-generation optoelectronics. Yet, their long-term stability must be established prior to commercialization. Edisonian, traditional trial-and-error methods for material screening, development, and stability testing are slow considering the vast hyper-parameter space entailing chemical composition and the potential influence of environmental stressors when acted in combination. To overcome this bottleneck towards the identification of stable HOIPs, we realize automated experimentation and machine learning (ML) to gain physical understanding of how these materials' behavior is affected by environmental stressors, such as relative humidity and temperature. We apply ML models to analyze high throughput, *in situ* steady-state photoluminescence and predict the changes in $Cs_yFA_{1-y}Pb(Br_xI_{1-x})_3$ perovskites while exposed to relative humidity cycles. We compare linear regression, echo state network, and seasonal auto-regressive integrated moving average with eXogenous regressor algorithms, and attain consistent accuracy of >90% for the latter, while following long-term changes for 50 hours. Our accurate time series predictions showcase the promise of ML to mimic non-linear response from a series of hybrid perovskite compositions.

2:00 PM EL14.02.02
AI-Guided Autonomous Materials Discovery for Organic Photovoltaics Seungjoo Yi[1], Nicholas Angello[1], Tiara Torres-Flores[1], Edward Jira[1], David Friday[1], Austin Cheng[2], Riley Hickman[2], Changhyun Hwang[1], Alan Aspuru-Guzik[2], Ying Diao[1], Nick Jackson[1], Martin Burke[1] and Charles M. Schroeder[1]; [1]University of illinois at Urbana Champaign, United States; [2]University of Toronto, Canada

In this work, we are pursuing an AI-guided, closed-loop approach to discover new organic photovoltaics (OPVs) with high device performance. Our work integrates autonomous synthesis, automated materials characterization, and AI-based molecular prediction methods in a closed-loop manner to discover new high-performance OPV molecules. We use a Bayesian optimization framework in which physicochemical descriptors of OPV candidates guide the search through a large molecular combinatorial space while maintaining a customizable tradeoff between exploitative and explorative sampling. Candidate OPV molecules suggested by the AI framework are prepared via automated synthesis methods using a "Lego-like" molecular building block-based approach relying on an iterative Suzuki cross-coupling reaction scheme. Following synthesis, the physical properties of candidate OPV molecules are characterized using an automated workflow, with experimental results passed back to the Bayesian optimizer for subsequent rounds of closed-loop materials discovery. Using this approach, our team has uncovered new high-performing OPV molecules after multiple rounds of AI prediction, synthesis, and materials characterization. Overall, our work aims to fill key knowledge gaps in understanding how molecular structure and properties encode OPV device performance. Moreover, our work is advancing the science of closed-loop autonomous discovery by learning how to synergistically integrate AI, automated synthesis, and automated testing and characterization into a common workflow. We aim to meet the "10-10" target (10% efficiency and 10-year stability for OPV materials) to make organic photovoltaics a commercial reality for next-generation energy capture applications.

2:15 PM EL14.02.03
Integrating Robotic High-Throughput Processing with Synchrotron Based *In Situ* Multimodal Analysis—Homogenous Crystallization of Mixed Br-I Perovskites Jiatu Liu[1], Matteo Ciambezi[1], Mahesh Ramakrishnan[1], Jinzhao Li[2], Eva L. Unger[2] and Justus Just[1]; [1]Lund University, Sweden; [2]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany

Optoelectronic material properties and especially conversion efficiencies of next-generation semiconductors are a result of the complex interplay between precursors, intermediates, spectators and products during synthesis processes. Therefore, the discovery of optimized synthesis processes has become an important part in material discovery approaches. A knowledge based discovery and tuning of synthesis processes requires a fundamental understanding of its systematics, pathways and kinetics. Due to the complexity of synthesis interactions, a multitude of experiments with a wide variation of parameters, investigated from complemental perspectives, is required.

To this extend we developed a platform (*in-FORM*), which integrates robotic high-throughput solution processing with synchrotron based in-situ multimodal process analysis. It is based on a small-footprint, robotic, roll-to-roll slot-die coating system, which is fully integrated into a hard X-ray beamline for real-time in-situ process analysis at the MAX IV synchrotron. We measure simultaneously and at the same spot from the same incident X-ray beam a combination of X-ray spectroscopy (X-ray absorption and fluorescence), X-ray diffraction (XRD) and X-ray excited optical luminescence (XEOL). This allows for a complementary investigation of the local structure, crystalline phase, chemical composition, oxidation states, and optoelectronic properties, unraveling formation and evolution processes during and after slot-die ink deposition.
Aiming to optimize the synthesis of mixed bromide-iodide metal-halide perovskites for a wide range of resulting absorber band-gaps while achieving high opto-electronic material quality, we utilized our in-situ platform. We investigated the full formation process, from precursor solutions to final films, under a wide range of synthesis parameters using a combinatorial approach. Our results show how the choice of solvents and co-solvents determines Br/I intermixing and segregation during the synthesis process. Measurements with high-temporal resolution (10ms) during rapid gas quenching reveal how rapid quenching processes can be utilized to achieve homogenous Br/I distributions. By enabling a fundamental understanding of the complex interplay between solvents and intermediates, we pave the way towards the development of greener solvent processes and environmental friendly up-scaling.

2:30 PM *EL14.02.04
Closing the Loop to Automate and Optimize the Synthesis of Halide Perovskites Simon Arnold[1,2], Corneel Casert[1], Edward Barnard[1], Stephen Whitelam[1] and Carolin M. Sutter-Fella[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Organic-inorganic halide perovskites have excellent optoelectronic properties which enables their application for example in photovoltaics, light emitting diodes, and detectors. The field is plagued by the fact that subtle variations in the synthetic protocol can lead to significant reproducibility challenges. In addition, the parameter space to optimize for desirable optoelectronic properties and stability is very large. Therefore, automation of halide perovskite synthesis at high throughput presents an attractive route to identify synthesis parameter-structure-function properties.
In this talk I will describe our joint effort in setting up a robotic platform, SpinBot One, to synthesize and characterize $FAPbI_3$ films. SpinBot One is coupled to neural networks which are trained using evolutionary reinforcement learning to realize time-dependent processes that optimize the optical properties of the material under study. SpinBot One fabricates halide perovskite thin films via spin coating and thermal annealing followed by optical characterization (UV Vis, photoluminescence) on the platform and external X-ray diffraction measurements. SpinBot One performed experiments to rationalize the influence of spin speed, spin duration, MACl content, and annealing profile on crystal phase formation and phase stability. The first part of this talk will describe the more technical/ engineering aspects of building our closed loop system while the second part discusses scientific findings enabled by the closed loop.

3:00 PM BREAK

3:30 PM *EL14.02.05
Robot-Accelerated Exploration of Perovskite Crystallization and Reaction Networks Emory Chan; Lawrence Berkeley National Laboratory, United States

Hybrid inorganic/organic materials offer modular platforms for generating libraries of custom materials, whose properties can be tailored to applications in lasers, photovoltaics, and other optoelectronic devices. The large number of components in these complex materials, and the numerous parameters that specify their synthesis, result in an experimental space that is challenging to explore with conventional laboratory techniques. I will discuss the development of data-enabled strategies for discovering new materials through the combination of robotic synthesis, physical models, and machine learning. I will discuss our Robot-Accelerated Perovskite Investigation and Discovery (RAPID) workflow, which has performed over 15,000 distinct reactions. We used these large datasets to train machine learning classification models for the crystallization of metal halide perovskites and to validate new software pipelines for experimental design and capture. We demonstrate how such robotic techniques have accelerated the application of data approaches such as meta-learning, active learning, and model fusion to perovskite crystallization. Finally, we discuss how expansive robotic datasets allowed us to uncover the dual roles of water in perovskite crystallization and to elucidate the reaction networks that govern chemical transformations of perovskites.

4:00 PM EL14.02.06
Accelerated Discovery of Ligand Molecules for Perovskite Nanocrystals via Machine Learning Guided High-Throughput Experimentation Min A Kim[1], Qianxiang Ai[2], Sandra Bueno[1], Joshua Schrier[2] and Emory Chan[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]Fordham University, United States

Surface binding ligands are critical component in nanoparticle studies, from growth to post-synthesis treatment process. Especially for particles with low chemical stabilities, ligands could act as a barrier preventing defect formations to prolong their intrinsic properties. Given vast chemical space available for ligand molecules, successful search will likely discover unseen ligands for the desired effects on nanoparticles. However, searching such large and complex pool of molecules requires high experimental cost and time, while still practically impossible to explore every candidate available. We combined high-throughput (HT) experimental workflow with machine learning model to accelerate exploration of ligand molecules. We implemented automated liquid handing robots to screen surface treatment reactions by exposing $CsPbBr_3$ perovskite nanocrystal solution to a library of ligands across a range of concentrations. We used perovskite nanocrystals as a model system; Our machine learning guided framework can be easily adopted to screen molecules and their surface interactions with other nanoparticles. Our developed workflow successfully screened 500 reactions in one 8-hour workday demonstrating high efficiency of our experimental method. Each reaction was characterized by HT absorption/fluorescence measurements to observe the change in photoluminescence (PL) intensity as they are exposed to various ligand molecules. Utilized optical measurements provided HT screening tool to correlate the ligand environment and luminescence of nanocrystal solution over time. The surface binding strength of ligand molecules were compared based on the relative change in PL intensity. Ligand selection in HT reactions was prioritized by an active learning (AL) approach with uncertainty quantified by twin regressors. Our model successfully found high performance ligand molecules with initial teaching dataset. Identified surface binding ligand molecules enhanced emission efficiency and chemical stability of perovskite nanocrystals. Feature importance analysis on our models helps the future investigations on uncovering fundamental correlations between molecular properties and their effects on the nanocrystal surface.

4:15 PM EL14.02.07
In-Loop X-Ray Phase Fraction and Structure Analysis for High-Rate Closed-Loop Autonomous Experimentation Ming-Chiang Chang[1], Sebastian Ament[1], Duncan Sutherland[1], Maximilian Amsler[1], Lan Zhou[2], John M. Gregoire[2], Carla P. Gomes[1], R. Bruce van Dover[1] and Michael O. Thompson[1]; [1]Cornell University, United States; [2]California Institute of Technology, United States

Recent advances in autonomous closed-loop experimentation have created new opportunities in high-throughput material discovery research. However, quantitative phase and phase fraction identification from x-ray scattering at speeds commensurate with synchrotron-based measurements remains challenging and limits full exploitation of autonomous searches. To address this challenge, we have developed a probabilistically quantitative, multi-phase labeling algorithm that provides in-loop full structural information for AI agents controlling high-throughput autonomous experiments; data include quantitative lattice strains, peak broadening and grain size effects, and probability estimates for likely multi-phase combinations. In conjunction with non-equilibrium laser spike annealing of compositional libraries to explore composition and processing spaces, we demonstrate the ability of the autonomous agents to utilize the additional data from x-ray scattering to implement a two-stage objective function, switching between *exploration* and *exploitation* modes based on uncertainty of the whole material processing space with structurally labeled phase fields. By providing in-loop data at rates commensurate with the laser spike annealing and synchrotron measurements, we allow active learning AI agents to explore the phase space efficiently and to identify optimal conditions to synthesize high phase-purity structures. With further design of targeted acquisition functions and incorporating additional property measurements, we expect to extend this method for on-the-fly modeling of structure-property relationships and enable practical multi-objective optimization.

4:30 PM *EL14.02.08
A Robotized Screening Platform for Renewable Energy Materials—Building a Pipeline and Proof of Principle Studies Per H. Svensson[1,2], Allan Starkholm[3] and Lars Kloo[2]; [1]RISE - Research Institutes of Sweden, Sweden; [2]KTH Royal Institute of Technology, Sweden; [3]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany

Novel materials constitute the core challenge for all ambitions towards new technologies in the field of renewable energy. A grand challenge for humanity is sufficiently fast discovery of new sustainable materials to solve many of the existing societal challenges. In general, it takes an alarmingly long time to screen and discover new materials, and the time to implement new energy technologies into the commercial market from the time of discovery is in the realm of decades. This is very problematic considering the immediate demand of novel materials and efficient energy storage technologies. Consequently, accelerated discovery and development of new systems/devices are urgently required and robotized materials screening represents a promising tool to accelerate this process significantly.

To meet these challenges, society requires new methodologies and techniques. Our group has for many years been working on an initiative to develop a robotized platform, Poseidon, for the discovery of new materials in different application areas. This talk will present the developed robot pipeline and workflows for solar cells and batteries, as well as results from the screening.

SESSION EL14.03: High Throughput Characterisation
Session Chairs: Hannah Barad and Emil List-Kratochvil
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3014

10:30 AM *EL14.03.01
Model Supported In-Line Characterizaton of Roll-to-Roll Coated Solar Cells Jens W. Andreasen[1], Michael K. Sørensen[2], Anders S. Gertsen[1], Marcial F. Castro[3], Moises E. Rodriguez[2], Suraj Manikandan[1] and Luise T. Kuhn[1]; [1]Technical University of Denmark, Denmark; [2]FOM Technologies, Denmark; [3]CIC energiGUNE, Spain

The application of scalable processing methods like roll-to-roll coating is being adopted with increasing intensity in the field of organic and hybrid perovskite solar cells. This development calls for characterization methods matching the speed and volume of such deposition techniques. One such method is *in situ* X-ray scattering which has followed step, allowing high-throughput analysis of the effect of fine-grained variation of processing parameters and inline analysis of the kinetics of structure formation.
Analyses of non-crystalline nanostructure in thin films coated on flexible substrates are still few and low in detail. The analysis is complicated by the overlapping contributions of scattering from substrate and other nanostructured layers, but there are also considerable advantages by working with coatings on a flexible substrate. Besides studying the coated thin films under the actual processing conditions that allow scaling to mass production, it also facilitates large scale analysis of processing parameters with high resolution. Böttiger *et al.*[1] demonstrated this as a structural analysis extension to an earlier large scale solar cell device analysis experiment, where constituent concentration ratio and film thickness was varied over tens of meters of roll-coated devices[2]. In this manner, "recording" thousands of experiment variations along the substrate foil, high-resolution analysis of parameter space is allowed by "playing back" the coating, either on a fast testing device to record solar cell device parameters (IV-curves), or through a high-flux X-ray beam to record the small- and wide-angle scattering from the coated film. Acquisition times down to a few hundred milliseconds can be realized corresponding to a spatial resolution along the coated foil of a millimeter to a centimetre for foil speeds between 0.5 to 5 m/min[3]. For an experiment where a component concentration is varied from 0% to 100%, this corresponds to a resolution in concentration parameter space of better than 0.01%, or better than 0.001% for the case of additive concentration, varied from 0% to 5%[1]. This is well below what can be expected in mixing accuracy from syringe pumps and uncertainties in the flow dynamics of the microchannel solution mixing structure. With fewer measurements along the coated foil and thus a lower resolution of parameter space similar experiments can be completed in a few days with an optimized laboratory instrument where acceptable counting statistics can be achieved in 100 s exposures[4-6].
We have focused on developing an in-line methodology that is supported by molecular dynamics simulation[7] in order to disentangle the scattering fingerprints that may eventually be used to steer mesoscale structure formation to achieve the optimal photovoltaic performance of a bulk heterojunction. As will be shown, the methodology may be applied both on laboratory scale setups[8] as well as on synchrotron beam lines, and may even be used in conjunction with coating conditions far removed from ambient, i.e. with fully heated solution, coating head and substrate to handle materials that otherwise quickly aggregate and gelate. In combination with optical probes and machine learning techniques, the methodology is expected to close the lab-to-fab gap

that continues to hold back the commercial breakthrough of organic solar cells.

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11:00 AM EL14.03.02
Automatic Identification by Deep Learning of New Hybrid Perovskites from X-ray Diffraction Patterns Florian Massuyeau and Romain Gautier; CNRS-IMN, France

Hybrid lead halides of perovskite type have recently shown a great potential in optoelectronic applications. For this reason, many research groups are currently exploring this chemical system to discover new low dimensional hybrid perovskites. However, discovering such materials is challenging as the necessary structure determination by X-ray crystallography is time consuming and non-perovskite compounds are very often synthesized instead of the more interesting perovskites. In this context, we developed a deep learning approach, which automatically and accurately assign the structure type from the X-ray diffraction patterns of new hybrid lead halides.[1] The models could automatically identify new hybrid perovskites with an accuracy as high as 92%. Interestingly, we were able to identify and explain the key features in the diffraction patterns, which allow the machine learning algorithms to discriminate between perovskites and non perovskites. From this information, the scientists' ability in discriminating the different structure types is largely augmented and such algorithms could be included in autonomous materials discovery cycles in the future.
[1] F. Massuyeau, T. Broux, F. Coulet, A. Demessence, A. Mesbah, R. Gautier, *Advanced Materials* **2022**, *Accepted*, 2203879.

11:15 AM EL14.03.03
Automating 4D-STEM Data Acquisition for Perovskite Imaging Alexander J. Pattison[1], Wolfgang Theis[2] and Peter Ercius[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of Birmingham, United Kingdom

Scanning transmission electron microscopy is a key tool for characterizing the structure and composition of optoelectronic materials at atomic scales [1]. More recently, the advent of high-speed pixelated electron detectors has enabled the collection of full 2D convergent beam electron diffraction patterns for every scan position in a normal 2D raster scan, producing 4D datasets. As well as being used to generate standard STEM images with variably defined collection angles, new 4D-STEM techniques such as center-of-mass [2], ptychography [3], nanoscale strain mapping [4] and STEM holography [5] are now also available.

Despite its widespread usage, however, taking STEM data remains a mostly manual process, which limits the efficiency of microscope sessions and introduces subjective bias into the selection of regions of interest (ROI). With the processing power of modern desktop computers and the availability of open-source computer vision and image analysis software, it is now feasible for computers to decide which ROIs are worth interrogating during an experiment and where to move a microscope stage next to take more useful data. A major challenge is developing workflows that are sufficiently customisable for the range of samples and experiments conducted in EM investigations.

In this presentation, we demonstrate the operation and applications of a custom-built automation program to acquire data on an aberration corrected STEM. This program is integrated with a high speed direct electron detector capable of acquiring large 4D-STEM scans with 87,000 frames per second. The program's pipeline architecture allows rapid development of custom workflows based on basic methods, making it highly customisable for different samples and experiments. We demonstrate its use in acquiring 4D-STEM data sets of many regions of interest suitable for atomic resolution phase contrast STEM of dose sensitive materials. This shows the potential to study large amounts of materials such as perovskites at high resolution without human intervention leading to statistically meaningful results.

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11:30 AM EL14.03.04
A High-Throughput, Multi-Approach Platform for Discovery of Phosphosulfide Semiconductors Andrea Crovetto; Technical University of Denmark, Denmark

Despite the success of Group III phosphides as optoelectronic semiconductors, phosphorus-containing materials for optoelectronics are still largely unexplored. This is unfortunate, because phosphorus is one of the most versatile elements in the periodic table, as it can take a range of positive and negative oxidation states giving countless possibilities for materials discovery.

One of the many intriguing possibilities is to explore P-containing materials containing both a more electropositive and a more electronegative species than phosphorus. Very interesting materials (phosphosulfides) can be obtained using sulfur as the electronegative species. Many phosphosulfides are predicted to be semiconductors with band gaps in the visible. Yet, there are less than 5 five reports of phosphosulfides in thin-film form and hardly any optoelectronic characterization. Phosphosulfides with phosphorus in the -3 oxidation state are completely unexplored by experiment, although recent calculations show direct band gaps, disperse bands, and a high degree of versatility.

To try to harness some of these possibilities in a time- and resource-efficient manner, I propose an integrated platform for discovery of phosphosulfide materials. This platform includes:
- High-throughput/high versatility modular synthesis apparatus for combinatorial growth of inorganic phosphosulfide thin films. This includes sulfur- and phosphorus partial pressure control (both at atmospheric and low total pressures), separate chambers for volatile metal incorporation, and creation of perpendicular combinatorial gradients in the metal-to-metal ratio as well as in the S/P ratio.
- High-throughput characterization apparatus, focusing on the properties that are expected to be correlated with the final optoelectronic performance and are difficult to simulate with sufficient accuracy.
- A tiered approach to material property simulation, which complements the information available from experiment. The simulation tools can be roughly

divided into first-principles quantum mechanical methods, semiclassical methods, and classical “rule-of-thumb“ methods.
- Data management tools to accommodate both experimental and simulation data
- Various artificial intelligence tools to be used both for decision-making in the lab and for understanding complex composition-structure-process-property-performance relationships.
- Public access to the data generated by the tools listed above

To make the presentation more concrete, I will show preliminary optoelectronic characterization of a new phosphosulfide thin-film material to demonstrate the general potential of phosphosulfides for optoelectronics. Finally, I will show recent results on Cu_3P thin films, where a similar (integrated) approach resulted in discoveries that could not have been made by a single-methodology approach.

11:45 AM EL14.04.09
Design Optimization of Bifacial Perovskite Minimodules for Improved Efficiency and Stability Hangyu Gu and Jinsong Huang; The University of North Carolina-Chapel Hill, United States

Bifacial solar modules can produce more energy than monofacial ones, but efficient bifacial perovskite modules have not been demonstrated yet. Here we report bifacial perovskite minimodules with front efficiency comparable to that of the best opaque monofacial minimodules while gaining additional energy from albedo light. The addition of hydrophobic additive in bottom hole transport layer surprisingly protects the perovskite films from moisture damage during atomic layer deposition. Integrating silica nanoparticles with proper size and spacing in perovskite films recovers the absorption loss induced by the absence of reflective metal electrodes while maintains the charge collection properties of perovskites. The small-area single-junction bifacial cells have an equivalent stabilized efficiency of 26.4% at an albedo of 0.2. The bifacial solar minimodules show front efficiency of over 20% and bifaciality of 74.3%, and thus an equivalent efficiency of over 23% at an albedo of 0.2. The bifacial minimodule retained 97% of its initial efficiency after light soaking under one simulated sun for over 6000 hours at 60±5 °C.

SESSION EL14.04: Theory and High Throughput Approaches
Session Chairs: T. Jesper Jacobsson and Hampus Näsström
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3014

1:30 PM *EL14.04.01
Interweaving Synthesis, Theory, Experiment, Devices, Data Tools and Machine Learning for Exploring Materials—Example of Halide Perovskites Claudia Draxl; Humboldt-Universität zu Berlin, Germany

Every material or material class comes with its individual properties and functions that may be useful for a certain type of application. Understanding the respective peculiarities, is particularly interesting from a fundamental point of view. Employing first-principles theory, one can explore the relevant interactions on the electronic scale. A broad variety of available experimental probes allows for in-depth characterization. Bringing both together, often highlight discrepancies between computational results, typically obtained for perfect crystals, and measurements performed on real materials. Moreover, uncertainties may arise coming from the preparation and/or treatment of the investigated samples. On top of all this, every technique – be it experimental or theoretical – comes with its own subtleties. Taking the halide perovskites as an example, for instance, a reliable calculation of the electronic structure even with forefront methodology is still a remarkable challenge [1]. This makes it even more challenging to relate these results to real-world halide perovskites used in state-of-the-art devices. This is also in part due to the sample quality, concerning structural disorder, instability issues, and complex compositions.

Augmented datasets that combine knowledge derived from all perspectives – sample synthesis, experiments, devices, and *ab initio* calculations – have the power of overcoming this barrier and answering scientific questions that cannot be resolved from their individualistic perspectives. Within the FAIRmat consortium [2] (https://fairmat-nfdi.eu), the NOMAD Laboratory [3] (https://nomad-lab.eu), originally developed for computational materials science, is now adapting towards managing experimental material-science data and their various applications, one of them being solar cells.

In this presentation, we demonstrate with the example of organic-inorganic halide perovskites how NOMAD enables the exploration of materials in an interoperable manner from both, the theoretical and the experimental perspective, including synthesis, characterization, and device properties. This enables not only scientific insight through in-depth comparison and analysis but provides also a basis for employing novel artificial-intelligence based workflows and tools. For example, users may train their machine-learning models with theoretical results or experimental data either coming from NOMAD or from their own labs, or from curated datasets like the Perovskite Database Project [4], or with a combination of all of them.

Work carried out in collaboration with J. Márquez Prieto, E. Unger, T. Unold, L. Himanen, M. Scheidgen and the entire FAIRmat team.

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2:00 PM EL14.04.02
High-Throughput Optical Absorption Spectra for Inorganic Semiconductor Ruoxi Yang, Matthew Horton, Jason Munro and Kristin A. Persson; Lawrence Berkeley National Laboratory, United States

An optical absorption spectrum constitutes one of the most fundamental material characteristics, with relevant applications ranging from material identification to energy harvesting and optoelectronics. However, the database of both experimental and computational spectra are currently lacking. In this study, we designed a computational workflow for optical absorption spectrum and integrated the simulated spectra into the Materials Project. Using density-functional theory, we computed the frequency dependent dielectric function and the corresponding absorption coefficient for more than 1000 solid compounds of varying crystal structure and chemistry. The computed spectra show excellent agreement, as quantified by a high value of the Pearson correlation, with experimental results when applying the band gap correction from the HSE functional. The demonstrated calculated accuracy in the spectra suggests that the workflow can be applied next-generation perovskite materials for optoelectronic applications.

2:15 PM EL14.04.03
Computational Discovery of Novel $Ln_2M_2O_5Ch_2$ Materials for Photocatalytic Water Splitting Katarina Brlec, Joe Willis and David O. Scanlon; University College London, United Kingdom

Worldwide, 96% of all hydrogen is produced from fossil fuels in steam methane reforming or coal gasification processes, leading to large greenhouse gas emissions.[1] In addition to fossil fuels, another major source of hydrogen on Earth is water. Hydrogen can be sustainably produced using photocatalytic water splitting – a biomimicry of photosynthesis. TiO_2 and other d^0 oxides have been extensively studied over the last 50 years, however their electronic band structure with low-lying oxygen-dominated valence band prevents efficient hydrogen evolution photocatalysis.[2]

Mixed anion systems (ON, OX, OCh systems) opened a new paradigm in the search for better photocatalysts, as the second anion can be engineered to have a higher-lying p orbital to optimise the band edge positions for water redox. A series of $Ln_2Ti_2O_5S_2$ (Ln=Y, Sm, Gd, Tb) compounds exhibited visible-light photocatalytic water splitting, with $Y_2Ti_2O_5S_2$ showing simultaneous O_2 and H_2 evolution.[3,4]

In this work we explore the 26 previously unknown members of the $Ln_2M_2O_5Ch_2$ (Ln = Sc, Y, La; M = Ti, Zr, Hf; Ch = S, Se, Te) series using state-of-the-art density functional theory (DFT). In total, 289 competing phases of the entire Ln-M-O-Ch chemical space were evaluated at hybrid-DFT level to accurately determine the thermodynamic stability of the proposed materials. Phononic stability of the systems was confirmed using the supercell lattice dynamics approach, with any instabilities mapped out to obtain the true ground state structure. Finally, the relevant optoelectronic properties and bulk band alignments were calculated at hybrid-DFT level to assess the suitability of materials for photocatalytic applications.

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2:30 PM BREAK

3:30 PM *EL14.04.05
Machine Learning to Investigate Material Properties—Autoencoders as a Powerful Tool to Reveal Material Properties Alessio Gagliardi; Technische Universitat Munchen, Germany

Machine learning (ML) is emerging as a new tool for many different fields which now span, among the others, chemistry, physics and material science [1,2]. The idea is to use ML algorithms as a powerful machinery to identify, starting from big data analysis, subtle correlations between simple elemental quantities and complex material properties and then use these to predict them. This approach can help to screen many material properties directly *in-silico* avoiding more computational expensive ab-initio calculations and experimental measurements.
However, adapting existing ML architectures to problems in chemistry, physics and material science is not straightforward. Several aspects need to be addressed to improve machine performance which can be summarized into prediction accuracy and generalization skills. Improving these aspects require to go into the details of the machine and analyze the way they learn from a training dataset. This allows to identify which architecture, training algorithm and dataset are relevant for the problem at hand.
In the present talk I will discuss about the use of a special class of algorithms, i.e. Autoencoders, and how their latent space can be directly used to understand structure-to-property relations in materials and boost numerical simulations.

[1] Wei Li, Ryan Jacobs, Dane Morgan Computational Materials Science 150, 454-463 (2018)
[2] G. Pilania, A. Mannodi-Kanakkithodi, B. P. Uberuaga, R. Ramprasad, J. E. Gubernatis & T. Lookman, Scientific Reports volume 6, Article number: 19375 (2016).

4:00 PM EL14.04.07
Forbidden Optical Transitions—A New Design Metric for Transparent Conductors Rachel Woods-Robinson; Lawrence Berkeley National Laboratory, United States

Many semiconductor materials have weak or forbidden transitions at their fundamental band gaps, as is the case in many high-performing n-type transparent conductors (TCs) including Sn-doped In_2O_3 (ITO) and which induces a widened region of transparency. Finding a high-performing p-type TC could enable breakthroughs in optoelectronic devices such as photovoltatics and several high-throughput screenings have been performed. However, most of these screenings assume that the direct fundamental band gap is a good proxy for absorption edge energy, and so far the presence of forbidden transitions has been overlooked in searches for new p-type TCs. To address this, we compute absorption spectra across a set of ~18,000 semiconductors from the Materials Project database, demonstrating that over half have forbidden or weak optical transitions at the band gap and nearly 10% have at least 0.5 eV between their direct gap and allowed gap (a descriptor we call "forbidden energy difference"). We show that compounds with highly localized states at the band edges (as determined by the inverse participation ratio) are most likely to have forbidden transitions, and for these compounds high orbital overlaps correlate with large forbidden energy differences. Next, we use this data set to perform a screening for p-type and n-type TCs that may have been previously overlooked due to the forbidden nature of their band gap, and defect calculations yield a set of new promising candidate ambipolar TCs, p-type TCs, and n-type TCs. Notably, the two best known n-type TCs, In_2O_3 and SnO_2, would have been filtered out in previous screenings, yet we show they emerge successfully from our screening. We have shared our data set via the MPContribs platform, and we recommend that future screenings for optical properties use metrics representative of absorption features rather than band gap alone.

4:15 PM EL14.04.08
High-Throughput Computing and Screening Thermodynamic and Phonon Transport Properties of 13,205 Dynamically Disordered Perovskites Ming Hu; University of South Carolina, United States

Although first-principles based anharmonic lattice dynamics method coupled with the phonon Boltzmann transport equation has been developed to obtain the phonon properties including lattice thermal conductivity at highest accuracy ever, the costly and time-consuming nature of the required interatomic force constants calculations renders high-throughput infeasible when facing tens of thousands of new materials. Here, a high-dimensional multi-element deep neural network is trained, dubbed Elemental Spatial Density Neural Network Force Field (Elemental-SDNNFF), achieving a competitive force root mean square error and a speed-up of 3 orders of magnitude in comparison to first-principles. The effectiveness and precision of the Elemental-SDNNFF approach is demonstrated on a set of >100,000 inorganic crystalline structures spanning 63 elements in the periodic table by prediction of complete phonon properties such as phonon dispersions and lattice thermal conductivity. We then use our trained neural network model to predict and screen full phonon properties of 13,205 perovskite structures. Due to the inherent structural feature of dynamical disorder, the perovskite structures have shown diverse thermodynamic and phonon transport properties. Thermodynamic stability of all 13,205 perovskite structures is predicted by screening negative frequencies in the Brillouin zone. Four-phonon scattering and two-channel thermal transport are also analyzed and screened. The underlying mechanism is analyzed in deep at the electronic level. This study demonstrated that our algorithm is very powerful for predicting phonon properties of large-scale inorganic crystals and is also promising for accelerating high-throughput search of novel phononic materials for emerging applications.

4:30 PM EL14.04.10
Combinatorial Slot-Die Coating of Metal Halide Perovskite Semiconductors Jinzhao Li, Natalia Maticiuc and Eva L. Unger; Helmholtz-Zentrum Berlin, Germany

Metal-halide perovskite semiconductors are of interest for various optoelectronic devices: photovoltaics, light-emitting diodes, lasers, and photodetectors.[1] In order to explore the vast compositional space of perovskite materials, high-throughput approaches are of strong interest. Current, the approach to compositional engineering is based on manually mixing perovskite precursor inks and fabricate samples individually. To more efficiently fabricate a large amount of perovskite compositions in a single deposition or automizable step, high-throughput fabrication methods based on scalable methods such as slot-die coating, inkjet printing, and evaporation have been developed. Among them, slot-die coating is a promising technique for solution fabrication of high-efficiency perovskite solar cells. This method can be easily modified to make combinatorial sample by implementing a differential feed of two or more precursor inks into the slot-die head, which we refer to as combinatorial slot-die coating. As we will present in this talk, this generic methodology offers very interesting opportunities for high-throughput screening of the of perovskite compositions.
Here, we demonstrate the use of combinatorial slot-die coating to fabricate perovskite semiconductors varying the compositions from $FAPbI_3$ to $MAPbBr_3$. It provides a direct method for synthesis and mixing of perovskite compositions by varying the pump rate. We fabricated solar cell devices and found devices with the composition $FA_{0.8}MA_{0.2}Pb(I_{0.8}Br_{0.2})_3$ yielded the best performance, which is consistent with the previously published result.[2] To characterize the homogeneity and quality of samples, we carried out morphological, optical and crystallographic measurements on thin-films. We found that the coverage of high bromine samples is poor, which is due to the different crystallization pathways of bromide compared to iodide-based perovskite.[3] The $FAPbI_3$-rich devices give better performance due to the improved morphology, which suggests the combinatorial slot-die coating method is suitable for fabrication of solar cells. This work highlights both the potential and obstacles using a high-throughput strategy for screening and exploring the compositional and structural properties of metal halide perovskite semiconductors.
Reference:
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SESSION EL14.05: Poster Session
Session Chairs: Jens Andreasen and Udo Bach
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL14.05.02
SnF_2-Doped Cs_2SnI_6 Ordered Vacancy Double Perovskite for Photovoltaic Applications Rubaiya Murshed, Sarah Thornton, Curtis Walkons and Shubhra Bansal; University of Nevada Las Vegas, United States

Cs_2SnI_6, an emerging inorganic perovskite variant is considered an environmentally benign lead-free option for photovoltaic application. Cs_2SnI_6 offers favorable optoelectronic properties as well as high stability due to the presence of the tetravalent oxidation state. Owing to its p-type semiconducting nature, Cs_2SnI_6 has previously been reported as an efficient hole transport material. However, its candidacy as a potential light absorber is still being explored in different strategical investigations. In this study, for the first time, Cs_2SnI_6 has been used in a superstrate *n-i-p* planar device structure enabled by a spin-coated absorber thickness of ~2 mm on a chemical bath deposited Zn(O,S) electron transport layer. The crystalline Cs_2SnI_6 phase is obtained with CsI, SnI_2, and SnF_2 salts in a solvent mixture of Gamma-Butyrolactone (GBL) and N, N-Dimethylformamide (DMF) and a bandgap of 1.6 eV has been demonstrated. The best device power conversion efficiency reported here is 5.18% with V_{OC} of 0.81 V, J_{SC} of 9.28 mA/cm^2 and a fill-factor of about 68%. The devices exhibit a high V_{OC} deficit, and higher device efficiency can be expected by improvement of material quality, charge transport and device engineering.

5:00 PM EL14.05.04
0D–2D Hybrid Photodetectors using Multilayer MoS_2 and Lead Halide Perovskite Quantum Dots with Tunable Bandgap SeockJin Jeong and Jong-Soo Lee; Daegu Gyeongbuk Institute of Science & Technology (DGIST), Korea (the Republic of)

We report high-performance 0D–2D hybrid photodetectors integrated with tunable band gap perovskite ($CsPbI_3$, $Cs_XFA_{X-1}PbI_3$, and $FAPbI_3$) quantum dots and MOCVD-grown bilayer MoS_2. In our hybrid structure, the lead halide PQDs can be utilized as an absorbing layer of the light of specific wavelengths and transfer the photogenerated carriers to the MoS_2 transport layer. With tunable wavelength lead halide PQDs, the 0D–2D hybrid photodetector shows a high responsivity up to 10^7 AW^{-1} and high specific detectivity exceeding 10^{13} Jones due to the difference in the built-in potential between PQDs and multilayer MoS_2 layers. This work proposes the possibility of fabricating high-performance photodetectors by hybridizing PQDs of various band gaps with 2D materials.

5:00 PM EL14.05.05
High Throughput Screening of Composition in Multicomponent Organic Based Photovoltaics Mariano Campoy-Quiles; ICMAB-CSIC, Spain

Combining two acceptors and one donor in the active layer of organic solar cells, also referred to as ternary blending, has become a very important strategy in this field in order to improve light harvesting, as well the preventing morphological evolution. The efficiency strongly depends on the exact ternary composition, as the optimum mixing will be a compromise between transport and optical properties. Despite its importance, predicting how the final efficiency of a system depends on composition has been, thus far, elusive [1].
In this talk, we will first describe a novel methodology for the fast evaluation of binary and ternary systems for photovoltaics. The new approach is based on the fabrication of samples with gradients in the relevant parameters of interest that represent a large fraction of the corresponding parameter space. In particular, we fabricate gradients in thickness, microstructure, and composition, and apply hyperspectral imaging to correlate material and device properties [1]. Then, we will show how this machinery, which is ca 100 faster than conventional optimization protocols [2], can be used to cartograph the complex composition phase diagram for ternary organic solar cells based on a single polymer donor (such as P3HT, PTB7-Th or PM6) and two acceptors (e.g. IDTBR, IDFBR, Y6, ITIC, PCBM, etc.) [3,4]. We find that, depending of the specific system, the ternary land scape can exhibit either one or more efficiency maxima. We also observe that the optimum composition is often found outside the 1:1 donor:acceptor ratio trajectory. Finally, we will discuss different options to choose the third material in the ternary, including the use of an experimental genetic algorithm method that we have developed.

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X. Rodríguez-Martínez, E. Pascual-San-José, M. Campoy-Quiles, *Energy & Environmental Science*, 14, 3301 (2021)
[3] Efficient exploration of the composition space in ternary organic solar cells by combining high-throughput material libraries and hyperspectral imaging, A. Harillo-Baños, X. Rodríguez-Martínez and M. Campoy-Quiles, *Advanced Energy Materials*, 10, 1, 1902417 (2020).
[4] Suppressing CoCrystallization of Halogenated NonFullerene Acceptors for Thermally Stable Ternary Solar Cells, S. Hultmark, et al, Advanced Functional Materials, 30, 2005462 (2020).

5:00 PM EL14.05.06
Metal-Organic Chemical Vapor Deposition of Hybrid Perovskites Alicia Bryan, Jonathan Meyers, Lorenzo Serafin and James Cahoon; University of North Carolina at Chapel Hill, United States

Hybrid perovskites (HPs) have become widely recognized in the chemistry and materials science communities as a promising candidate for the next generation of efficient optoelectronic and photovoltaic devices. Their unique hybrid organic-inorganic nature affords HPs an exciting blend of electronic and structural properties, and yields both advantages and challenges in fabrication. The vast majority of HP fabrication methods to date have focused on simple solution processing, while comparatively few vapor-phase HP deposition methods have been developed, and these broadly rely on single-source evaporation of solid HP perovskite crystals or dual-source coevaporation of precursor salts. However, these methods suffer from limited control over reactant vapor pressures and temperatures that in turn lead to limited control over final film composition and morphology. In light of this, we have developed a metal-organic chemical vapor deposition (MOCVD) method for HP fabrication to enable precise control of composition, stoichiometry, and film morphology. Using our custom-built reactor equipped with vapor precursors including methylamine, tetraethyllead, and hydrogen halide gasses, we have successfully deposited $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ perovskites as confirmed using X-ray diffraction, UV-visible spectroscopy, and scanning electron microscopy. We have further probed deposition on a variety of substrates including silicon oxides, glass, and organic-functionalized materials to investigate the vital relationship between substrate identity and film nucleation and growth dynamics.

SESSION EL14.06: Virtual Session: High Throughput Discovery of the Next-Generation Perovskites for Opto-Electronics

Session Chairs: T. Jesper Jacobsson and Eva Unger
Tuesday Afternoon, April 25, 2023
EL14-virtual

9:00 PM EL14.06.01
Materials Screening of Interface Passivation Layer in Perovskite Photovoltaic Devices Using Machine Learning Zhe Liu, Chongyang Zhi, Suo Wang and Zhen Li; Northwestern Polytechnical University, China

Machine learning (ML) has increasingly gained attention in the field of materials science, especially to accelerate the development of new energy materials. Particularly, we tackle the materials screening challenge of interface passivation layers in perovskite solar cells (PSC). Perovskite solar cells with quasi-2D passivation layers is known to be effective to achieve record-high efficiencies (*e.g.*, 2D/3D PSCs). However, the large number of available organic compounds has made the trial-and-error experimental approach very inefficient. In this study, we demonstrated a materials screening framework using ML methods, with experimental validations using new data collected from our lab as well as scientific literature. The ML method is applied to investigate the relationship between the molecular features of ammonium salts and the PCE improvement ratios. We establish an accurate predictive model with a dataset of 19 ammonium salts via the following two methodological innovations: (1) data-bias correction by adding diversely sampled data in the material feature space, and (2) ensemble ML learning with five base learners of distinct model architectures. Along with the Shapley Additive Explanations (SHAP) analysis method, four molecular features (*i.e.*, hydrogen atom, hydrogen bond donor, partition coefficient, and complexity) are identified as the most important, having suitable value ranges for screening the ammonium salts for a better passivation effect. Therefore, the molecular feature criteria are used to downselect 10 candidates from a pool of approximately 112 ammonium iodides available in the PubChem database. Finally, PSCs are fabricated using the predicted ammonium iodides for the model validation. We demonstrated efficient PSCs with a 3-phenylpropan-1-aminium iodide (PPAI) induced interface layer, achieving PCEs of 21.87% and 24.32% in PSCs with $(FA_{0.83}MA_{0.17})_{0.93}Cs_{0.07}Pb(I_{0.83}Br_{0.17})_3$ and $FA_{0.92}MA_{0.08}PbI_3$ absorber layers, respectively. We believe that ML-assisted material screening can help us interpret the crucial molecular features for perovskite interface passivation, and effectively predict the materials candidates. The proposed ML workflow can be easily adapted for screening a wide range of organic molecules to improve the performance and stability of optoelectronic devices.

9:15 PM EL14.06.02
High-Throughput Screening of Organic Solar Cells Based on PTQ10:NFA to Determine the Best Compromise Between Efficiency and Stability
Sergi Riera-Galindo[1], Arnau Guiteras[1], Marta Sanz[2], Laura López-Mir[2] and Mariano Campoy-Quiles[1]; [1]ICMAB-CSIC, Spain; [2]Eurecat Technology Center, Spain

High power conversion efficiency (PCE) and stability are essential for the industrial viability of organic photovoltaic (OPV). The optimization of device

PCE and stability is a multi-parameter complex system. High-throughput screening offers tremendous opportunities to accelerate the discovery of optimal material composition and structure of efficient and stable organic solar cells.

In this work, we present the stability of organic solar cells based on PTQ10 with different acceptors. First, we evaluate the impact of the molecular weigth (MW) of the PTQ10 donor polymer blended with three differente non-fullerene acceptors (NFAs) (ie. IDIC, Y6 and Y12) on the performance of organic solar cells. By increasing the MW from 10 to 147 kDa, the efficiency improves by one order of magnitude, from around 2% up to 12%. The devices with higher molecular weights also show better thermal stability. We also characterized the active layer materials by photoluminicence, Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) and charge carrier mobility.

Moreover, we explore by combinatorial screening the dependence of the stability with the active layer thickness following ISOS protocols, in order to determine if the optimal thickness for power conversion efficiency matches the thickness of the most stable devices.

As a result, we report stable and promising systems of organic solar cells for industrialisation of low cost organic photovoltaics.

9:30 PM *EL14.06.03
Accelerating Perovskite R&D Using Direct Multi-Material Printing Tonio Buonassisi, Alexander E. Siemenn and James Serdy; Massachusetts Institute of Technology, United States

In this study, we present a hardware and software platform that could accelerate deposition and characterization of perovskite solar cell materials by a factor of >1000x relative to spin coating. The hardware is a “direct multi-material printing” method known as “chemjet.” We utilize multiple positive-displacement fluid dispensers, combine fluids using a joiner valve, and dispense the mixture *via* a nozzle onto a substrate at a rate of up to 2000 unique formulations per minute.

It is natural to ask, to what extent perovskite materials deposited *via* chemjet are similar to those deposited via spin coating or slot-die coating methods. To build trust, we demonstrate the equivalence of X-ray diffraction patterns and optical absorption (UV-Vis) profiles between perovskite materials in the $(MA,FA)PbI_3$ family with both chemjet and spin coating.

We discuss the machine-learning control loops employed to optimize for materials properties, and aid the researcher in extracting scientific insights. This presentation concludes with a prospectus of the scientific questions currently being addressed using this platform, as well as an overview of the future strengths and challenges of chemjet.

*credit to Aldair Gongora for introducing Buonassisi to the term “direct multi-material printing.”

SYMPOSIUM

April 11 - April 25, 2023

Symposium Organizers
Brandon Durant, Naval Research Laboratory
Ahmad Kirmani, National Renewable Energy Laboratory
Lyndsey McMillon-Brown, NASA Glenn Research Center
Bibhudutta Rout, University of North Texas

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National Renewable Energy Laboratory (NREL)
University of North Texas, COS Grant Support

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* Invited Paper
\+ Distinguished Invited

SESSION EL15.01: Next-Generation Lightweight Technologies for Space Photovoltaics and Electronics
Session Chairs: Ahmad Kirmani and Lyndsey McMillon-Brown
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3000

1:30 PM *EL15.01.01
Perovskite and Organic Solar Cells for Space Applications Peter Muller-Buschbaum; Technical University of Munich, Germany

Due to massive research, the champion devices for perovskite solar cells have passed the 25% device efficiency threshold and organic solar cells approach

20%. In general, perovskite and organic solar cells only require comparatively thin absorber layers on the order of 100 nm, which enables a reduction in device thickness of the total solar cells well below 1 µm. Moreover, processing of the perovskite and organic layer can be done from solution on flexible substrates at low temperatures via potential scalable methods like printing and spray coating. Thereby, flexible solar cells can be fabricated. Combining these advantageous factors, enables fundamentally higher specific energy densities compared to the classical solar cell types used in space so far. Moreover, it will open up new possibilities in transport, deployment, and application of perovskite and organic solar cells in space. However, so far, performance data of perovskite and organic solar cells in space environment is very limited. Besides promising laboratory experiments that can never capture the full set of ambient conditions present in space, some near-space experiments have been performed in the upper atmosphere with appealing results regarding the performance and stability.
Here, we present the first electrical characterization of perovskite and organic solar cells at orbital altitudes [1]. Space flights are an ideal platform to investigate the behavior of solar cells in conditions that are characterized by ultra-high vacuum, strong UV solar irradiation, and the absence of oxygen or water outside Earth's atmosphere. During a suborbital rocket flight, we measured the voltage-current response of perovskite and organic solar cells under different illumination conditions. The combination of the solar cell measurements with irradiance data obtained from simultaneous light sensor measurements allows for deducing the performance parameters. Our results show that the solar cells survived the harsh conditions during transport, the start preparation procedure, and the rocket launch, where the best solar cells reached power conversion efficiencies of more than 10% for perovskite-based solar cell modules. Our results show the versatility of perovskite solar cells for application in various environmental conditions, with promising potential to revolutionize future renewable energy production in space.

[1] Reb et al. Joule **4**, 1880-1892 (2020)
[2] Reb et al. Rev. Sci. Instr. **92**, 074501 (2021)

2:00 PM *EL15.01.02
X-factors that Might Determine How Perovskite Solar Cells are Deployed Michael D. McGehee; University of Colorado, United States

Metal halide perovskite solar cells might be deployed as single junctions or in tandems that could consist of wide bandgap perovskites paired with silicon, copper indium gallium dye selenide or a narrow-bandgap perovskite. Modules might be made with singulated cells that are connected by wires or ribbons or in a monolithically integrated architecture made with several laser scribes. Researchers often discuss the efficiency, stability under standard operating conditions and cost of the various options when making the case that one approach is the most attractive. These factors are indisputably important, but there are other factors that do not get as much attention, but could end up determining which approach is the best one. We will discuss reverse bias degradation that can occur when a panel is partially shaded and comment on which architectures are likely to be the most resistant to this type of degradation. We will discuss why some architectures are likely to have higher yield than others and point out that laser scribing along with metal vias could introduce degradation mechanisms that are not seen in the cells that are frequently put through accelerated lifetime testing.

2:30 PM BREAK

3:00 PM *EL15.01.03
Radiation Effects in Quantum Well Multi-Junction Solar Cell Seth Hubbard, Stephen Polly and Brandon Bogner; Rochester Institute of Technology, United States

The space III-V photovoltaic industry relies on multijunction solar cell technology meeting high-efficiency, low weight, and radiation tolerance metrics. Incorporation of nanostructures in the current-limiting subcell of the III-V multijunction solar cells has been shown to be an efficient way to achieve current matching between the subcells. Adding QWs to the intrinsic region of the limiting GaAs subcell of a standard triple junction InGaP/GaAs/Ge solar cell, on the one hand, enables absorption of the sub-band edge photons, effectively lowering the bandgap of the middle cell, and at the same time can allow for efficient carrier extraction. Engineering of the energy states in the strained QWs for enabling carrier escape via tunneling and thermalization can be approached by tuning the width of the QWs, as well as by changing the separating energy barriers height and width. Increasing the number of strained QWs strongly impacts the absorption in the QWs, however, the strain energy accumulation in the QWs has to be carefully balanced with appropriate and oppositely strained barrier material to maintain low non-radiative recombination. Alternatively, using rear-side distributed Bragg reflectors (DBR) structures, the optical thickness of the QW region can be nearly doubled.

In this talk, I will demonstrate development of both single-junction GaAs and tandem InGaP/GaAs solar cells incorporating $In_{0.08}Ga_{0.92}As$ strain balanced quantum wells. This work builds on previous reports of the integration of InGaAs quantum wells in an InGaP/GaAs heterojunction solar cell with minimal loss in Voc, as well as significant effort to understand the growth conditions required for strain compensation with GaAsP including the effects of phosphorus content, growth temperature, gas switching sequence, and substrate orientation. Up to 50 layers of strain balanced QWs have been added to a single junction device with minimal degradation in Voc and monotonic increase in Jsc. A distributed Bragg reflector (DBR) was added below the structure centered at the collection energy of the QWs to increase the optical path length of the QW region and further increase subgap current collection. Finally, these components were assembled into dual-junction device comprised of an InGaP homojunction and InGaP/GaAs heterojunction optimized with and without the incorporation of 50x QWs and a DBR for AM0 and AM1.5G spectra. These developments have resulted in radiation tolerant 2-junction solar cells incorporating QWs, with a 27.5% AM0 (>30% AM1.5G) efficiency, representing a 2.5% absolute efficiency increase over a control 2-jucntion solar cell without QWs. Radiation testing is currently ongoing.

In addition, we have also investigated the impact of integrating advanced textured photonic structures to increase the optical path length (OPL) in thin and ultra-thin GaAs and $In_{0.3}Ga_{0.7}As$. In particular, we have demonstrated a facile *in situ* method for back surface textures that can be accomplished using standard metal organic vapor phase epitaxy. The textured films were characterized using specular and diffuse reflectance measurements as an indicator of improved angular reflectance.

3:30 PM *EL15.01.04
Development of Electronics Technologies for Space Radiation Environments Jesse Mee; Air Force Research Laboratory, United States

The United States Space Force (USSF) space systems are growing rapidly in complexity to meet the needs of the future Department of Defense (DoD) space architecture. These national assets provide surveillance, communications, navigation, positioning and timing functions for both the DoD and commercial sectors, and all ultimately rely on advanced electronics circuits, systems and devices. Operation in a space radiation environment puts unique constraints on the types of electronics that can be deployed into these systems depending on the orbit altitude, inclination and mission duration. Adding to the complexity, the future USSF architecture is envisioned to include a hybrid mix of large, long-lived, high-value assets augmented by a layer of smaller, shorter-duration, satellite constellations. This creates a spectrum of space radiation tolerant and radiation hardened electronics needs to support these systems. It is the mission of the Air Force Research Laboratory Space Vehicles Directorate (AFRL/RV) Space Electronics Technology (SET) team to provide trusted, affordable, radiation hardened/tolerant, high-performance, and reliable electronics for future USSF space systems. This presentation will discuss the trade-space in electronic components development to meet "new-space" requirement for high-performance with good-enough radiation tolerance, while continuing to support legacy radiation hardened electronics needs for long lived systems.

4:00 PM *EL15.01.05
Metal Halide Perovskites for Space Applications - An Industry Perspective Giles Eperon; Swift Solar, United States

TBD

4:30 PM EL15.01.06
Ultra-high Properties of Carbon and Boron Nitride Nanomaterials toward Space Materials Jun Kyung Kim, Se Gyu Jang, Hyeonsu Jeong, Seokhoon Ahn, Bon-Cheol Ku, Seung Min Kim and Jin Sang Kim; Korea Inst of Science and Technology, Korea (the Republic of)

The space elevator is an earth-to-space transportation system, and carbon nanotube (CNT) fibers and boron nitride nanotubes (BNNTs) which can protect CNT fibers from the space environment have been considered as core materials. To develop core technologies for these materials, Korea Institute of Science and Technology (KIST) has been carrying out the "4 Ultrahigh-performance Composites Development Project" since 2017, where 4U stands for ultra-light weight, ultra-high strength, conductivity, and shielding. In this presentation, we will share major achievements through the 4U project.
For high-performance CNT fibers, we have developed various techniques based on both the direct and wet-spinning methods. The main achievement among the direct spinning-based techniques is the fast densification method derived from the principle of wet-spinning method [1]. Directly-spun CNT fiber usually possesses poor internal structure with less aligned CNTs and lots of voids, which critically limits the properties of directly-spun CNT fiber. To overcome this issue, we developed the method in which swollen CNT fiber by chlorosulfonic acid was stretched and coagulated. This method allowed us to fabricate highly-aligned and densified CNT fiber with excellent properties in a minute. Furthermore, the high-performance CNT fibers by wet-spinning technique were fabricated after optimizing fiber orientation and defects. The highly oriented and densified CNT fibers were then thermally treated, which resulted in producing ultra-high strength and modulus CNT fibers with high electrical and thermal conductivity [2].
For BNNTs, we have intensively studied the synthesis, purification, dispersion, and fibers of BNNTs. For example, the growth mechanism of BNNTs was identified through the discovery of open tip growth mode by radicals, and BNNT purification and dispersion technology was developed through polymer functionalization.

Reference

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[2] D. Lee et al., "Ultrahigh strength, modulus, and conductivity of graphitic fibers by macromolecular coalescence," Sci. Adv., 8(16), eabn0939 (2022).

4:45 PM EL15.01.07
Radiation Tolerance of $GaAs_{1-x}Sb_x$ Solar Cells—A Candidate III-V System for Space Applications Hadi Afshari[1], Brandon Durant[1], Tristan Thrasher[1], Logan Abshire[1], Vincent R. Whiteside[1], Shun Chan[2], Dongyoung Kim[2], Sabina Hatch[2], Mingchu Tang[2], Jeremiah McNatt[3], Huiyun Liu[2], David Smith[4] and Ian R. Sellers[1]; [1]University of Oklahoma, United States; [2]University College London, United Kingdom; [3]NASA Glenn Research Center, United States; [4]Arizona State University, United States

The high radiation tolerance of $GaAs_{0.86}Sb_{0.14}$ based solar cells with a bandgap suitable for PV is demonstrated at the low intensity low temperature (LILT) conditions. This system shows remarkable radiation hardness at AM0, and more prominently, at the conditions of several outer planetary targets. The photovoltaic behavior of the system after electron irradiation is attributed to an irradiation induced change in the absorber bandgap due to local heating and strain relaxation, and the generation of less prohibitive shallow Sb-based defects in the $GaAs_{1-x}Sb_x$ absorber.
Both high efficiency and radiation tolerance are the two essential factors required for solar cells working in space. While III-V multi-junction solar cells are used ubiquitously in space, the radiation tolerance of such systems, particularly in deep space brings added complexity to their design since there is large variability in the sub cell radiation tolerance. Although, numerous studies have been performed to improve radiation resistance of the tandem structures; still thick cover glass is required, which increases the weight and reduces the specific power of the systems. GaAs as one of the most successful PV technologies has now reached record PCE levels, but its response to high radiation levels under LILT conditions is concerning (particularly around Jupiter and its moons) requiring very thick cover glass which removes the ability for compact stowage and deployment. Recently, ultrathin GaAs has been shown to offer potential as a more radiation hard system for space, if appropriate optical management can be designed to improve the absorption. Here, we propose GaAsSb as an alternative candidate system for space power applications, particularly in the regions of harsh radiation conditions of outer space and under LILT conditions. We show remarkably radiation tolerant performance in optically thick optimized $GaAs_{0.86}Sb_{0.14}$ without encapsulation suggesting this material should be further considered for hostile space missions including those to Jupiter or for satellite applications in Highly Eccentric Orbits (HEO) being considered to provide better internet coverage which require more robust systems than are currently available.

SESSION EL15.02: Perovskite Photovoltaics for Space Applications
Session Chairs: Giles Eperon and Joseph Luther
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3000

8:30 AM *EL15.02.01
Perovskite Solar Cells a New Horizon for Space Power Systems? Ian R. Sellers; University of Oklahoma, United States

In this presentation the potential of metal halide perovskite solar cells for space power applications will be presented. This discussion will focus on recent work at the University of Oklahoma, which includes the assessment of the systems in low-intensity-low-temperature (LILT) conditions for outer planetary missions, in addition to exposure to high temperatures and variable radiation conditions that directly and independently impact the absorber material and transporting layers of the solar cells. This presentation will discuss a number of perovskite systems including mixed Pb-Sn systems and the FAMACs family of metal halide perovskites. It will be shown that perovskites display remarkable tolerance to high radiation exposure and that while measurements *do* suggest high energy radiation negatively affects the transporting layers and interfaces in the devices: the perovskite absorber *is not affected* in any significant way. Moreover, these systems are observed to self-heal under ambient conditions in the dark demonstrating the unique behavior of perovskite solar cells and their potential for future space applications. This is further substantiated by high temperature measurements that indicate specific triple cation perovskites displays no appreciable or permanent degradation up to 500 K, supporting in particular their potential as candidate systems for future lunar missions.

9:00 AM *EL15.02.02
Perovskites and Other Emerging Photovoltaic Technologies for Space Applications Michael Kelzenberg, Phillip Jahelka and Harry A. Atwater; California Institue of Technology, United States

Perovskite solar cells have emerged as promising candidates for space applications owing to their high absorption coefficient, which allows for sub-micron cell thicknesses, and to their promising radiation tolerance. They have been fabricated on thin (<2 µm) flexible polymer superstrates, allowing for specific power up to ~30 kW/kg at the cell level, dramatically higher than other cell technologies. However, the space environment subjects solar cells to ionizing radiation and elevated operating temperatures, which for conventional space photovoltaics, requires the addition of radiation shielding coverglass for radiative cooling and to prevent premature degradation of the efficiency. Conventional coverglass typically ranges from 70—200 µm in thickness, and would substantially erode the specific power advantage of ultrathin perovskites. It is thus of interest to study the stability of perovskite solar cells in the space environment, to determine how much shielding or cooling materials would be necessary for use in various orbits or mission lifetimes. We will present the results of prior and ongoing radiation studies including high-energy electrons and low-energy protons, and discuss the viability of thin polymer substrates and shielding materials. Our research also includes other emerging photovoltaic technologies for space applications, including luminescent solar concentrators, nanostructured III-Vs for improved radiation hardness, and low-cost diffused-junction GaAs cells. We will discuss developments in these cell technologies and our present effort to measure the behavior of research devices in low-earth orbit.

9:30 AM BREAK

10:00 AM EL15.02.03
Radiation Tolerance Testing and Materials Analysis of Perovskite Solar Cells Utilizing a Versatile Ion Beam Facility at the University of North Texas Bibhudutta Rout; University of North Texas, United States

Recently, several groups have shown that perovskites based solar cells show significant tolerance to proton radiation, however, perovskites also suffer from beam-induced damage in simple SEM characterization. Understanding the full extent of the various radiation-induced effects will greatly de-risk the perovskites for various non-terrestrial as well as terrestrial PV applications. Recently, we have performed several studies on the effects of proton and alpha irradiance at various fluences and energies, enabling the comprehensive assessment of the relative contribution of both nuclear and electron ionization losses in these materials. Using the stopping range of ions in matter simulations (SRIM) and damage displacement dose analysis in conjunction with targeted experimental irradiation energies and fluences we have developed a semi-empirical approach to evaluate the performance, radiation tolerance, and self-healing of solar cells. The correlation between the structural evolution of materials and device performance under irradiation can be estimated before the experiments by calculating the contributions to the total vacancies by the individual constituent elements.
At the University of North Texas, Ion Beam Laboratory, we have two dedicated accelerator facilities providing proton beams of energies from a few tens of KeV to several MeV enabling targeted irradiation of various layers of the devices. We have also a novel and powerful set of integrated in-situ analytical techniques for defect characterization in PV devices along with simultaneously performing irradiation of targeted layers of the devices.
In this presentation, we will provide updated results of these ion irradiation tolerance testing, radiation induced defect generation, as well as an in-situ elemental and charge collection analysis of the various layers of the perovskite-based solar cells.

10:15 AM EL15.02.04
Low-Cost and Lightweight Oxide Barriers for Space and Terrestrial Perovskite Solar Cells Ahmad R. Kirmani; Rochester Institute of Technology, United States

With parallel improvements in device efficiency and operational stability of perovskite solar cells, efficient and lightweight packaging schemes become the next frontier of research in this direction. Such schemes are also important for deployment of perovskite photovoltaics in aerospace applications, given their promising radiation hardness.[1] I will present our latest metal oxide based ul1tralight barrier layers that can be deposited using low-cost scalable techniques atop perovskite solar cells. 1-micron thick silicon oxide (SiO_X) will be shown to improve device tolerance against the most critical space and terrestrial stressors including low- and high-energy protons, alpha particles, atomic oxygen, moisture, and polar solvents (DI water, and dimethylformamide, DMF).[2] The barrier layer is electrically insulating, mechanically dense, crack-free, uniform, and chemically inert to the perovskite device stack. Based on these experiments, the calculated lifetime of the device in the low-Earth orbit (LEO) increases from ~0.3 years for bare cells to ~6 years after SiO_X encapsulation. The technology is attractive simultaneously for terrestrial and space applications, minimizing packaging costs and module weights, and maximizing specific power.

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2). Kirmani, A. R.; Ostrowski, D. P.; Bramante, R. C; Heinselman, K. N.; Tong, J.; Byers, T. A.; Stevens, B.; VanSant, K. V.; Zhu, K.; Sellers, I. R.; Rout, B.; Luther, J. M., Metal Oxide Barrier Layers for Terrestrial and Space Perovskite Photovoltaics. *Nature Energy* (accepted), **2023**

10:30 AM *EL15.02.05
Sublimed Perovskite Based Photovoltaics for High Altitude and Space Applications Henk J. Bolink[1], Javier Sebastián[1], Claus Zimmermann[2] and Michele Sessolo[1]; [1]University of Valencia, Spain; [2]Airbus Defense and Space, Germany

Metal halide perovskite solar cells (PSCs) are of interest for high altitude and space applications due to their lightweight and versatile form factor. However, their resilience toward the particle spectrum encountered in space is still of concern. For space cells, the effect of these particles is condensed into an equivalent 1 MeV electron fluence. The effect of high doses of 1 MeV e-beam radiation up to an accumulated fluence to 1016 e� cm�2 on methylammonium lead iodide perovskite thin films and solar cells is probed. By using substrate and encapsulation materials that are stable under the high energy e-beam radiation,
its net effect on the perovskite film and solar cells can be studied. The quartz substrate-based PSCs are stable under the high doses of 1 MeV e-beam irradiation. Time-resolved microwave conductivity analysis on pristine and irradiated films indicates that there is a small reduction in the charge carrier diffusion length upon irradiation. Nevertheless, this diffusion length remains larger than the perovskite film thickness used in the solar cells, even for the highest accumulated fluence of 10E16 e� cm�2. This demonstrates that PSCs are promising candidates for space applications.

11:00 AM EL15.02.06
Stress Testing of Perovskites Solar Cells For Stable Operation in Space Kaitlyn VanSant[1,2], Ahmad Kirmani[3], Kyle Crowley[1], Xiaopeng Zheng[2], Joseph Luther[2], Timothy Peshek[1] and Lyndsey McMillon-Brown[1]; [1]NASA Glenn Research Center, United States; [2]National Renewable Energy Laboratory, United States; [3]Rochester Institute of Technology, United States

Perovskite solar cells (PSCs) could transform space energy generation by providing a low-cost alternative to existing space photovoltaic (PV) technologies. They exhibit promising radiation tolerance, high specific power and low costs could be obtained with high volume manufacturing. NASA has significant interest in designing a PSC resilient to stress conditions relevant to the lunar surface, with a specific focus on understanding contacts and barrier layers to maximize stability.

To achieve this goal, the cell must be able to withstand extreme ultraviolet light, harsh radiation, hard vacuum and temperatures up to 75°C, assuming thermal management will protect the cells from the lunar ambient temperature extremes.[1] In order to be a viable space PV technology, the perovskite solar cells will also need to be space-qualified, which will require either encapsulation or a barrier layer to protect the cells from the terrestrial environment (prior to launch) and on the lunar surface. Space-qualified cells must also meet NASA's strict out-gassing requirements.[2]

In our research, we focused on the down-selection of both the contacts and the barrier layers for solar cells designed to operate in the lunar environment. We used a p-i-n device architecture, with a triple cation perovskite absorber.[3] We explored contacts composed of bathocuproine (BCP)/Ag, BCP/Au and a contact consisting of SnO_x/Indium tin oxide (ITO)/Au, referred to as ITO contacts.[4] For the barrier layers, we investigated a SiO barrier layer alone; a space-grade two-part silicone, DC93-500, with cover glass; and a combination of these two schemes (i.e. SiO/DC93-500/cover glass). Preliminary results from stressing the cells at 75°C under modest vacuum conditions (10 – 20 mTorr) were used to select the most thermally robust combination of contacts and barrier layers. We then used a cryostat to apply light, heat and vacuum conditions simultaneously to these selected cells. To augment these cell-level stress studies, synchrotron X-ray diffraction data was measured as a function of temperature at SLAC to assess the crystallographic structural stability of the full cell stack, over a similar temperature range to that used for the thermal vacuum stress testing.

In this presentation, we will summarize the optimal combination of contacts and barrier layer(s) that we devised, based on the results of this stress testing. We will also report on how cells with the selected architecture performed, when exposed to electron-beam irradiation.

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SESSION EL15.03: Radiation Tolerance of Perovskite Photovoltaics
Session Chairs: Bibhudutta Rout and Ian Sellers
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3000

1:30 PM *EL15.03.01
Perovskites Built for Space—Radiation, Thermal Cycling, Cell Design and Packaging Joseph Luther; National Renewable Energy Laboratory, United States

The space power market is now undergoing rapid growth with many more small satellites to be launched over the coming years with significant cumulative power requirements. Perovskites offer a unique potential alternative to both Silicon photovoltaics and III-V multijunction technology used today due to perovskites unique defect/radiation tolerance, packaging/lightweight configurations coupled with their low cost. However, they must first be shown to withstand the harsh environments which can involve proton, electron, neutron, and alpha particle irradiation, coupled with rapid and extreme thermal cycling, and high temperatures reached under the more powerful AM0 spectrum (1347 W/m2 vs 1000 W/m2 for AM1.5G) Perovskites devices offer many design flexibilities which can be exploited to construct devices specifically for space conditions but must each be tested for nuances in stability and performance. One such example is that perovskite cells with "PIN" geometry (which is defined as a structure with hole contact deposited before the Perovskite and electron contact after the perovskite) can be designed to operate with a temperature coefficient as low as 0.08 %/K, which is among the best in all photovoltaics, whereas other configurations show much more undesirable decrease in performance at high temperature. Thus, when designing a cell specifically for space application, it is critical to explore each of the space stressors as a function of the layers, compositions, and packaging. Here, I will discuss guidelines and initial testing results for perovskites using earth-based radiation sources for evaluation radiation tolerance in various space orbits. These results will be discussed with the community at MRS to better understand the feasibility of perovskite technology and potential collaboration opportunities for space applications.

2:00 PM *EL15.03.02
Scalable Halide Perovskites—Radiation Tolerance and Processing Sensitivities Samuel D. Stranks; University of Cambridge, United Kingdom

Halide perovskites have opened up a new world of semiconductors that can be processed inexpensively by solution or vapour yet perform exceptionally well. These materials are realising new paradigms for solar cell manufacturing at high throughput, including lightweight, high power modules that could enable new applications in space, aerial communications and electric vehicles. Here, I will show new results in which we have vapour-deposited tunable halide perovskite absorbers, which we in turn use in high-performance tandem cells. I will show how sensitive the fabrication can be to processing conditions, and how to control such parameters to realise high performance including with passivation approaches. I will also show tests of halide perovskite devices for proton radiation hardness required for space applications, and characterise the devices on different length scales. The materials demonstrate extremely good resilience to proton radiation even at very high doses. However, I will also show their limitations when bombarded with electrons or X-rays.

2:30 PM BREAK

3:00 PM EL15.03.03
Anneal Recovery Post-Proton Irradiation of Hybrid Organic-Inorganic Metal Halide Perovskite Solar Cells and Study of Radiation Effects on Each Component Material Nina Vaidya[1,2], Samuel Loke[1], Jing Shun Huang[1], Michael Kelzenberg[1], Pilar Espinet-Gonzalez[1], Arky Yang[1], Stepan Demchyschyn[3,1], Jonathan Grandidier[4,1], Martin Kaltenbrunner[3] and Harry A. Atwater[1]; [1]California Institute of Technology, United States; [2]University of Southampton, United Kingdom; [3]Johannes Kepler University Linz, Austria; [4]NASA Jet Propulsion Laboratory, United States

Nina Vaidya*[1] and Samuel Loke*[1], Jing-Shun Huang[1], Michael D. Kelzenberg[1], Pilar Espinet-Gonzales[1], Arky Yang[1], Jonathan Grandidier[1,2], Stepan Demchyschyn[1,3], Martin Kaltenbrunner[3], Harry A. Atwater [1]
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We propose the recently expanding field of hybrid organic-inorganic metal halide perovskites solar cells to offer avenues to achieve high specific power (power/mass) needed for space-based power systems. These perovskites present tuneable band gaps ideal for a solar cell absorber layer, when combined with their favourable carrier diffusion lengths arising from high carrier mobility and lower ease of formation of deep-band defects, have thus far resulted in single-junction record efficiencies of 25.7% -perovskite solar cell have over taken efficiencies of thin-film Silicon solar cells. The ability to process the perovskite family of materials at temperatures below 473K via solution processing techniques such as spin-coating, spray coating, and even printing offers avenues for low-cost fabrication of perovskite solar cells. Moreover, work has been done to investigate the viability of perovskite solar cells on a flexible substrate, and it has been shown to be robust enough for flexible and ultralightweight cells, achieving power densities as high as $23Wg^{-1}$ [1]. As such, perovskite solar cells present themselves as a potential candidate for the high specific power technology necessary to enable space based solar power. More critically, perovskites are sensitive to oxygen and water vapor, both of which are not present in space and hence they inevitably become an extremely important opto-electronic energy materials to investigate for space applications.

Hybrid organic-inorganic lead halide perovskite solar cells and their constituent device material layers were irradiated to examine their viability for space energy applications. Perovskites cells, hole and electron transport material films, and transparent conducting films were irradiated with 30keV and 75keV protons at fluences ranging from 4.3×10^{13} p^+ cm^{-2} to 1.7×10^{14} p^+ cm^{-2}. The optical transmission and electrical resistances of the charge-transport material films were characterized before and after irradiation to deconvolve and assess the individual contribution of these materials on the degradation of perovskite devices. We conclude, some materials like PEDOT do become more opaque. Apart from these, electrically, the damage to many of these materials is low enough that there is only a small impact on the perovskite cell performance. The results of this proton irradiance study can serve as material selection guide for space cells. Furthermore, we characterized the perovskite solar cells through light-IV curves and EQE spectra before and after irradiation. Further to our initial study [2], we observed large scale degradation trends post large doses of proton irradiation. However, we demonstrate temperature-dependent anneal recovery post irradiation. We note that while heating a cell can recover most of its performance, this recovery peaks at 80°C and this reversible recovery starts reaching its limit when proton irradiation energy gets high, up to 75KeV.

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3:15 PM EL15.03.04
Radiation Tolerance, High Temperature Stability and Self-Healing of Triple Halide Perovskite Solar Cells Hadi Afshari[1], Sergio Chacon[1], Brandon Durant[1], Rose Crawford[1], Bibhudutta Rout[2], Giles Eperon[3] and Ian R. Sellers[1]; [1]University of Oklahoma, United States; [2]University of North Texas, United States; [3]Swift Solar, United States

$FA_{0.8}Cs_{0.2}PbI_{2.4}Br_{0.6}Cl_{0.02}$ triple halide perovskite solar cells are studied for potential space power applications including exposure to high temperatures and variable radiation conditions. The radiation tolerance of these devices is investigated in response to increasing levels of proton irradiation and fluence. Parameters were chosen to investigate the relative effects of nuclear displacement and electron ionization processes upon the solar cells being assessed. The change in the photovoltaic (PV) parameters was monitored with regards to energy and fluence of irradiation at various temperatures. The experimental results indicated a considerable reduction in the PV parameters affecting *Jsc* and FF with minimal effect on *Voc* as the energy and fluence of the irradiation increased. However, a suite of complementary measurements suggests that while the irradiation negatively affects the transporting layers and interfaces in the devices: the perovskite absorber is not affected in any significant way. Moreover, these systems were observed to self-heal under ambient conditions in the dark demonstrating the unique behavior of perovskite solar cells and their potential for future space power systems. This is further substantiated by high temperature measurements that indicate that the system under investigation displays no appreciable loss up to 490 K, supporting in particular their potential as candidate systems for future lunar missions.

3:30 PM *EL15.03.05
Potential, Radiation Tolerance and Damage Mechanisms of Perovskite Multijunction-Based Space PV Felix Lang[1], Giles Eperon[2], Jarla Thiesbrummel[1], Eike Köhnen[3], Francisco Pena-Camargo[1], Heinz-Chris Neitzert[4], Steve Albrecht[3], Samuel D. Stranks[5], Dieter Neher[1] and Martin Stolterfoht[1]; [1]Universität Potsdam, Germany; [2]Swift Solar, United States; [3]Helmholtz-Zentrum Berlin fuer Materialien und Energie GmbH, Germany; [4]Salerno University, Italy; [5]University of Cambridge, United Kingdom

Perovskite multijunction-based space PV systems promise excellent power conversion efficiencies beyond the detailed balance limit of their single junction counterparts while requiring only ultra-thin absorber layers. Their high power-weight (W/g) potentials consequently make them a dream power source for private-driven space exploration, planned satellite mega-constellations, and future habitats on Moon and Mars. Yet there are still questions regarding their long-term stability under light, bias, and ambient conditions, and application outside Earth’s protective atmosphere place even more extreme demands on material and device stability.

In this presentation, I will review lessons learned during various high-energy proton irradiation experiments we conducted on perovskite single-junctions, as well as perovskite/Silicon, perovskite/CIGS, and perovskite/perovskite tandem PV. [1–4] With perovskite subcells being highly radiation tolerant perovskite/perovskite tandems, even exceed commercially available, industry-standard III-V semiconductors on Ge triple-junction space solar cells in terms of radiation tolerance.

To enable a deeper understanding of potential degradation mechanisms, I will present various subcell-specific characterization techniques that allow disentangling of the different losses and limiting factors in monolithic interconnected perovskite-based multijunction solar cells. Contrary to standard *JV* characterizations, this approach allows us to assess the performance and loss mechanisms of the individual subcells, even after their assembly in a monolithic tandem stack. I will begin with subcell-specific characterizations after high energetic irradiation mimicking the harsh radiation environment in space and then continue with various examples in which we identify limiting loss mechanisms and efficiency potentials in perovskite/silicon and perovskite/perovskite tandems.[5,6,7] After all, such deep understanding is pivotal to further optimizing the efficiency as well as the stability for space applications.

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4:00 PM *EL15.03.06
Impact of the Ionizing Radiation on the Halide Perovskite Crystal, Thin Films and Devices Aldo Di Carlo[1,2], Arthur Istheev[3,4,5], Danila Saranin[3], Fabio Matteocci[1], Daniele Trucchi[2] and Marco Girolami[2]; [1]CHOSE - Univ of Rome Tor Vergata, Italy; [2]ISM-CNR, Italy; [3]Laboratory of Advanced Solar Energy (LASE), NUST-MISIS, Russian Federation; [4]Moscow Center for Diagnostics & Telemedicine, Russian Federation; [5]N. Semenov Federal Research Center for Chemical Physics, RAS, Moscow, Russian Federation

Halide perovskites (HP) have demonstrated great potential for photovoltaics and detector applications, due to the strong absorption, large mobility lifetime product, structural defect tolerance, and wide range of chemical compositions with high Z atoms. Ionizing radiation sensing is one of the emerging directions for the use of halide perovskites, which already demonstrated high radiation hardness. Indeed, the progress in the development of the HP science can demonstrate potential technological breakthrough for ionizing radiation detectors in terms of detection performances, stability, low-temperature processing and conformable lightweight integration thanks to its possible flexibility. The typical composition of HP contains heavy elements (Cs, Pb, Ag, Bi, Sn, I, Br) with atomic numbers in the range of 47-82, which is even larger in comparison to widely used X-ray absorber - CZTS (max atomic number is 52). Moreover, in contrast to state-of-art materials for ionizing radiation detection, the band gap of HP can be easily varied, through cationic and/or anionic substitution, between 1.2 to 2.8 eV. One principal technological advantage of the halide perovskite technology is a low-temperature (100°C) solution processing, that permits the fabrication of devices with various printing methods, such as ink-jet, slot-die, spray etc., all are compatible to flexible substrates (plastic and glass).

In this talk we will discuss the radiation properties of some members of the halide perovskite family, such as $MAPbBr_3$ and in single crystals and in thin film $FAPbBr_3$ and $CsFAPbI_{3-x}Cl_x$ configuration under inizing radiation such as E-beam and X-ray. We investigate the changes in structural and optical properties of perovskite crystals induced by e-beam irradiation with high flux (10^{15} electrons per cm^2, energy 5 MeV) and an extremely high dose (25 MRAD). Ellipsometry measurements demonstrated a strong increase of the Urbach tails related to radiation-induced defects. A trap-induced Fermi level pinning at +0.56 eV was observed by Kelvin probe microscopy analysis of the irradiated $MAPbBr_3$ monocrystals with respect to pristine crystals. However, X-ray diffraction analysis and optical depth analysis with two-photon excitation microscopy photoluminescence reveal that, despite the large irradiation dose, the structural and optical properties are stable. This clearly shows that $MAPbBr_3$ crystals are stable for high energy applications. To evaluate defects related parameters such as activation energy and density we fabricated HP Schottky diodes with rectifying electrodes and we performed deep level transient spectroscopy at different absorbed dose of the radiation. DLTS analyses clearly demonstrated the self-healing properties of halide perovskite to the radiation damage.
X-ray photocurrent measurements, performed on $FAPbBr_3$ thin films, highlight their outstanding properties in terms of signal stability with time, high bulk specific sensitivity, excellent linearity with dose-rate, all extremely desirable properties for a detector conceived for X-ray imaging or radiotherapy applications. In addition, the possibility of working in photovoltaic mode (i.e., at zero-bias), is an added value, making $FAPbBr_3$ thin films appealing for the fabrication of portable detectors with no need for power supply.

4:30 PM EL15.03.07
Monolayer-Modified Hole Transporter Improves Space Compatability for Perovskite Photovoltaics Calton J. Kong[1,2,3], Mohin Sharma[4], Mritunjaya Parashar[4], Kaitlyn VanSant[3,5], Brian Wieliczka[3], Bibhudutta Rout[4], Joseph Luther[3] and Ahmad R. Kirmani[3]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]National Renewable Energy Laboratory, United States; [4]University of North Texas, United States; [5]NASA Glenn Research Center, United States

Perovskite solar cells demonstrate great promise as the next generation photovoltaic technology and interest is also rising in their operation under harsh environments such as near-Earth orbits and deep space. In this talk, we develop one of the most space tolerant perovskite solar cell device designs reported to date. To achieve this, we first modify the commonly used poly[bis(2,4,6-trimethylpheneyl)amine] (PTAA) hole transporter with a self-assembled monolayer of 2-(9H-carbazol-9-yl)ethyl]phosphonic acid (2PACz) molecules. This monolayer-modified charge transporter results in columnar perovskite grain growth minimizing grain boundaries, suppressing bulk defects, and increasing open-circuit voltage by ~40 mV. Compared to control devices based on PTAA hole transporter, these cells remarkably show a 22% radiation tolerance increase when irradiated with 10^{13} cm^{-2} fluence of 75 keV protons, and a 18% increase in thermal tolerance when aged at 110 °C, conditions commonly experienced during space operation. Replacing silver with ITO as a back contact further boosts tolerance to these stressors due to its encapsulation benefits. The wide-ranging advantages offered by this low-cost device design make it appealing for terrestrial and space photovoltaic applications.

4:45 PM EL15.03.08
Probing the Ion Migration and Radiation Tolerance of Triple-Cation Perovskite Solar Cells via Rutherford Backscattering Spectrometry
Mritunjaya Parashar[1], Mohin Sharma[1], Darshpreet Kaur Saini[1], Todd Byers[1], Ahmad Kirmani[2], Joseph Luther[3], Ian R. Sellers[4] and Bibhudutta Rout[1]; [1]University of North Texas, United States; [2]Rochester Institute of Technology, United States; [3]National Renewable Energy Laboratory, United States; [4]University of Oklahoma, United States

Mixed organic-inorganic halide perovskites (OIHPs) based solar cells have attracted the interest of researchers in recent years due to their potential for both terrestrial and space applications. As a result of the photovoltaic community's ongoing efforts, the triple-cation perovskite photoabsorber, ($Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$) has emerged as one of the most promising compositions for perovskite solar cells (PSCs) in terms of stability and power conversion efficiency (PCE). Ion migration of the various cations/anions in OIHPs is considered one of the possible reasons for device degradation and hysteresis in the PSCs. Furthermore, PSCs are becoming viable candidates for space photovoltaic applications thus, it is critical to investigate the impact of radiation-induced degradation in PSCs. Ion beam techniques such as Rutherford backscattering spectrometry (RBS) can be a useful method to probe the elemental depth profile of multilayer PSCs as well as to study the inter-diffusion of various ionic species of OIHPs between the different interfaces. In the present work, we have used a 2 MeV He^+ beam to probe the evidence of ion migration between different interfaces in a state-of-the-art PSC having a device architecture as: Glass/ ITO/ SnO_2/ $Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$/ Spiro-OMeTAD/$MoO_3$/ Au. During the analysis, the active area of the device were exposed up to irradiation equivalent to 5.5×10^{15} He^+/cm^2 which is orders of magnitude higher than the annual proton fluence (~10^{10}-10^{14} p^+/cm^2) in various outer space trajectories, and still any measurable evidence (with a depth resolution ~1 nm) of ion migration was not observed which suggests that the perovskite solar cells with the above device architecture have a high tolerance to the radiation. We will be presenting elemental compositional depth profiles as well as any beam-induced diffusion of the elements.

SESSION EL15.04: Radiation Detection Using Perovskite and Organic Semiconductors
Session Chairs: Felix Lang and Kaitlyn VanSant
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3000

8:15 AM *EL15.04.01
Spectroscopic Radiation Detection Using Perovskites Jinsong Huang; University of North Carolina-Chapel Hill, United States

Metal halide perovskites are promising candidates for room temperature gamma-ray spectrum detectors, however, it is challenging to grow high-quality single crystals under operation conditions to make them performance competitive to existing materials. I will report the growth of centimeter-size organic-inorganic lead halide single crystals at high yield from low purity precursors using a relatively low-temperature solution method. By identifying the defects in these materials, a method will be presented to make most perovskite composition to have spectroscopic detection capability. We will report the application of perovskites for both direct and indirect detection. Finally the radiation hardness of these materials under X-ray and gamma-ray will be briefed.

8:45 AM *EL15.04.02
Radiation Monitoring with a Dosimeter Conformal to the Human Body Oana D. Jurchescu; Wake Forest University, United States

Radiation is used extensively in healthcare both for establishing diagnostics and as a powerful treatment tool. From visualizing features within bones, tissues, and organs to treating cancer, the radiation dose and point of contact to the human body are tailored to each patient’s needs. Administration of the correct dose is critical to the outcome of the procedure, and precise control of its path prevents serious damage that the ionizing radiation can induce to the healthy tissues surrounding the target volumes. Conventional dosimetry techniques used in clinical settings, however, are limited to providing only the absolute radiation dose a patient receives, and accurately measuring variations in its value over large areas remains a challenge. In this presentation I will discuss radiation detectors based on large area arrays of organic field-effect transistors (RAD-OFETs) that allow for high-resolution *in vivo* dosimetry at the skin surface. These dosimeters absorb radiation similar to the tissue, are low-cost, mechanically flexible and conformal to the human body, allowing for direct measurement of the radiation dose without the need for extensive data processing faced by current technologies. The mechanism responsible for radiation detection, as well as the sensitivity of the devices, are discussed. 2D-mapping the spatial distribution of the dose revealed non-uniformities in the received dose, with hotspots near the center beam. Our results are important because they provide the much-needed tools that can generate the information on the variations in the radiation dose over a large area, relevant to diagnostics and therapy in a clinical setting. The spatial control over the administered dose would allow for maximizing the target dose, while minimizing normal tissue dose when planning a patient’s radiation regimen.

This work has been performed in collaboration with Derek Dremann, Dr. Andrew Zeidell, Prof. James D. Ververs, Prof. J. Daniel Bourland, and Prof. John E. Anthony.

9:15 AM EL15.04.03
***Ab initio* Molecular Dynamics Calculations of Threshold Displacement Energies in Halide Perovskites** Mario F. Borunda[1], Rosty B. Martinez[1], Ahmad Kirmani[2] and Ian R. Sellers[3]; [1]Oklahoma State University, United States; [2]National Renewable Energy Laboratory, United States; [3]The University of Oklahoma, United States

Ab initio molecular dynamics (AIMD) simulations have been performed for different halide perovskites to investigate their response to low-energy radiation. The threshold displacement energy (E_d) is the minimum amount of transferred kinetic energy to an atom so that it generates a stable defect in the lattice of a particular material. The E_d is a critical physical parameter for simulating non-ionizing radiation damage in materials, the primary degrader of optoelectronic properties under radiation environments. AIMD allows us to probe atoms in different lattice directions and establish the E_d of the species in the halide perovskite. These efforts would allow for a better understanding of the radiation hardness of materials.

9:30 AM BREAK

10:00 AM *EL15.04.04
Fully Organic Thin Film Based Dosimeters for High Energy Ionizing Radiation Beatrice Fraboni[1,2]; [1]Univ of Bologna, Italy; [2]INFN, Italy

The development of novel high performing, thin and flexible sensors for the detection of ionizing radiation in real-time at affordable costs is rapidly increasing, as the technology currently available still fails to address the requirements of large-area, conformability and portability, lightweight and low power operation.
Organic small molecules and polymers are promising active layers for advanced dosimetry purposes, as their mechanical features allow the development of devices able to adapt to complex contoured surfaces, with outstanding portability (low power operation) and lightweight. Organic semiconductors can be processed from solution and deposited at low temperature (<150 °C), leading to the possibility to realize 2D matrices of pixels onto flexible and large-area substrates. They also provide the unique possibility to develop human-tissue-equivalent detectors, thanks to their density and composition, which makes

them ideal candidates for medical dosimetry applications. Their low average atomic number and density also grants a low absorption of the incoming radiation, making them extremely radiation-tolerant. The physical process of radiation detection for organic thin- film based detectors will be discussed in two different configurations: 1) the direct one, based on a simple planar device with an organic thin film as active conversion layer, and 2) the indirect one, based on a polysiloxane-based scintillating layer effectively coupled to an organic phototransistor (OPT)

Both configurations are thus fully organic devices and have been assessed for flexibility and operation at low power. We report on their performance under exposure to intense photons and MeV protons radiation fields, to evaluate their suitability as space crew members personal dosimeters. The direct configuration (planar 2-terminal device) can quantitatively and reliably measure the dose of protons impinging on the sensor both in real-time and in integration mode. This contribution will discuss how to detect and exploit the energy absorbed both by the organic semiconducting layer and by the plastic substrate, allowing to extrapolate information on the irradiation history of the detector. Their measured sensitivity S = (5.15 ± 0.13) pC Gy-1 and limit of detection LOD = (30 ± 6) cGy s-1 assess their efficacy and their potential as proton dosimeters in several fields of application. As for the indirect configuration, we will present its stability and operation for biases as low as 1V we will discuss a new kinetic model, developed to describe the detector response mechanism, able to precisely reproduce the dynamic response of the device under proton irradiation and to provide further insight into the physical processes controlling its response.

10:30 AM *EL15.04.05
Solution Preparation of Optical and Electronic Metal Halides Bayram Saparov[1], Zheng Zhang[1], Mehran Amiri[2] and May Nyman[2]; [1]University of Oklahoma, United States; [2]Oregon State University, United States

Perovskites and perovskite-inspired halides are continuing to attract the interest of a broad community of researchers as prospective materials for optoelectronic applications. In addition to their outstanding optical and electronic properties, the solution-processability of metal halides is among their greatest advantages. Low-temperature solution preparation not only reduces the processing cost but is also partly responsible for the remarkable diversity in chemical compositions and crystal structures of this class of materials. However, the solution chemistries of most metal halide systems and their relationship with the observed structural and chemical diversity are poorly understood. This is exemplified by the great variety of solution processing conditions reported for both new materials synthesis and solution deposition of thin films reported in the literature. In this talk, our ongoing research efforts to study and develop understanding of several metal halide systems will be summarized. Our combined computational and experimental approach includes UV-vis spectroscopy and electrospray ionization mass spectrometry (ESI-MS) measurements, small-angle X-ray scattering (SAXS) and density functional theory (DFT) calculations. Our early success in several pseudoternary systems will be described along with the outstanding challenges in studying more complex multicomponent systems will be discussed. This study shows that understanding the solution chemistry of multinary metal halide systems could be a valuable tool for discovering new functional materials for practical applications.

11:00 AM EL15.04.06
Direct Detection of 5 MeV Protons by Mixed 3D-2D Perovskite Flexible Films Laura Basiricò[1,2], Ilaria Fratelli[1,2], Matteo Verdi[1,2], Andrea Ciavatti[1,2], Luisa Barba[3], Olivia Cesarini[2], Giorgio Bais[4], Maurizio Polentarutti[4], Massimo Chiari[2] and Beatrice Fraboni[1,2]; [1]University of Bologna, Italy; [2]National Institute for Nuclear Physics, Italy; [3]National Council of Research, Italy; [4]Elettra-Sincrotrone Trieste, Italy

The development of detectors for protons and heavy particles is a long-lasting research topic not only for fundamental applications, but more recently, in the medical field for hadron therapy of cancer. In this application, ion beams are used for the controlled treatment of cancer by focusing them onto small volumes, to avoid the spreading of the radiation to healthy tissues. For this reason, there is an increasing demand of systems optimized for the accurate in-situ, real-time recording and mapping of the dose delivered during a treatment plan.
Metal halide perovskites are rapidly emerging as active materials in low cost high performing ionizing radiation detectors thanks to strong absorption of ionizing radiation, high charge carrier mobilities, long exciton diffusion, long charge carrier lifetime, and excellent optical properties. [1] Further, they combine the high performance of traditional inorganic semiconductors with the low cost, large area scalable, deposition methods (i.e., printing technologies) typical of organic semiconductors. However, the direct proton beam detection or dose-monitoring by perovskite based devices has not been explored yet and only one paper has been published so far on direct proton detection, implemented by fully organic flexible devices.[2]
In this work, we propose a novel flexible proton detector based on mixed 3D and 2D perovskites films deposited from solution. Mixed 3D-2D perovskites are formed by mixing 3D (based on methylammonium (MA) cations) and 2D (based on larger organic ammonium (OA) cations) structure perovskites. Their employment has been reported as an effective strategy to retain the exceptional transport properties of 3D perovskites and the high stability induced by the layered structure of 2D perovskites. By adding the 3D phase ($MAPbBr_3$) we here aim to enhance the radiation absorption of protons by the perovskite film, thanks to the higher density of $MAPbBr_3$ and to the higher thickness of the active layer for mixed compounds.
The here proposed devices demonstrate an accurate monitoring of proton dose with instant feedback and low limit of detection, and provide a stable response even after hard and long-lasting proton irradiation.
In fact, the detector exhibited a stable response to repetitive irradiation cycles with sensitivity up to (290 ± 40) $\text{nC Gy}^{-1}\text{mm}^{-3}$ and a radiation tolerance is also assessed up to a total of $1.7 * 10^{12}$ protons impinging on the beam spot area, with a maximum variation of the detector's response of 14%.
The presented results provide an effective solution to the challenge of identifying novel functional materials and portable devices for real-time accurate monitoring of proton dose, addressing the quest for radiation hardness, low-cost scalability over large areas and mechanical flexibility, still unsolved for a range of application which span from personal dosimetry to large area and lightweight detectors for large accelerators facilities and space missions.
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11:15 AM EL15.04.07
Record Stability for Fully Passive Perovskite-Based X-Ray Detectors Using Starch as Polymeric Template Andrea Ciavatti[1,2], Antonella Giuri[3], Matteo Verdi[1], Aurora Rizzo[3], Laura Basiricò[1], Silvia Colella[3] and Beatrice Fraboni[1]; [1]DIFA - University of Bologna, Italy; [2]INFN - Bologna, Italy; [3]CNR NANOTEC, Italy

Lead-Halide hybrid Perovskites are recently emerging as promising materials for high energy radiation detection thanks to the combination of excellent transport properties, even in polycrystalline films, and their solution processability. Since 2015 hybrid lead-halide perovskites have attracted increasing attention as an interesting alternative to traditional semiconductors used for radiation detection. The presence of heavy elements inside the atomic structure ensures a high X-ray absorption coefficient, together with the high crystal density, make them ideal for direct detection of ionizing radiation. High performance detectors were demonstrated in both polycrystalline and single crystal forms [1], outperforming traditional Si- or CZT-based sensors. Despite top performance of perovskite single crystals, they do not fully exploit the solution processability on flexible substrates, the deposition over large area and the low-voltage operation, typical of thin-film devices. Flexible thin-film perovskite X-ray detectors have been recently reported [2,3]; however, low operational and environmental stability is limiting their further development toward commercialization.
Here we report a strategy based on using starch as a polymeric template for the fabrication of stable thin film perovskite direct X-ray detectors, which confers to the film a series of characteristics that cannot be achieved with pristine perovskites, in particular higher stability in ambient conditions, improved

homogeneity of the film also at greater thicknesses, enhanced mechanical flexibility and robustness. The approach is highly reliable and versatile, in fact, we demonstrate it in this work for different perovskite compositions, namely $MAPbI_3$ and $FA_xMA_{1-x}PbI_3$. Moreover, the starch polymer allows excellent tuning of the active layer thickness, since acting as a rheological modifier enhances the viscosity of perovskite precursors' ink.
The proposed p-i-n photodiodes can operate with no external bias applied (fully passive devices), thus strongly improving the operation stability by decreasing the ion migration. We monitored the current response at 40kVp of X-ray radiation for detectors with different active layers compositions and thicknesses. We found that a 20 wt% starch concentration in the perovskite precursor solution, corresponding to 1050 nm thick perovskite layer provides the best trade-off between X-ray absorption, charge collection efficiency and performance stability. We measured an X-ray sensitivity of 5.5±0.2 $\mu C\ Gy^{-1}\ cm^{-2}$ (at 0 V), with no degradation on the electric characteristic after 9.4 Gy irradiation.
The device degradation was monitored for samples stored in air for a time window of 630 days. During this period, the samples were subjected to temperatures and relative humidity as high as 30°C and 70% respectively during summer times. After 1.7 years the films retained their dark color and nice dynamics curves under X-rays were measured, demonstrating an exceptional stability: 97% of the initial sensitivity was retained for the best perovskite-starch composite formulation making it the most stable unencapsulated perovskite X-ray detector reported so far.

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SESSION EL15.05: Wide Bandgap Lightweight Electronics for Harsh Environments
Session Chairs: Bayram Saparov and Kaitlyn VanSant
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3000

1:30 PM *EL15.05.01
Novel AlGdN Alloys for Integrated Detection in Radiation Environments Nancy Haegel; NREL, United States

Metastable ternary nitrides are a growing class of materials that offer broad potential for both new functionality and heterogenous integration. In this work, we are synthesizing $Al_xGd_{1-x}N$ as a radiation hard ultrawide bandgap semiconductor, with potential for integrated detection high energy particles including neutrons and gamma rays. Metastable $Al_{1-x}Gd_xN$ alloys have been synthesized via non-equilibrium radio frequency co-sputtering in a combinatorial system allowing exploration of a range of Gd compositions. First-principles calculations show that the limiting critical composition for a wurtzite to rocksalt phase transition is $x_c = 0.82$. Theory suggests that at temperatures below 1000 K there is a large miscibility gap limiting Gd incorporation in AlN to only a few percent. However, by accessing higher effective temperature through non-equilibrium growth we have achieved Gd concentrations up to 24%, the highest Gd^{3+} incorporation into the wurtzite phase reported to date. Single-phase compositions up to $x \approx 0.24$ are confirmed by high resolution synchrotron grazing incidence wide angle X-ray scattering and transmission electron microscopy (TEM).
These new materials have been characterized using a range of analytical tools, including X-ray diffraction, Rutherford Backscattering Spectroscopy, cathodoluminescence, temperature dependent X-ray, ellipsometry, and transmission electron microscopy with high resolution energy dispersive X-ray. Energy dispersive X-ray (EDX) imaging in the scanning electron microscope and cathodoluminescence, monitoring an internal UV transition within the Gd atoms, indicate uniform distribution of Gd in thin films with columnar grains. High resolution EDX in the TEM shows homogeneous incorporation of Al, Gd and N in films on the order of ~ 200 nm in thickness, and TEM imaging indicates a wurtzite structure based on fast Fourier transform (FFT) analysis, consistent with the synchrotron grazing incidence wide angle X-ray scattering.
Because $Al_{1-x}Gd_xN$ is a heterostructural alloy (AlN is a wurtzite structure, GdN is a rocksalt structure), a key part of the project is to explore the fundamental science to enable stable integration of new tunable metastable nitride materials into thin film structures for high radiation and high temperature environments. Interfacial understanding and control are critical and could potentially provide both enhanced structural stability for these metastable alloys (e.g., via designed lattice matching) and tunable electronic functionality (e.g., ohmic to rectifying behavior). We will review the status of contact materials for high resistivity high energy particle detectors and discuss paths to device integration.

2:00 PM *EL15.05.02
Influence of Mechanical Hotspots on Radiation Susceptibility of GaN HEMTs Md Rasel[1], Nahid Al-Mamun[1], Sergei Stepanoff[1], Aman Haque[1], Khalid Hattar[2], Douglas Wolfe[1], Fan Ren[3] and Stephen Pearton[3]; [1]The Pennsylvania State University, United States; [2]Sandia National Laboratories, United States; [3]University of Florida, United States

Performance and reliability of microelectronic devices are governed by the mechanical strain. Typically, strain engineering implies uniformly distributed strain. However, we offer a different perspective by hypothesizing that very small but localized strain (or stress) may have significant impact on the overall behavior of AlGaN/GaN high electron mobility transistors (HEMTs). Micro to nanoscale confined mechanical stress fields may develop unavoidably and are ignored because their spatial average is insignificant. We exploit high resolution techniques such as transmission electron microscopy (TEM) and micro-Raman spectroscopy to spatially resolve the stress field in GaN HEMTs to demonstrate the stress localization and then radiation effects.

To study stress localization effects on the global electrical characteristics, we introduced a highly localized strain relief by milling a 20×30 μm^2 micro trench about 70 µm deep on the backside of an 800×840 μm^2 size HEMT die. The resulting local relaxation of in-plane residual strain was mapped using micro-Raman technique. Our results show that a decrease of only 0.02% strain can decrease the overall output saturation current up to ~20 %. The drop of output current is attributed to reduced two-dimensional electron gas (2DEG) sheet carrier density and electron mobility due to the strain relief in the device layers. However, the mechanistic process of strain relief also causes defect generation at the interfaces, which increases leakage current. Our technique for localized strain re-distribution could be an effective tool to surrogate the influence of inherent localized strain build-up across the channel of electronic devices.

To study radiation effects, we exposed the HEMTs to gamma rays (up to 10 megaRads dose at 180 kiloRads per hour). We report the thermal and mechanical responses in terms of the changes in lattice strain and temperature, which were simultaneously characterized by changes in phonon frequency of E2 (high) and A1 (LO) from on- state and unpowered/pinched off reference states. Lower doses of radiation improved the electrical properties, however degradation initiated at about 1 megaRads. We observed about 16% decrease in saturation current and 6% decrease in transconductance at the highest dose. However, leakage current increase by 3 orders of magnitude was the most notable radiation effect. We observed temperature increase by 40% and mechanical stress increase by a factor of three at dose of 10 megaRads compared to the pristine devices. Spatial mapping of mechanical stress along the

channel identifies the gate region as mechanically affected area, whereas the thermal degradation was mostly uniform. Transmission electron microscopy showed contrast changes reflecting high vacancy concentration in the gate region. These findings suggest that localized stress (mechanical hotspots) may increases vulnerability to radiation damage by accommodating higher concentration of defects that promote leakage current.
Finally, we present experimental results on a novel concept of electron wind force driven room temperature annealing of GaN and SiC devices. This technique was applied on Gamma irradiated HEMT and SiC diodes. We demonstrate full recovery of the HEMTs irradiated to 10 mega-Rads gamma radiation. About 200% performance improvement was recorded for the SiC diodes. Our hypothesis is that mechanical stress waves are instrumental in eliminating interfacial defects.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

2:30 PM BREAK

3:30 PM EL15.05.03
Chemical Modifications of Low-dimensional MoS$_2$ in Radiation-Harsh Environments Kory D. Burns[1], Christopher M. Smyth[2], Alex M. Boehm[2], Eric Lang[3], Taisuke Ohta[2], Jordan A. Hachtel[4] and Khalid Hattar[5]; [1]University of Virginia, United States; [2]Sandia National Laboratories, United States; [3]The University of New Mexico, United States; [4]Oak Ridge National Laboratory, United States; [5]The University of Tennessee, Knoxville, United States

The resilience of MoS$_2$ to energetic particles and understanding the chemical modifications induced are of great interest for the realization of long-term space-based electronics incorporating low dimensional materials. In this contribution, we probe these properties in MoS$_2$ using 10 keV He$^+$ ion irradiation to alter the chemical composition of MoS$_2$ enabling selective alterations of the work function. By combining photoemission electron microscopy (PEEM), optical spectroscopy, X-ray photoelectron spectroscopy (XPS), structural characterization, and monte carlo simulations we unveil the role of structural defects in the band onset potential, work function, electron binding energy (E_B) of the occupied states, and ionization energy. Here, we assess the influence of layer number and substrate interactions in the defect formation process at different fluences. Ultimately, we provide an avenue for efficient testing of the radiation tolerance of low-dimensional materials and analyze the defect-property relationship progression in extreme environments. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

3:45 PM EL15.05.04
Negative Capacitance HfO$_2$-ZrO$_2$ Superlattice Gate Stack Towards High-Performance Radiation-Hard Electronics Nirmaan Shanker[1], Suraj Cheema[1], Li-Chen Wang[1], Sergei Stepanoff[2], Douglas Wolfe[2] and Sayeef Salahuddin[1,3]; [1]University of California, Berkeley, United States; [2]The Pennsylvania State University, United States; [3]Lawrence Berkeley National Laboratory, United States

There is an increasing demand for high-performance, low-power microelectronics that can operate in extreme radiation environments for space, nuclear, and avionic applications [1]. One route towards high-performance, low-power transistors is to increase the gate capacitance, i.e. lower equivalent oxide thickness (EOT), which reduces the operating voltage and therefore power. However, EOT scaling has been stagnant since the adoption of the high-κ metal gate SiO$_2$/HfO$_2$ gate stack [2], as conventional EOT scaling approaches, such as SiO$_2$ interlayer (IL) scavenging, in which the IL EOT contribution is reduced, result in significantly degraded gate leakage, carrier mobility, and reliability characteristics due to the closer proximity of the Si channel to the high-κ dielectric [2]. In contrast, integrating a ferroelectric negative capacitance (NC) gate oxide [3] can scale EOT while maintaining gate leakage, mobility, and reliability, as the IL thickness is no longer reduced [3]. We have previously demonstrated a 1.8 nm ferroelectric-antiferroelectric HfO$_2$-ZrO$_2$ superlattice (HZH) gate stack boasting a capacitance enhancement over the 8 Å SiO$_2$ IL layer via the NC effect [3]. Furthermore, once the HZH gate stack was integrated into 90 nm L_g silicon-on-insulator (SOI) nMOS transistors, gate leakage, electron mobility, and the PBTI reliability were unchanged relative to a conventional high-κ dielectric HfO$_2$ gate stack [3, 4], while maintaining the capacitance enhancement and demonstrating a 14% and 25% increase in ON current (I_{on}) and transconductance (g_m) at the same operating voltage, respectively [3, 5].
In this work, we investigate the total ionizing dose effect (TID) of gamma radiation (^{60}Co source) up to 10 Mrad on the NC HZH gate stack integrated into bulk metal-oxide-semiconductor (MOS) capacitors and 90 nm L_g SOI (~20 nm) nMOS transistors. In the bulk MOS capacitors, both EOT and gate leakage are maintained up to 10 Mrad dose with negligible flatband voltage shifts, suggesting minimal charge trapping within the NC HZH gate stack. In the 90 nm L_g SOI (~20 nm) nMOS transistors, the only significant change was a dose-dependent negative threshold voltage (V_T) shift (-250 mV at 10 Mrad), while changes in transistor metrics such as EOT, I_{on}, g_m, and subthreshold swing were negligible. The negative V_T shift was attributed to electrical coupling to trapped charges in the buried oxide (BOX) layer of the SOI substrate, consistent with previous reports of TID effects on short-channel SOI transistors incorporating conventional high-κ dielectrics [1] and can be mitigated by employing an ultrathin BOX layer (~10 nm) [1]. Overall, we demonstrate that the NC HfO$_2$-ZrO$_2$ gate stack can be integrated into radiation-hard electronics and serve as an avenue for next-generation high-performance radiation-hard electronics in extreme environments.

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4:00 PM EL15.05.05
A High-Detectivity, Fast-Response, and Radiation-Resistant TiN/CdZnTe Heterojunction Photodiode Mykhailo Solovan[1], Andriy Mostovii[1], Hryhorii Parkhomenko[1], Marat Kaikanov[1], Nora Schopp[2], Ernest Asare[1], Taras Kavalyuk[3], Dmytro Korbutyak[4] and Viktor Brus[1]; [1]Nazarbayev University, Kazakhstan; [2]University of California, Santa Barbara, United States; [3]Charles University, Czechia; [4]National Academy of Sciences of Ukraine, Ukraine

Photodiodes have found wide practical applications as sensing and information transmission technology. However, some fields of their possible applications require added features besides excellent performance characteristics. For instance, the rapid development of commercial and scientific space programs and large-scale nuclear safety efforts in radioactively contaminated areas considerably demands next-generation radiation-resistant optoelectronic materials and devices. The heterojunction photodiode device concept opens a broad range of possibilities in combining different semiconductor materials with unique properties resulting in added functionalities, but with the price of detectivity and response time compared to conventional silicon photodiodes.
In this work, we proposed a novel *high-performance and radiation-resistant* UV-vis-NIR (300 – 820 nm) heterojunction photodiode based on radiation-resistant functional semiconductor materials: titanium nitride (TiN) 'window' layer and cadmium zinc telluride solid solution (CdZnTe) photoactive layer. The developed TiN/CdZnTe heterojunction photodiodes **concurrently revealed outstanding detectivity D^* = 4.14×10^{12} Jones @ -0.2 V and rise/fall response times of 3.5/3.8 μs @ -1.5 V** outperforming existing similar heterojunction optoelectronic devices based on photoactive compound semiconductor materials.[1] Moreover, the added feature of the proposed heterojunction photodiodes is their **advanced radiation resistance**,

experimentally demonstrated under *extreme conditions* of short impulse proton irradiation (170 keV) with an accumulated fluence of 2×10^{12} proton/cm^2. This unusual synergy of high performance and radiation resistance of the TiN/CdZnTe photodiodes is crucial for their reliable, long-term operation under the detrimental influence of ionizing radiation in extreme environments like space or radioactively contaminated zones.
We have a strong belief that our work is of interest to a broad range of material scientists and device engineers, as it pushes the current detectivity-response time boundaries, defined by the long-standing materials science and device engineering problems in developing **simultaneously highly sensitive, fast-responding, and radiation-resistant optoelectronic devices** based on compound semiconductors.

[1] Mykhailo M. Solovan, Andriy I. Mostovyi, Hryhorii P. Parkhomenko, Marat Kaikanov, Nora Schopp, Ernest A. Asare, Taras Kovaliuk, Petr Vertat, Kostiantyn S. Ulyanytsky, Dmytro V. Korbutyak and Viktor V. Brus*, A High-Detectivity, Fast-Response, and Radiation-Resistant TiN/CdZnTe Heterojunction Photodiode, *Advanced Optical Materials* (in press).

4:15 PM EL15.05.06
Fast Engineering Models for Radiation-Induced Defect Production in Thin Materials Henry R. Little, Christopher Lenyk, Darren Holland, Adib Samin and Whitman Dailey; Air Force Institute of Technology, United States

Due to the rapid evolution of electronic devices based on advanced lithography techniques and the commercialization of space, methods are needed to assess and predict performance in adverse radiation environments of both the transient and long-term response to irradiation. Experimental measurements of radiation damage generally exist on the order of hours after irradiation, and simulations are able to provide detailed predictions of damage out to the order of picoseconds. Additionally, radiation damage and interactions at depths below the mean free path of radiation in a particular material have long proven difficult quantities to measure and challenging to predict. A potential method is explored for predicting the concentration of defects in a material resulting from neutron irradiation, and the method's output is compared against experimental results for the well-studied material, MgO. The Monte Carlo Neutral Particle transport code (MCNP), leveraging the PTRAC module, is used to simulate irradiation of MgO samples with dimensions that are sub-mean free path, in the Oak Ridge National Laboratory's High Flux Isotope Reactor (HFIR). Cluster dynamics results and atomic displacement theory are used to compute the total number of defects in transient phase and account for the effects of defect saturation and thermal annealing. Comparison of the long-term response is then compared against actual experimental results of MgO irradiation in the HFIR and shown to agree within a factor of two. The method is then broadened to examine the spatial distribution of defects in the sample. Other materials are also explored for comparison including Si and GaN.

SESSION EL15.06: Virtual Session: Radiation-Hard and Lightweight Next-Generation Semiconductor Electronics
Session Chairs: Ahmad Kirmani and Bibhudutta Rout
Tuesday Afternoon, April 25, 2023
EL15-virtual

4:30 PM *EL15.06.01
In-situ and ex-situ Spectral Response Characterization of the Radiation Damage and subsequent Recovery during Proton Irradiation of Silicon and Perovskite based Solar Cells Heinz-Chris Neitzert[1], Felix Lang[2], Andrea Denker[3], Juergen Bundesmann[3], Lucio Gialanella[4], Paola Delli Veneri[5], Lucia Mercaldo[5], Maryamsadat Heydarian[6], Alexander J. Bett[6] and Martin Schubert[6]; [1]Universita di Salerno, Italy; [2]University of Potsdam, Germany; [3]Helmholtz Zentrum Berlin fuer Materialien und Energie GmbH, Germany; [4]Universita della Campania "Luigi Vanvitelli", Italy; [5]C.R. ENEA Portici, Italy; [6]Fraunhofer Institute for Solar Energy Systems ISE, Germany

The dynamics of the radiation induced degradation of space solar cells is complex and often degradation and annealing are competing processes, in particular if elevated solar cell operation temperatures are reached. In-situ characterization of the degradation process during exposure of the solar cells to high energy particles can be simply performed by monitoring of the radiation-induced current, that is strongly correlated to the photoelectric properties of the solar cells. In order to detect also fast annealing processes, however, the in-situ monitoring of the photocurrent is needed. Spectrally resolved measurements of the photocurrent allow to distinct between different degradation and annealing mechanisms, like bulk effects and interface modifications, but are usually only performed ex-situ due to the bulky equipment.
A very simple and compact measurement setup will be shown, that enables the spectral response measurement with good temporal resolution also in a vacuum system without the need of optical windows already during irradiation. It is based on the pointwise photocurrent generation with LEDs with different emission wavelength and a detection unit, that converts the small resulting photocurrents directly into a proportional frequency, that can then easily be monitored for example by using the audio card of a PC [1].
First measurement during the degradation of conventional single junction monocrystalline silicon solar cells with protons are reported, confirming the good temporal resolution and the excellent signal-to-noise ratio even in the complex environment of a high energy particle accelerator. In a further evolution the setup has been modified for the characterization of Tandem type solar cells and the, in this case ex-situ, characterization of a micromorph silicon Tandem cell (2) has been successfully demonstrated. By comparing ex-situ photocurrent spectra of these micromorph cells to the spectra of all-perovskite Tandem cells it is shown, that the micromorph cell can be used as a stable reference cell for the calibration of the in-situ setup, that will in future be used for the in-situ characterization of all-Perovskite or Perovskite/CIGS cells. These both types of Perovskite cells have been already shown to be very stable under proton irradiation [3,4]. For this latter types of thin film solar cells with very promising properties for space applications the in-situ photocurrent monitoring, with excitation with a simpler two-LED irradiation system will be reported and also compared to the radiation induced current monitoring results.

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5:00 PM DISCUSSION TIME

5:30 PM *EL15.06.03
Proton Radiation Hardness of Organic Photovoltaics Harrison Ka Hin Lee[1], Katherine Stewart[2], Declan Hughes[1], Jérémy Barbé[1], Adam Pockett[1], Rachel Kilbride[3], Keith Heasman,[4], Zhengfei Wei[1], Trystan Watson[1], Matthew Carnie[1], Ji-seon Kim[2] and Wing Chung Tsoi[1]; [1]Swansea University, United Kingdom; [2]Imperial College London, United Kingdom; [3]The University of Sheffield, United Kingdom; [4]Surrey university, United Kingdom

Recent developments of solution-processed bulk-heterojunction organic photovoltaic (OPV) cells have demonstrated power conversion efficiencies (PCEs) as high as 18.7% for single-junction devices. Such a high PCE in addition to its desirable lightweight property and high mechanical flexibility can realize high specific power and small stowed volume, which are key considerations when choosing PV for space missions. To take one important step forward, their resilience to ionizing radiation should be well studied. Herein, the effect of proton irradiation at various fluences on the performance of benchmark OPV cells is explored under AM0 illumination. The remaining device performance is found to decrease with increasing proton fluence, which correlates to changes in electrical and chemical properties of the active layer. By redissolving the devices, the solubility of the active layer is found to decrease with increasing proton fluence, suggesting that the active materials are likely cross-linked. Additionally, Raman studies reveal conformational changes of the polymer leading to a higher degree of energetic disorder. Despite a drop in performance, the retaining percentage of the performance is indeed higher than the current market-dominating space PV technology—III–V semiconductor-based PV, demonstrating a high potential of the OPV cell as a candidate for space applications.

6:00 PM DISCUSSION TIME

6:15 PM EL15.06.05
Radiation Tolerance of Hybrid Perovskite Solar Cells Studied with 8 MeV Proton Irradiation Tsutomu Miyasaka[1] and Yu Miyazawa[2]; [1]Toin University of Yokohama, Japan; [2]Japan Aerospace Exploration Agency, Japan

Perovskite solar cells (PSCs) can be fabricated as lightweight, flexible, and highly efficient solar power devices at low cost. This advantage matches their applications to spacecrafts. We have evaluated the resistance of PSCs to high energy radiations, which is the biggest deterioration factor of the solar cells in the space. PSCs exhibit high radiation tolerance when the device is exposed to high fluences of 1 MeV electron and 50 keV proton beams, and perovskite crystals show a low minority-carrier diffusion length (DL) after irradiation of 1MeV electrons. It has been reported that the photocurrent-voltage (I-V) characteristics of InP solar cells, which have a low DL, recovers after radiation deterioration. To clarify whether or not that the perovskite crystals are introduced with substantial defects by radiation, I-V characteristics of PSC immediately after irradiation and its change over time have been evaluated. At room temperature, 8 MeV proton beam (an energy that can penetrates the PSC by causing deterioration to the all layers in PSC) was irradiated to high-efficiency PSCs with $CsMAFAPb(IBr)_3$ perovskite absorber. The energy incident on the PSC (<1 μm) after passing through the 0.3 mm thick quartz glass substrate was 4.4 MeV. We measured the remaining factor of the parameters of I-V characteristics of PSC (short-circuit current (Isc), open-circuit voltage (Voc) and fill factor (FF)) as a function of proton beam fluence. Up to a radiation dose of 1×10^{13} /cm^2, no significant degradation occurs in all parameters. With a radiation dose of 1×10^{14} /cm^2, degradation of less than 5% was observed in the Isc while FF decreased by 24% and Voc decreased by 9% immediately after irradiation. However, FF and Voc were almost recovered in 3 min after irradiation. The deterioration and recovery of I-V characteristics is considered to be due to some change of conductivity in the charge transport layers. The above investigation endorses that no defects are introduced into the perovskite crystals to deteriorate power generation performance with a radiation dose of 1×10^{14} /cm^2 and corroborate high radiation tolerance of the hybrid perovskite semiconductor.

SYMPOSIUM

April 10 - April 26, 2023

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SESSION EL16.01: Lasing and Radiation Engineering with Metasurfaces and Metamaterials
Session Chairs: Ho Wai (Howard) Lee and Yang Zhao
Monday Morning, April 10, 2023
Moscone West, Level 3, Room 3016

9:00 AM EL16.01.02
All-Dielectric Transmissive High-Q Active Metasurfaces for Thermo-Optic Beam-Steering Morgan D. Foley, Claudio Hail, Ruzan Sokhoyan, Souvik Biswas and Harry A. Atwater; California Institute of Technology, United States

All-dielectric nanophotonics has the potential for designing active metasurfaces that exploit highly localized high-quality-factor modes, yielding new ways to individually address each element to shape the overall wavefront. We have designed an all-dielectric metasurface capable of actively steering light via thermo-optic tuning. Our metasurface consists of subwavelength high-index amorphous silicon resonators on a thin SiO_2 spacer layer and a crystalline silicon substrate. The dielectric resonators support high-quality-factor Mie modes (Q ~ 1000 - 10,000) that are optically capable of two-dimensional beam steering. Furthermore, by tailoring the SiO_2 layer thickness to specific values, we can tune the Fano asymmetry parameter of the resonance, and hence the transmittance of the modes. By adding doped amorphous silicon electrodes across one of the two principal axes of the array, metasurface elements can be actively index modulated under electrical actuation via Joule heating ($\triangle n \sim 0.01$). We have demonstrated via finite-difference-time-domain simulations that our metasurface can steer light to a range of angles by generating one-dimensional phase gradients via dynamic refractive index modulation. From three-dimensional finite element thermal simulations, we calculate a response time for our system of ~ 7μs, corresponding to a modulation frequency of ~ 140kHz. Importantly, our design operates in transmission, opening the possibility of cascading with other transmissive metasurfaces to perform multiple operations, such as optical edge detection for imaging. Our work contrasts with previous active designs, such as active plasmonic metasurfaces which primarily operate in reflection and exhibit strong loss, or liquid crystal systems which have a slower modulation time. We also report on our experimental progress towards realizing an all-dielectric active metasurface capable of performing dynamic beam steering. Thermo-optic modulation of two-dimensional dielectric metasurfaces has many potential applications for optical sensing, lensless imaging and display technologies.

9:15 AM EL16.01.03
Selective Placement of Nanocrystals in Plasmonic Arrays for Tailored Directionality and Polarization of Photoluminescence Maya Ramamurthy, Pavlos Pachidis, Bryan M. Cote and Vivian Ferry; University of Minnesota - Twin Cities, United States

Light-emitting metamaterials are promising candidates for applications where polarization and directional control of photoluminescence is desired, including security tagging, beam shaping, 3D displays, and photonic circuits. While most work to date involves uniformly coating the metasurface with light emitters, placing emitters in specific locations enables more complex and controlled effects. Here, we are interested in metamaterials comprised of Au nanobars and *patterned* light emitters that form their own, collective solids. These solids can be realized using direct-write electron beam lithographic patterning of luminescent semiconductor nanocrystals.
In this work, we use finite difference time domain (FDTD) simulations and experiments to study how the placement of luminophores in plasmonic arrays affects the circular polarization and directionality of photoluminescence. We modeled the luminophores as incoherent dipole sources with peak photoluminescence emission at 630 nm. The plasmonic array was modeled as a 23 x 23 square periodic array of Au nanobars with dimensions 160 nm x 300 nm x 70 nm and a pitch of 600 nm. To compare the effects of patterning light emitters into specific locations versus a uniform coating, the dipoles were either placed within a cylindrical disk (diameter = 140 nm, n = 1.75) adjacent to each nanobar, or uniformly distributed within a film (n = 1.59) placed on top of the nanobar array.
These luminescent metamaterial arrays were fabricated on ITO-coated glass slides using a two-step lithographic patterning process where the Au nanobars were fabricated in the first step, and CdSe/CdS core/shell nanocrystals were patterned resist-free in the second step.
We show that selective placement of luminophores in certain locations around the Au nanobar produces systems that preferentially outcouple either right or left circularly polarized light (RCP/LCP). Additionally, the angular distribution of RCP/LCP light outcoupling reflects the symmetry of the metamaterial array. Therefore, the metamaterial comprised of a uniform film of luminophores emits polarized light at certain angles, but no net polarization is observed when averaged over all angles of emission. By contrast, when luminophores are placed in locations that render the metamaterial chiral, polarized light is emitted not only at specific angles, but also when averaged over all angles.
We also find that the distinctive placement of emitters changes the direction of light outcoupling by changing the Raleigh-Wood modes of the periodic array, compared to when the emitters comprise a uniform film. Finally, we demonstrate how to create metamaterials that emit light with any desired circular polarization or direction by analyzing the near-fields around the Au nanobar and placing luminophores in regions of high circularly polarized field enhancement. This creates systems that simultaneously achieve a high degree of circular polarization (DCP) and a high photoluminescence intensity at the desired angle of emission. These studies advance understanding of light-mater interactions in nanostructured arrays and are broadly relevant in nano-optics.

9:30 AM BREAK

10:00 AM *EL16.01.04
Flat Optics for Dynamic Wavefront Manipulation Mark L. Brongersma; Stanford University, United States

Since the development of diffractive optical elements in the 1970s, major research efforts have focused on replacing bulky optical components by thinner, planar counterparts. The more recent advent of metasurfaces, i.e. nanostructured optical coatings, has further accelerated the development of flat optics through the realization that nanoscale antenna elements can be utilized to facilitate local and nonlocal control over the light scattering amplitude and phase. In this presentation, I will highlight recent efforts in our group to realize electrically-tunable metasurfaces employing nanomechanics, tunable transparent oxides, electrochemistry, microfluidics, phase change materials, and atomically-thin semiconductors. Such elements are capable of dynamic wavefront manipulation for optical beam steering, holography and future display technologies. The proposed optical elements can be fabricated by scalable fabrication technologies, opening the door to a wide range of commercial applications.

10:30 AM EL16.01.05
Metasurface-Enabled Full-Space Structured Light Illumination for Depth Imaging Jooyeong Yun[1], Gyeongtae Kim[1], Yeseul Kim[1], Inki Kim[2] and

Junsuk Rho[1]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of)

Laser-based imaging technology has shown promising potential in three-dimensional (3D) depth sensing platforms enabling variety of applications such as autonomous driving, robot vision, and face recognition in mobile devices. To image 3D objects over a wide field of view (FOV), the laser beams illuminate the objects, and the backscattered light is monitored through detectors. Structured light (SL)-based imaging system splits the light into an array of dots or a specific pattern into the object scene, enabling imaging of multiple objects simultaneously. So far, diffractive optical elements (DOEs) or spatial light modulators (SLMs) have been used to form the laser dot arrays. However, such architectures suffer from small FOVs, low efficiency, and bulkiness due to the large micron-scale pixel size. Here, we propose a metasurface-based SL imaging platform, allowing for subwavelength scale manipulation of incident light. The scattered light from the metasurface covers the full 180° FOV, with a high-density ~10K dot array. The metasurface is composed of a periodic supercell, and the properties of diffraction patterns are analyzed by convolution theorem regarding the supercell as a kernel function. As a proof-of-concept, we place face masks one on the laser beam axis and the other 50° apart from axis within distance of 1 m and estimate the depth information from the backscattered light using a stereo matching algorithm. Furthermore, we demonstrate the replication of our metasurface on a glass surface using the nanoimprinting of a nanoparticle-embedded-resin (nano-PER) for high-throughput fabrication.

10:45 AM EL16.01.06

Dislocation Study in InGaAs QW Metamorphic Lasers Nicholas Stephen[1], Praveen Kumar[1], Agnieszka Gocalinska[2], Emanuele Pelucchi[2] and Miryam Arredondo[1]; [1]Queen's University Belfast, United Kingdom; [2]Tyndall National Institute, Ireland

There has been a drive to produce novel InGaAs Quantum Wells (QW) on GaAs substrate lasers for telecommunication applications that can replace current InP based lasers. The In concentration in the InGaAs QW can be fine-tuned so that the emission is in the C-band (1330nm) or O-band (1550nm) telecommunication bands. Furthermore, compared to the current InP substrates, GaAs is less brittle, cheaper and available large wafer sizes: making them ideal for mass fabrication [1]. Difficulties can arise due to lattice mismatches between the InGaAs QW and GaAs substrate, which causes an increase in non-radiative recombination centres (whereby phonons instead of photons are produced) [2]. One proposal that has been used to overcome this problem is metamorphic growth, where a buffer layer is grown between the substrate and active region. In turn, this creates an artificial substrate with a lattice constant that can be tailored to greatly reduce the lattice mismatch between active region and substrate.

In the metamorphic buffer layer, strain is relieved via the creation of dislocations. These dislocations are confined to a certain region within the metamorphic buffer [3]. It is well known that these can be classified in many ways such as 60° or 90° (pure edge) dislocations and it is common for the burgers vectors to be identified using techniques such as weak beam dark -field transmission electron microscopy [4,5]. However, to date, few studies have provided in-depth details on the distribution of the type dislocations within an InGaAs metamorphic buffer and how this could be linked to the performance of the laser.

This work investigates a series of InGaAs QWs on GaAs substrate metamorphic lasers grown by Metal Organic Vapour Phase Epitaxy (MOVPE) using transmission electron microscopy techniques. This study identifies and characterises properties of dislocations within the metamorphic buffer. We also address the In concentration of the metamorphic buffer which these dislocations are based around.

Finally, our data elaborates further on the distribution of the dislocations. These findings lend themselves towards the understanding of laser emission behaviour and the mechanism of relaxation in the buffer. In turn, allowing novel metamorphic lasers to be manufactured with characteristics similar to current commercial semiconductor lasers.

ACKNOWLEDGEMENTS

This work was supported by the Engineering and Physical Sciences Research Council (Grant number EP/S023321/1)

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11:00 AM *EL16.01.07

Engineered Hydrogenated Amorphous Silicon (a-Si:H) and Nanoparticle-Embedded-Resin (nano-PER) for Low-Loss and Scalable Optical Metasurfaces Junsuk Rho; Pohang University of Science and Technology, Korea (the Republic of)

Here, we present a printing-based highly-productive scalable nanofabrication method to manufacture dielectric metasurfaces working in the visible and near-infrared (NIR) regime. A main idea is that transferred patterns of UV-curable resin from a printing mold directly work as metasurfaces without any secondary operations such as thin film deposition and etching, but the problem is that the refractive index of the typical resin is not high enough for metasurfaces. Therefore, we develop the effective medium of nanoparticle composite (NPC) that consists of high-index dielectric nanoparticle (NP) inclusion in the matrix of UV-curable resin. This hierarchy enables to achieve the sufficiently-high refractive index for metasurfaces. By using our method, we demonstrate various metasurfaces such as metaholograms and metalenses. The fabricated metalens and metahologram based on titanium dioxide NPs exhibits a high conversion efficiency of 90.6% at the wavelength of 532 nm. Theoretically, the efficiency can be further increased up to 96.4% by optimizing the nanostructures of the metasurfaces. A 4 mm-diameter NIR metalens made of the silicon NPC is also demonstrated to verify that the metalens can be fabricated by one-step printing without any thin-film deposition nor etching processes4. The fabricated NIR metalens shows focusing efficiency of 47% at the wavelength $\lambda = 940$ nm. We also use the NIR metalens to realize a compact NIR camera and confirm its imaging capability by capturing the distribution of veins underneath human skin. Therefore, this work will pave the way for practical applications of metalenses such as night vision, thermal imaging, biometric technologies and light detection and ranging (LiDAR) devices. Considering that the proposed nanoimprinting method enables low-cost production of metasurfaces, we expect that NPC-based functional metasurfaces will be implanted on various photonic applications from infrared to visible frequencies. Also, if time allows, I will discuss the materials and fabrication progress.

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SESSION EL16.02: Controlling Thermal Emission with Nanostructure and Active Control Plasmonic Devices
Session Chairs: Mark Brongersma and Wenshan Cai
Monday Afternoon, April 10, 2023
Moscone West, Level 3, Room 3016

1:30 PM *EL16.02.01
Free-Form Plasmonic Meta-Optics via Machine Learning Wenshan Cai; Georgia Institute of Technology, United States

Advanced neural networks and optimization algorithms have enabled a paradigm shift in the discovery and design of structured photonic materials and devices. In this talk we report a diverse set of inversely designed meta-optical structures, devices, and systems for wavefront control, imaging, computing, and nonlinearity.

Flat optics, represented by metamaterials and metasurfaces, foresees a promising route to ultra-compact optical devices. Conventional designs of such meta-structures start with a certain structure as the prototype, followed by extensive parametric sweeps to accommodate the requirements of phase and amplitude of the emerging light. Regardless of how computation-consuming the process is, a predefined structure can hardly realize the independent control over polarization, frequency, and spatial channels, which hinders the potential of metasurfaces to be multifunctional. Besides, achieving complicated and multiple functions calls for designing meta-systems with multiple cascading layers of metasurfaces, which introduces exponential complexity. We have developed a series of deep-learning enabled generative frameworks for the inverse design of plasmonic structures in response to on-demand optical properties, with extended case studies and experimental demonstrations. Moreover, we further present a hybrid deep learning framework for designing multilayer meta-systems with multifunctional capabilities, as well as nonlinear metasurfaces for the generation of new spectral components and active control of light waves.

Metasurfaces composed of meta-molecules with spatially variant building blocks, such as gradient metasurfaces, are drawing substantial attention due to their unconventional controllability of the amplitude, phase, and frequency of light. However, the intricate mechanisms and the large degrees of freedom of the multi-element systems impede an effective strategy for the design and optimization of meta-molecules. We propose a hybrid artificial intelligence-based framework consolidating compositional pattern-producing networks and cooperative coevolution to resolve the inverse design of meta-molecules in metasurfaces. The efficacy and reliability of the design strategy are confirmed through experimental validations. This framework reveals a promising candidate approach to expedite the design of free-form, large-scale metasurfaces in a systematic manner.

We further introduce a deep learning framework for the discovery and design of a multilayer multifunctional meta-system, which is too complicated to be accomplished through conventional design processes. As solid illustrations, we report three examples designed by our framework: a polarization-multiplexed dual-functional beam generator, a second order differentiator for all-optical computing, and a space-polarization-wavelength multiplexed hologram. These functions are barely achievable by single-layer metasurfaces, and the devices are hardly approachable by conventional design means. The designed devices are constituted of arbitrary patterns, which indicates the extremely high degrees of freedom of the structures involved.

The machine learning methods developed here is applicable to the inverse design of other photonic components and systems, including photonic crystals, chip-scale silicon devices, quantum-optical devices, and nonlinear optical materials. This design methodology is also significant to other disciplines of natural sciences, such as the design of nano materials, searching for new topological insulators, planning of chemical syntheses, prediction of protein structures, and many more.

2:00 PM EL16.02.02
Electronic Steering of Directional Thermal Emission based on Delocalized Photonic Mode Resonator Combined with Graphene-Metal Hybrid Metasurface Joel Siegel[1], Shinho Kim[2], Margaret Fortman[1], Phillip Hon[3], Luke Sweatlock[3], Min Seok Jang[2] and Victor Brar[1]; [1]University of Wisconsin-Madison, United States; [2]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [3]Northrop Grumman Corporation, United States

There have been various studies to control the thermal emission of hot objects to obtain a narrowband or directional emission spectrum that is difficult to achieve by the conventional blackbody emitter. Recent studies have reported that elaborately designed metasurface/metamaterial combined with active materials enables dynamic control of the emission spectrum by external stimuli. However, previous studies have focused on emissivity modulation for the frequency spectrum, and the steering of directional thermal emission has not yet been demonstrated.

In this report, we experimentally demonstrate an electrically tunable directional thermal emission from a delocalized optical mode resonator combined with a graphene-metal hybrid metasurface. The wavelength scale thick dielectric layer is sandwiched by the metal electrode layer and the metasurface, supporting vertically oscillating Fabry-Perot mode. The delocalized Fabry-Perot mode has a sufficiently long coherence length, resulting in phase alignment of random thermal dipoles to obtain sufficient interference effect between emissions of each metasurface element.

The dynamical behavior of emissivity is estimated by calculating the absorption of the proposed structure for various incident angles of TM polarized light and Fermi levels of graphene. Due to the metasurface's non-resonant scattering, the proposed structure's resonant absorption spectrum could be completely explained by the Fabry-Perot reflection model. The phase of the reflection coefficient of the metasurface is modulated by altering the Fermi level of graphene, resulting in the resonance frequency shift of Fabry-Perot reflection. The maximum absorption of the proposed structure is achieved by nearly complete destructive interference of direct and Fabry-Perot reflections. From the constraint of wavevector for the direction of oscillation imposed by the

Fabry-Perot resonance condition, the difference of resonance frequencies for different Fermi levels is equivalent to the steering angle of thermal emission. For a fixed frequency, the angle of directional thermal emission is continuously modulated by varying the Fermi level of graphene. We measured the emissivity of the device by collecting the thermal emission of the device on the 250°C heating stage through Fourier transform infrared spectroscopy. The Fermi level of graphene is modulated by applying the voltage on the backside metal reflector and the graphene layer. The experimental measurement of the device shows maximum emissivity over 0.9 for each resonance frequency. For the change of 1.15 x 10^{13} cm^{-2} carrier density in graphene, the steering angle at 1508 cm^{-1} is larger than 10°. This work inspires new approaches to controlling thermal emission and pave the way for expanding applications of thermal emitters beyond conventional limitations

2:15 PM EL16.02.03

Exploring the Design of Mid-Infrared Thermal Emitters Using Graphene-Si Hybrid Resonances with Coupled Mode Theory Arun Nagpal[1], Ming Zhou[2], Ognjen Ilic[3], Zongfu Yu[4] and Harry A. Atwater[1]; [1]California Institute of Technology, United States; [2]Stanford University, United States; [3]University of Minnesota Twin Cities, United States; [4]University of Wisconsin–Madison, United States

Thermal emission is typically spontaneous, broadband, and isotropic. Modifying the emissivity and absorptivity of a nanostructure allows for the development of devices for heat management and leads to advances in beamforming metasurfaces for generally incoherent light or emissive sources. Here we discuss the use of coupled-mode theory to design metasurfaces whose working principle couples the guided mode resonance of a silicon photonic crystal to the localized surface plasmons of a graphene ribbon array. The resultant devices are predicted to have a Q factor of greater than 10,000 and can be tuned through the application of a gate voltage from a peak emissivity of more than 0.98 to nearly 0. We show that predictions made using coupled mode theory run two orders of magnitude faster than equivalent FEM simulations, allowing us to quickly define the phase space of device geometries that produce critically coupled, narrowband TM-polarized thermal emission. We will also present results of experimental measurements of tunable graphene resonators coupled to high quality factor photonic crystals. We show through the choice of realistic material parameter modelling, the resultant structures are amenable for fabrication.

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2:30 PM BREAK

3:00 PM *EL16.02.05

Multipole Mie Resonances in Lattices of Lossy Materials Amanda Romero, Md Sakibul Islam and Viktoriia Babicheva; University of New Mexico, United States

Due to the high losses, achieving high light confinement and efficient harvesting in the nanostructures of lossy materials is challenging. We design, fabricate, and experimentally characterize resonant nanostructures to achieve efficient mode concentration and dynamic tuning of nanophotonic elements made of lossy materials, such as titanium and nickel. We have achieved the excitation of strong lattice resonances and more significant absorption in the arrays of lossy nanoparticles, which can result in a higher generation of hot electrons. We explore the optical properties of novel nanostructures, intending to use them in laser devices and for enhanced emission. We have shown that the narrowband or broadband functionality of such lossy nanostructures can be improved using a multiple-period array and can be applied to photodetectors. Arranged in the periodic array, nanoparticles facilitate a strong enhancement in the resonances and absorption profiles. We also show that these nanostructures can provide high-efficiency hot-electron generation.
This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Los Alamos National Laboratory (Contract 89233218CNA000001) and Sandia National Laboratories (Contract DE-NA-0003525). The work is also supported by Contract DE-2375849.

3:30 PM EL16.02.06

Tuning the Generation of Luminescent Silver Nanodots with Printed ssDNA on the Surface Junhua Yu and Sungmoon Choi; Seoul National Univ, Korea (the Republic of)

Stable luminescent silver clusters, named as silver nanodots (AgNDs), have been successfully encapsulated in several scaffolds, such as dendrimers, [1] microgels, [2] peptides, [3] and single stranded DNA (ssDNA). [4] ssDNA with varying sequences have produced the widest variety of and most robust nanodot emitters with spectrally pure emissions from the blue to near-IR wavelengths. Besides the much better brightness due to the competitive luminescent quantum yield and excellent molar extinction coefficient, silver nanodots exhibit excellent stability, at least 15-fold more photostable than organic dyes, illustrating great potential as a new generation of fluorophores. [5]

Silver nanodots are usually generated by reducing a mixture of silver ions and their protective group in solution, followed by the rearrangement of the reduced silver to form luminescent clusters. [6-8] Their characterizations are conducted thereafter or in a polyvinyl alcohol) (PVA) film. However, the generation and activity of silver nanodots on the surface has not been studied well. Surface chemistry plays an important role in determining the functionality of nanomaterials. [9] The interactions between the surface and the reactive molecules on the surface, as well as between these reactive molecules, may influence the reactivity of the surface molecules. Moreover, the stabilization of the silver cluster core in the nanodot is mainly related to coordinated covalent bonding. This indicates that the interactions between the silver cluster and the surrounding ligands are critically important, and therefore, the surface chemistry plays an even more essential role in the stabilization of silver nanodots. Herein, we have investigated the factors that determine the generation of silver nanodots and selectively controlled the spectrum of the silver nanodot.

We found that the fundamentals for the generation of silver nanodots on surfaces is different from that in solution.[10,11] Adsorbed ssDNA molecules cannot efficiently assist the generation of silver nanodots by either direct chemical reduction or photoactivation. Instead, silver nanodots can be instantly generated on the surface by silver cluster transfer, significantly faster than other methods to generate the same emitter in solution. Contrary to the most easily generated red emitter in solution, the predominant species on the surface is the near-IR emitter. This is likely due to the surface structure that stabilizes the near-IR emitter. Moreover, the kinetic trapping of ssDNA molecules on the surface also limits the reorganization of the resulting silver nanodots for other silver nanodot emitters. Adjusting the freedom of the adsorbed ssDNA on the surface can tune the generation of various silver nanodots on the surface.

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3:45 PM EL16.02.07

Optically Tunable Wavefunctions of Plasmonic Metals Kanij Mehtanin Khabir, Leila Hesami and Mikhail A. Noginov; Norfolk State University, United States

Active plasmonics and nanophotonics are of great interest for fundamental science and applications of light.
In our recent studies, we researched (i) effects of dye-doped polymers (Rh590:PMMA) on workfunction of Au and Ag [1,2] as well as (ii) effects of metal-dielectric substrates on photopolymerization of BITh molecules [3]. At this time, we report on control of the workfunctions of Ag and Au films coated with BITs by external light.
Our samples were thin Ag and Au films deposited on glass and spin coated with BITh molecules. They were exposed to radiation of a broadband quartz lamp, which was a part of the Kevin Probe (KP) apparatus, and their workfunctions as well as the reflection spectra were studied using the Kelvin Probe and the spectrophotometer, respectively.
We have found that in BITh-coated Ag and Au films, the workfunction decreased by several hundreds electron-volts during the photoexposure and almost returned to its original value when the light was turned off. The characteristic time scale of the process was ~15 minutes and it did not correlate with the rate of photopolymerization. (In particular, we did not see any reversibility of the photopolymerization.)
As the workfunction is expected to affect the optical properties of metals and metal-based waveguides, the observed phenomenon paws the road to tunable Fabry-Perot resonators, Metal-Insulator-Metal (MIM) waveguides, and control of strong coupling of excitons with cavities and surface plasmons.

[1] Kanij Mehtanin Khabir, Mohammad Shahabuddin, Jalyn-Rose L. Clark, Natalia Noginova, Mikhail A. Noginov, “Workfunction studies of constituents of Fabri-Perot cavities and MIM waveguides”, 2022 MRS Spring Meeting and Exhibit, May 8 -13.; Honolulu, Hawaii, USA.
[2] Kanij Mehtanin Khabir, Mohammad Shahabuddin, Jalyn-Rose L. Clark, Natalia Noginova, Mikhail A. Noginov, "Kelvin probe work-function studies of components of Fabry-Perot cavities and MIM waveguides," Proc. SPIE PC12195, Metamaterials, Metadevices, and Metasystems 2022, PC121951Z (3 October 2022); https://doi.org/10.1117/12.2635137
[3] Leila Hesami, Chi Yang, Elias Anwar, Mikhail A. Noginov, “Effect of metal-dielectric environments on photopolymerization of the [2,2′-bi-1H-indene]-1,1′-dione-3,3′-diyldiheptanoatecarboxylate monomer”, 2022 MRS Spring Meeting and Exhibit, May 8 -13.; Honolulu, Hawaii, USA.

4:00 PM EL16.02.08

Active Wavefront Shaping in Transmission from Tunable Excitonic Resonances Melissa Li, Claudio Hail, Souvik Biswas and Harry A. Atwater; California Institute of Technology, United States

We demonstrate dynamic beam steering in transmission by utilizing the large tunability of the complex refractive index enabled by excitonic resonances. While reconfigurable metasurfaces have been explored using tunable materials such as transparent conducting oxides, liquid crystals, or phase change materials, these concepts rely on coupling to resonant antennas or optical cavities which are sensitive to geometric parameters. Rapid advances in understanding excitonic resonances intrinsic to materials have stimulated thinking about active metasurfaces where the excitonic material can act both as the resonant scatterer and the tunable material. However, demonstrations of active metasurfaces exploiting excitonic resonances for amplitude and phase modulation have been limited to operating in reflection. Here, we show how in excitonic materials where the quantum yield is over 70%, for example, in monolayer transition metal dichalcogenides, quantum dots, or perovskites, we can modulate the phase shift of the transmitted light by over 250°. By varying the voltages from ±5 V between adjacent electrodes, we can then dynamically steer the transmitted beam to ±39° near the exciton resonance. Our results suggest the potential of leveraging the tunability of excitonic resonances for arbitrary wavefront shaping in emerging photonic applications.

4:15 PM *EL16.02.09

Nanophotonics with Coherent and Temporally Controlled Single Photon Light Emission Harry A. Atwater; California Institute of Technology, United States

Advances in synthesis of excitonic materials and color-centers are giving rise to sources of coherent and single photon light emission that can enable new types of nanophotonic systems. Recent developments in color center-based single photon sources have demonstrated homogeneously broadened and electrically tunable single photon emission from color centers in hexagonal boron nitride. These color centers are optical frequency single photon emitters with linewidths of <100 MHz and are wavelength tunable over a >400 GHz frequency range under electrical gating, with precisely determined dipole orientation. I will discuss the implications of these results for electrical control of single photon emission, in which we can envision nanophotonic structures for tailoring the temporal and spectral characteristics of color centers and excitonic emitters to enable indistinguishability and photon correlation for applications such as emitter-emitter entanglement and quasi-noiseless amplification of weak optical signals by single photon addition to thermal light sources.

SESSION EL16.03: Nonlinear and Tunable Optics

Session Chairs: Yao-Wei Huang and Pin Chieh Wu
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3016

10:30 AM *EL16.03.01

High Quality Factor Meta-Atoms for Extremely Energy-Efficient Dynamic and Nonlinear Flat Optics Mark Lawrence[1], Lin Lin[1], Samuel Ameyaw[1], Bo Zhao[1], Jennifer A. Dionne[2], Sahil Dagli[2] and Jack Hu[2]; [1]Washington University in St Louis, United States; [2]Stanford University, United States

Phase gradient metasurfaces represent a new paradigm for designing diffractive optics that offer unprecedented spatial resolution combined with multifunctionality, all within an ultrathin footprint. By sculpting light waves via independent subwavelength pixels each with access to all possible phase values, a wide array of impressive wave transformations has been realized, including aberration-free high NA lenses, artifact-free holograms, and skin invisibility cloaks. An intriguing next step is the prospect of adding nonlinear, dynamic, and active functionality, to target new LiDAR sensors, AR/VR glasses, quantum and classical light sources, and all-optical analog signal processors, for example. Unfortunately, a combination of vanishingly small material coefficients and weak optical resonance (quality factors $(Q)\sim10$) has meant that nonlinear, dynamic, and active phase gradient metasurface demonstrations have suffered from exceedingly low efficiency and/or limited performance.

Here, we introduce metasurface building blocks that dramatically boost the light-matter coupling strength while maintaining the sub-wavelength continuous phase control that makes metasurfaces so powerful. Specifically, we reveal dielectric nanoantennas that support multi-polar guided mode resonances (MGMR) which, thanks to subtle symmetry breaking, exhibit huge Q-factors. Counterintuitively, these high-Q nanoantennas can be placed very close together while maintaining independent scattering signatures, making them excellent meta-atoms. We even demonstrate that by using interference to suppress residual coupling, we can build phase gradient metasurfaces with spacing $<\lambda/2$ between elements with $Q>10^4$. Beyond the strong resonant intensity enhancement that this represents, we reveal that MGMRs share the rich scattering characteristics of Mie resonators. To demonstrate the potential of this new platform within real-world applications, we realize efficient electro-optic and electro-thermal beam-steering as well as incident angle independent low-threshold Kerr switching.

11:00 AM EL16.03.02
Plasmonic Control of High Energy Ligh-Materials Interaction Pavel Shafirin, Pengli Feng and Artur Davoyan; University of California, Los Angeles, United States

Thermoplasmoncis offers an unprecedented potential for creating optically induced heat sources at the nanoscale. Importantly, by creating nanoscale structures heat transfer and related heat induced processed can be efficiently controlled. Here, we study experimentally and theoretically the effects of intense laser beams interaction with plasmonic nanostructures in the ablation regime. Specifically, at high laser beam fluences we create ablation plasmas and study their properties as a function of the underlying plasmonic nanostructure. Our work hints the possibility of controlling ablation plasmas with properly selected and structured thermoplasmonic systems, offering new opportunities for a range of applications from compact accelerators to additive and emerging manufacturing to plasma medicine.
To investigate laser driven ablation we study pulsed (5-50 ns) high energy laser (1064 nm, 10 mJ- 1J) interaction with plasmonic nanostructures. Upon focusing we observe formation of short lived plasmas, which we measure characterize with short gate time ICCD camera to produce time resolved images of the plasma plume and emission spectra with resolution down to 3 ns. With this approach we determine the temporal evolution of ablation plasma temperature, ionization state and its density. We then compare measured ablation dynamics for bulk metals (such as copper, aluminum, and steel) with micro and nanostructured metals (such as thin ~100 nm films). We show that the ablation dynamics for these systems is drastically different, which signifies that by nanostructuring heat generation and transfer are modified. To reveal the complex light materials interaction we develop a theoretical framework that couples optical absorption together with heat transfer and associated series of phase changes. Influence of fast nanosecond evolution and nanoscale interaction in structured plasmonic materials is discussed.

11:15 AM EL16.03.03
Excitation Dependent Saturation Intensity in Ultrathin Epsilon-Near-Zero Films Quynh T. Dang[1], Sudip Gurung[1], Kent Nguyen[1], Subhajit Bej[2], Aleksei Anopchenko[1], Andrea Marini[3] and Ho Wai (Howard) Lee[1]; [1]UC Irvine, United States; [2]Tampere University, Finland; [3]University of L'Aquila, Italy

Studies in epsilon near zero (ENZ) thin films have shown extreme nonlinear light-matter interactions leading to giant ultrafast nonlinearities. This corresponds to the excitation of ENZ modes and the associated electric field intensity enhancement (FIE) inside the material. Recent progress in the field mainly focuses on ENZ nonlinearity caused by electron absorption within the conduction band only, thus lacking an understanding of optical transition absorption near the ENZ regime. Therefore, an in-depth study of the nonlinearity, especially the nonlinear absorption behavior of the ENZ materials in the presence of optical transition, is crucial. With three-photon absorption, the intensity-dependent absorption coefficient can be written as: $\alpha = \alpha_{ns} + \alpha_0 / (1 + I/I_{sat}) + \gamma I^2$, where the 1st and the 2nd term are related to the saturable absorption caused by conduction band free electrons, and the 3rd term is related to the 3-photon absorption. α = total absorption coefficient, γ = 3-photon absorption coefficient, α_{ns} = nonsaturable absorption, α_0 = linear absorption coefficient, and I_{sat} = saturation intensity is defined as the intensity when nonlinear absorption becomes $\alpha_0/2$.
In this work, we demonstrated that at ENZ wavelength (1190 nm for a 300 nm thick ITO sample), where 3-photon absorption is absent, saturable absorption decreases as intensity and angle of incident of light increase. These are because of the increased absorption and enhancement field intensity caused by ENZ mode excitation at a larger angle of incidence. We also observed that near the ENZ regime (1090nm), where 3-photon absorption is possible, saturable and 3-photon absorption compete with each other. In contrast to the saturable absorption, 3-photon absorption increases with increasing intensity but decreases at larger angles of incidence. The decrease of 3-photon absorption at a large incident angle can result from increased absorption by the free electrons in the conduction band. Since ENZ mode excitation causes the free electrons to absorb more photons at larger incident angles, there are fewer photons available to contribute to multiple-photon absorption. These competing nonlinear absorption mechanisms can provide a new and significant optical-nonlinearity tuning mechanism to implement in optics/optomechanical devices (i.e., ultrafast all-optical switches/modulators).

11:30 AM *EL16.03.04
Metasurfaces from Tunable Materials Matthew D. Escarra; Tulane University, United States

Huygens metasurfaces, utilizing coupled electric and magnetic dipole resonances in nanophotonic structures, show promise for integrated photonics, flat optics, and optical modulators. Novel phase tunable materials such as antimony trisulfide (Sb_2S_3) and vanadium dioxide (VO_2) may be used directly as nanoresonators to take advantage of the high sensitivity of this type of metasurface, enabling highly tunable optics with binary (Sb_2S_3, non-volatile) or continuous (VO_2, volatile) variability. Amplitude and phase modulators, beam deflectors, varifocal lenses, and tunable holograms are possible with these materials. Here we report progress in design, nanofabrication, and characterization of tunable metasurface optics from these materials. Related advances with Huygens metasurface-based biosensing and 2D materials will be briefly mentioned.

SESSION EL16.04: Ultrafast Photonics and Quantum Emission in Metasurfaces Nanostructures
Session Chairs: Ho Wai (Howard) Lee and Pin Chieh Wu
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3016

1:30 PM *EL16.04.01

Engineering Quantum Phenomena with Epsilon-Near-Zero (ENZ) Materials Jeremy N. Munday; University of California, Davis, United States

Epsilon-near-zero (ENZ) materials have given rise to a rich variety of phenomena such as electromagnetic supercoupling, resonance pinning, perfect optical absorption, and ultrafast optical switching. In addition, ENZ materials have been successfully exploited to modulate the spontaneous emission intensity, including the spectrum and directionality, of quantum emitters. Here we present two additional phenomena that can arise as a result of ENZ materials interacting with quantum vacuum fluctuations. First, we will present the concept of electromagnetic bandgaps for nanoparticles comprising an ENZ material. The suppressed radiative emission is found to be invariant with respect to particle size and is therefore an intrinsic property of the ENZ material. Even for non-ideal ENZ materials (e.g., ITO), a suppression of ~90% is achieved within the bandgap region. Second, we will show how tunable ENZ materials can be used to convert electrical bias into mechanical motion through the Casimir force, resulting from a confinement of the quantum fluctuations of vacuum. Together, these effects show the potential of engineering quantum fluctuations through novel material systems for future device applications.

2:00 PM EL16.04.02
Perovskite Phonon Polaritonics in the Terahertz Gap Rui Xu[1], Tong Lin[1], Jiaming Luo[1], Xiaotong Chen[1], Elizabeth Blackert[1], Alyssa Moon[2], Khalil Jebailey[1] and Hanyu Zhu[1]; [1]Rice University, United States; [2]Texas A&M University, United States

Photonics in the "new terahertz (THz) gap" between 5 and 15 THz have numerous applications from molecular sensing to ultrafast materials manipulations. However, there are few choices of photonic materials in this frequency range due to prevalent phonon absorption in solids. Recent progress in phonon-polariton microstructures and metamaterials demonstrated low-loss and sub-wavelength photonic devices in the mid-infrared frequencies, but many require crystalline thin films and have small bandwidths. Crystalline ternary oxides were predicted to have great potential as broadband phonon-polaritonic materials in mid- and far-infrared frequencies, but the difficulty in fabrication has impeded further development. Here we report surface phonon-polaritonics based on single-crystalline SrTiO3 that realizes planar ultrafast concentrators with a tunable resonance in 7–13 THz. Our design principle allows simple fabrication without damaging the crystalline quality of the materials. Experimentally, we achieved polarization-independent field amplification by a factor of 5 and average spectral enhancement over 30 times. We measured the resonance spectra and transient electric fields of the concentrators by THz-field induced second harmonic generation (TEFISH), showing up to 0.5 GV/m field strength in a large, optically resolvable area with a table-top source. The ability to generate strong, multicycle, variable-polarized THz fields in the new terahertz gap offers a convenient platform for studying driven phases and nonlinear phononics in quantum materials.

2:15 PM EL16.04.03
Rectifying Effect of Ratcheting Quasi-ballistic Electrons in Plasmonic Resonators Hue T. Do[1,1,2], Lin Wu[3,2] and Michel Bosman[1,2]; [1]National University of Singapore, Singapore; [2]Agency for Science, Technology and Research, Singapore; [3]Singapore University of Technology and Design, Singapore

Geometric diodes exhibit current rectification by preferential scattering of quasi-ballistic electrons in designed resonator geometries. High rectification ratios at room temperature have been shown in graphene [1] and recently also in silicon geometric diodes [2], which enables energy harvesting from radiation in the THz and GHz domains. In this work, we present rectification in plasmonic resonators operating in the near-IR frequency range. We use Particle-in-cell simulations [3][4] that solve the full-wave Maxwell equations while also considering the electron dynamics at the resonator boundaries that result in preferential scattering. Our approach reveals AC rectifying behaviour of such geometric diodes, which was not possible in earlier analytical models [1][2]. We demonstrate up to 1.7 asymmetry ratio between the current density in forward and backward direction for resonators that are locally excited by fast-moving electrons; and significant charge accumulation upon continuous-wave laser illumination. Following these theoretical predictions, we have fabricated TEM samples of our designed geometric diodes and by using nano-optical spectroscopy in the TEM, we experimentally confirm our predictions. This work will open opportunities for energy harvesting from near IR radiation and surface plasmon polariton rectification in plasmonic circuits.

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2:30 PM BREAK

3:00 PM EL16.04.04
Epsilon-Near-Zero Mode Excitation in TCO Thin Film Coated Optical Fibers Stuart Love; University of California Irvine, United States

Epsilon near zero (ENZ) materials have been extensively studied recently due to their unique and extreme optical properties [1]. Ultrathin transparent conducting oxide (TCO) ENZ—the real part of permittivity approaches zero—layer can support plasmon polariton mode with enhanced and highly confined optical field [2]. Furthermore, the ENZ properties of TCO can also be tuned dynamically by field effect dynamic [3-6]. However, excitation of ENZ resonances in optical waveguides, more specifically optical fibers, has been under investigated.

In this work, we demonstrate the excitation of ENZ mode in optical fiber via direct phase matching between the fundamental mode of the fiber and the ENZ mode supported by the AZO thin film. With the TCO coating near the core of a D-shaped single-mode fiber, we have shown up to 10 dB of transmission resonance in the ENZ wavelength regime. Using a supercontinuum laser (500-1750nm) we couple directly to a single mode fiber that has partially polished cladding in the center, allowing for proximity to the core. By depositing aluminum zinc oxide (AZO) film on the polished surface, this can allow for coupling to the ENZ modes of the AZO while the light is propagating through the fiber. Varying thickness of AZO coating, which changes the central ENZ wavelength, further change the coupling of the ENZ mode in the fiber by shifting the resonance peak. In comparison with uncoated fibers, there is a clear excitation of hybrid ENZ mode. By launching ultrafast high power pulse laser into the ENZ optical fiber, nonlinear ENZ mode coupling and generation of harmonic light are expected to be observed, which will be presented at this conference.

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3:15 PM EL16.04.05
A Multifunctional Imaging Metalens for Arbitrary Structuring Quantum Emission Jaehyuck Jang[1], Chi Li[2], Trevon Badloe[1], Junsuk Rho[1], Igor Aharonovich[2] and Haoran Ren[3]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]University of Technology Sydney, Australia; [3]Monash University, Australia

Quantum emission is essential for realizing quantum photonic applications such as computing, communication, and cryptography. The representative example of a quantum light source at room temperature is solid-state single photon emission (SPE) observed in defects in two-dimensional (2D) hexagonal boron nitride (hBN). Recently, it is of great interest to arbitrarily modulate quantum light sources with multiple degrees of freedom, including directionality, polarization, and orbital angular momentum. However, modulating the SPE in a conventional way entails a bulky optical system such as an objective, wave plates, and diffractive optical elements, which is inappropriate in a confined on-chip quantum system. Metasurface, an array of ultra-thin subwavelength nanostructures, is capable of multiplexing multiple functionalities of bulky optical components on it. Therefore, multiplexed metasurface can dramatically reduce the volume of the optical system that engineers the quantum emission of SPE.
In this presentation, I will introduce our recent work in structuring quantum emissions using a multifunctional imaging metalens [1]. First, a beam-splitting metalens was proposed for splitting SPE from ultra-bright defect in hBN depending on its orthogonal polarization states. Next, multiplexed metalenses were designed to imprint any arbitrary wavefront onto orthogonal polarization states, manipulating directionality, polarization, and orbital angular momentum of the output quantum source. This hybrid quantum metalens could unleash the full potential of solid-state SPEs for their use as high-dimensional quantum sources for advanced quantum photonic applications.

[1] Li, C.*, **Jang, J.***, Badloe, T.*, Yang, T., Kim, J., *et al.* Arbitrary structured quantum emission with a multifunctional imaging metalens. *ArXiv* 2209.04571 (2022).

3:30 PM *EL16.04.06
Metamaterial Analogue of a Continuous Time Crystal Tongjun Liu[1], Bruce Ou[1], Kevin F. MacDonald[1] and Nikolay I. Zheludev[1,2]; [1]University of Southampton, United Kingdom; [2]Nanyang Technological University, Singapore

Time crystals are an eagerly sought phase of matter in which time-translation symmetry is broken. Quantum time crystals with discretely broken time-translation symmetry have been demonstrated in trapped ions, atoms and spins while continuously broken time-translation symmetry has been observed in an atomic condensate inside an optical cavity. Here we report that a classical metamaterial nanostructure, a two-dimensional array of plasmonic metamolecules supported on flexible nanowires, can be driven to a state possessing all key features of a continuous time crystal: continuous coherent illumination by light resonant with the metamolecules' plasmonic mode triggers a spontaneous phase transition to a superradiance alike state of transmissivity oscillations resulting from many-body interactions among the metamolecules, and which is characterized by long-range order in space and time. As the state can be manipulated optically, the phenomenon is of interest to topological and non-Hermitian physics and applications in frequency conversion, memory, modulation, nonreciprocity and amplification.

SESSION EL16.05: Poster Session: Low Dimensional Nanostructure Meta Surfaces and Metamaterials
Session Chairs: Yao-Wei Huang and Ho Wai (Howard) Lee
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL16.05.01
Twins of Ultrasmall Gold Nanoparticles (1-2 nm) by Covalently Attached DNA Oligomers Jonas Sager[1], Sebastian Kollenda[1], Kai Klein[1], Kateryna Loza[1], Marc Heggen[2] and Matthias Epple[1]; [1]University Duisburg-Essen, Germany; [2]Forschungszentrum Jülich GmbH, Germany

Ultrasmall gold nanoparticles (1-2 nm) are smaller than most biomolecules like proteins and DNA plasmids. DNA oligomers were covalently attached by azide-alkyne click chemistry to the nanoparticle surface. A thorough control over the reaction conditions permits to limit the number of DNA strands on each nanoparticle to one or two. This allows a hybridization of two nanoparticles that each carry a complementary DNA strand. Furthermore, each nanoparticle was labelled with a fluorescent dye. Thereby, supramolecular structures with nanophotonic effects are generated: Nanoparticle twins (dumbbell-like) with an adjacent FRET pair of dyes.
The nanoparticles and their hybridization products were thoroughly characterized by transmission electron microscopy, NMR spectroscopy, and UV spectroscopy. The twins were isolated and purified by gel electrophoresis, removing aggregates that consisted of more than one pair of particles. The successful hybridization was demonstrated by Foerster resonance energy transfer (FRET) from donor/acceptor dyes at the complementary DNA strands, opening the way for a control over nanophotonic properties by variation of the length of the DNA duplex that connects both particles.

5:00 PM EL16.05.03
Edge States with Spin-Valley Locking Characteristics Through Staggered Photonic Crystals with Honeycomb Lattice Yeseul Kim[1], Minkyung Kim[2] and Junsuk Rho[1]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Gwangju Institute of Science and Technology, Korea (the Republic of)

Topological photonics imitate topological condensed matter physics, which has created opportunities for efficient and reliable photon transport. In this poster presentation, we present the demonstration of spin-valley locking of edge states using staggered chiral photonic crystals with the two-dimensional honeycomb lattice[1]. With a bandgap in the spin-valley locked edge states and calculations using the coupled dipole technique, we show the bulk band dispersion. And the staggered chirality breaks the inversion symmetry, resulting in the spin-valley locking properties.

[1] Kim, M., Kim, Y., & Rho, J. (2020). Spin-valley locked topological edge states in a staggered chiral photonic crystal. New Journal of Physics, 22(11), 113022.

5:00 PM EL16.05.05
Size-Dependent Electron-Phonon Coupling in Monocrystalline Gold Nanoparticles Yannic U. Staechelin[1], Dominik Hoeing[1,2], Florian Schulz[1] and Holger Lange[1,2]; [1]Universität Hamburg, Germany; [2]CUI: Advanced Imaging of Matter, Germany

The absorption of light very effectively generates hot electrons in plasmonic nanoparticles. These hot electrons can be used to photocatalyze chemical reactions. Relaxation of the hot electrons takes place via thermalization with the lattice. In our recent study, we investigated this so-called electron-phonon coupling in gold nanoparticles (AuNPs). Size dependency of the electron-phonon coupling has been controversially discussed in literature. By comparing mono- to polycrystalline AuNPs, we could show that electron-surface scattering contributes substantially to electron-phonon coupling, giving rise to size-dependent electron-phonon coupling in monocrystalline AuNPs, while blurring the size dependency in polycrystalline AuNPs.[1] We investigated further aspects of the hot electron dynamics in plasmonic nanoparticles such as its temperature dependency or the excitation mechanism of breathing oscillations.

[1]: ACS Photonics 2021, 8, 752−757

5:00 PM EL16.05.06
Robust Metasurfaces Using Versatile Encapsulation Coating Without Critical Optical Losses Junhwa Seong, Younghwan Yang and Junsuk Rho; Pohang University of Science and Technology, Korea (the Republic of)

Metasurfaces, which are comprised of 2D subwavelength artificial structures, have been extensively studied owing to their unprecedented wavefront manipulations, especially for visible range. By virtue of these capabilities, metasurfaces can serve as highly functionalized photonic systems, such as metalenses, and metaholograms, with the great pliability of electromagnetic wave control. Despite these benefits, many professionals predict that metasurfaces are challenging to be utilized realistic devices, because of their low robustness. Nowadays, dielectric metasurfaces have been devised to avoid a decrease in efficiency. These optical losses are induced by the electron oscillation of metal when light comes. Particularly, hydrogenated amorphous silicon (a-Si:H) which has a high refractive index and low extinction coefficient has been developed to implement high-efficiency dielectric metasurfaces at the visible. Here, we propose high-efficient and high-robustness encapsulated metasurfaces through bandgap engineering of hydrogenated amorphous silicon, achieving 95% in 532 nm wavelength. We vary the atomic arrangement of hydrogenated amorphous silicon by optimizing process terms of plasma-enhanced chemical vapor deposition for high-efficient dielectric metasurfaces. Moreover, encapsulation coating using atomic layer deposition and spin-on glass enables self-cleaning and high abrasion-resistant metasurfaces, while maintaining high efficiency in the visible frequencies. Unlike conventional metasurfaces, the introduced encapsulated metasurfaces can strongly resist external contaminations and abrasions. We believe that our novel method, enhancing the robustness of metasurfaces, can be applied to pragmatic outdoor applications.

5:00 PM EL16.05.07
Purcell-Enhanced Single-Photon Emission in Hexagonal Boron Nitride Integrated with Bound States in the Continuum Cavity Jihae Lee[1], Minsu Jeong[1] and Junsuk Rho[1,1,2]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]POSCO-POSTECH-RIST Convergence Research Center for Flat Optics and Metaphotonics, Korea (the Republic of)

Hexagonal boron nitride (hBN) has drawn attention as a promising candidate for single-photon sources operating at room temperature.[1] Photonic cavities have been employed for single-photon emitters to enhance the spontaneous emission rate[2], which is known as the Purcell effect[3]. In this work, we demonstrate Purcell enhancement of the single-photon emission in hBN combined with the bound states in the continuum (BIC) cavity. The cavity is designed to support the BIC mode at the emission wavelength of single-photon emitters. Single-photon emitters in mechanically exfoliated hBN are activated by argon annealing, followed by the integration into the BIC cavity using a deterministic transfer. The lifetime of the single-photon emission is reduced in hBN coupled with the BIC mode.

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5:00 PM EL16.05.10
Multilayered Metal-Dielectric Structures for Control of Magnetic Dipole Emission MD Afzalur Rab, Shamaar R. Howard, John N. Munga and Natalia Noginova; Norfolk State University, United States

Metal-dielectric multilayers with nanoscale layer thickness exhibiting hyperbolic dispersion and infinite density of photonic modes, provide opportunities for modification and control of quantum processes in or in a close vicinity to such structures. In our work, we explore multilayered metal-dielectric structures for control of spontaneous emission of $Eu3^+$ ions at the magnetic dipole transition. Using COMSOL software, we model the structure consisting of metal, dielectric and emitting layers, study its optical and plasmonic properties, and explore the possibility to selectively enhance or suppress magnetic and electric dipole emission. This possibility presents the special interest for $Eu3^+$ organic systems where the electric dipole transitions are the main competitive channels for the magnetic dipole transition. Theoretical results are compared with the experiment.

5:00 PM EL16.05.11
Monitoring Electrochemical Growth of Copper on Gold Nanoparticle Ensembles Hyunsik Hwang and Hyunjoon Song; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Metals and semiconductor materials have been of interest due to their prominent intrinsic properties on the bulk scale. Nowadays, hidden optical, catalytic, and biomedical applications with enhanced physicochemical properties that go beyond intrinsic properties have newly emerged over decades by nanostructuring. Among them, the shape of structures also has contributed to improving the characteristics. The application of designed nanoparticles has become a key factor in the fields of batteries, catalysts, and energy storage. As a bottom-up approach for controlling sophisticated morphologies, using surface-regulating agents is the most general strategy in synthetic phases. Although strong binding to specific facets has a great effect on selective deposition, there is sometimes a critical disadvantage to shielding other surface reactions in applications. As an alternative to this, various nanostructures are formed without any additives in electrodeposition. Thermodynamic or kinetic preferential structures could be formed according to the degree of diffusion layer gradient during the particle shaping process. The electrochemical reactions on nanoelectrode ensembles, uniformly or non-uniformly continuous arrays of nanoparticles on an inert working electrode, selectively react only in a limited area. Nanoelectrode ensembles have high sensitivity with a good signal-to-noise ratio to resolve chemical reactions. Interestingly, nanoparticle electrode ensembles are the unique features the distance between the nanoelectrodes directly controls the diffusion modes. Also, it was confirmed that radial diffusion layers generated near nanoparticles change the degree of overlapping by scan rate and particle distance. Selective electrodeposition on the nanoparticles dispersed at an active working electrode occurs in certain metal ions for some reasons such as surface energy difference and underpotential deposition. This system behaves like nanoparticle ensembles electrodes, so it was speculated a change in diffusion mode might occur due to the interparticle distance. If the assumption is correct, particle density during diffusion

layer formation can be a decisive factor in morphological control.
Herein, without any variables except particle density, three well-defined morphologies of single Cu nanostructures were successfully synthesized on Au nanoparticle ensembles via electrochemical deposition. As the number of Au nanoparticles on the ITO substrate, it changed to octapods, holed cubes, and cubes. A similar growth mechanism was identified in anisotropy Au rods. Interestingly, the seed asymmetry was transferred to the final structures. In order to understand the progress of growth, in-situ monitoring using dark-field microscopy was performed to obtain both electrochemical and optical signals simultaneously. The strong plasmon properties of metals such as Au and Cu enabled the in-situ reaction monitoring in the solution phase with a simple optical dark-field microscope. The discussion of the diffusion layer near the nanoparticle-modified electrode is just now becoming an important topic in nanocatalysis. By applying these ideas to electrodeposition, we expect to produce functional improvements with only a simple manipulation in the original direct electrodeposition process.

SESSION EL16.06: Plasmonic in the Visible
Session Chairs: Yao-Wei Huang and Yang Zhao
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3016

8:15 AM EL16.06.01
The Design Principles and the Experimental Characterization of Electrically Tunable Bifocal Metalens System in Visible Range Yeseul Kim[1], Trevon Badloe[1], Inki Kim[2], Joohoon Kim[1] and Junsuk Rho[1]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of)

One of the key components for three-dimensional light focusing and imaging is multifocal lens systems. As electronic devices get smaller, there is an increasing demand for light and thin multifocal systems. Metalens, a kind of flat lens that can focus light by arranging components with subwavelength range, has attracted a lot of interest since it is possible to construct a lens that is extremely light and has a thickness measured in micrometers.
In this presentation, we present how to develop an integrated liquid crystal and electrically tunable multifocal metalens system[1]. The existence of two focal points with a 4 mm difference between them has been experimentally verified. A variety of optical devices, including variable beam control and holographic devices, focusing camera modules, AR/VR display technologies, and depth of field measurement, can use the metalens' quick, millisecond-based focal length adjusting speed.
[1] Badloe, T., Kim, I., Kim, Y., Kim, J., & Rho, J. (2021). *Adv.Sci*., 8(21), 2102646.

8:30 AM EL16.06.02
Scalable Manufacturing of Visible Metalenses Toward High-efficiency Virtual Reality Applications Junhwa Seong[1], Joohoon Kim[1], Wonjoong Kim[2], Heon Lee[2] and Junsuk Rho[1]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Korea University, Korea (the Republic of)

Metasurface-based flat optics is recently in the process of transitioning from science to technology. For instance, metalenses, that have superior light-modulating performance with sub-micrometer-scale thicknesses, have emerged as alternatives to conventional optical lenses to resolve bulky systems and aberrations. However, many experts forecast that metalenses are arduous to commercialize because of serious materials and pattering limitations such as high production costs and low throughputs. To overcome these crucial bottlenecks, we introduce the mass production of visible metalenses with cost- and throughput-effective skills using argon fluoride lithography and wafer-scale nanoimprint lithography integrated with a high-index atomic layer. Once a 12-inch wafer-scale master mold is imprinted, hundreds of 1 cm metalenses are produced with a resolution of 40 nm which is high enough to fabricate the visible metalens. To increase efficiency, we thinly coated the high-index TiO2 atomic layer on printed metalenses, making it a drastic increase of conversion efficiency from 10% to 90%. As a proof of concept, we further apply our scalable produced metalens to a virtual reality device. Furthermore, this approach can also be employed for the scalable manufacturing of various metasurfaces like holograms and biosensors. We believe that our work will enable the extension of metasurfaces to the industry.

8:45 AM EL16.06.03
Imaging NIR to Visible Upconversion Luminescence from Single $NaYF_4$:Yb^{3+},Tm^{3+} Nanoparticles on Ag Nanowire Composites Kim Yip Chiok[1], Anahita Haghizadeh[1], Aravind Baride[2], Steve Smith[1] and Robert Anderson[1]; [1]South Dakota School of Mines and Technology, United States; [2]University of South Dakota, United States

Tm-doped energy transfer upconversion (ETU) $NaYF_4$: Yb^{3+}:Tm^{3+} nanoparticles have potential applications in deep tissue imaging and energy conversion devices due to their visible (450nm) and infra-red (800nm) upconversion emission, but suffer from low quantum efficiency. We use single particle spectroscopic imaging and statistical analysis to assess the plasmonic enhancement of NIR-to-visible upconversion luminescence (UCL) from single β-$NaYF_4$:Yb^{3+}:Tm^{3+}upconverting nanoparticles (UCNPs) supported on substrates consisting of random arrangements of Ag nanowires or nanowire composites (NWCs). By examining the effects at the single particle level, and accumulating a statistical sampling of single particle emitters, both on and off the plasmonic substrates studied, we obtain a statistical description of UCL emission enhancement in the Tm-doped UCNPs and map out the statistical distribution of excitation and luminescence enhancement on the plasmonic substrates. The distributions obtained are compared to Finite Difference Time Domain (FDTD) calculations of the fields near the plasmonic substrate, assuming the variations are due to variations in UCNP coupling to the plasmonic substrate based on an exponential decay with distance. We use both wide field and confocal spectroscopic imaging of single UCNPs on and off the plasmonic substrates in combination with energy and time resolved spectroscopy and compare these results to a coupled rate equation analysis to elucidate the energy transfer upconversion enhancement mechanisms for these substrates.

K.Y. Chiok acknowledges support from the MonArk NSF Quantum Foundry supported by the National Science Foundation Q-AMASE-i program under NSF award No. DMR-1906383

9:00 AM *EL16.06.04
Emerging Materials for Plasmonics in the Visible Region—From Discovery to Application Yu-Jung Lu[1,2]; [1]Academia Sinica, Taiwan; [2]National Taiwan University, Taiwan

Progress in understanding resonant subwavelength optical structures has fueled a worldwide explosion of interest in both fundamental processes and nanophotonic/plasmonic devices for imaging, sensing, solar energy conversion, and information processing. However, plasmonic platforms in the visible region with robust, high-performance, thermo-stable, and low-cost remains remain unexplored. In this presentation, I will particularly discuss emerging plasmonic platforms based on transition metal nitrides. I will present an overview of my research works over the past five years on the plasmon-enhanced light-matter interactions in the visible regions and their applications [1-6], including the plasmonic nanolasers [1-2], tunable plasmonic modulators [3], plasmonic phototransistors [4], plasmon-enhanced solar energy harvesting [5], and the refractory plasmonic colors for back-light free displays [6]. My group discovered several unique working mechanisms that utilize plasmonic nanostructures to improve optoelectronic device performance. By engineering the local electromagnetic field confinement, the light-matter interaction strength can be enhanced, which results in efficient energy conversion in the designed nanosystem. The detailed mechanisms and possible applications will be discussed. These results have broad implications for the use of plasmonic crystals/metasurfaces in high-performance optoelectronic devices with efficient energy conversion.

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[5]. M-J Yu, C-L Chang, H-Y Lan, Z-Y Chiao, Y-C Chen, H W H. Lee, Y-C Chang, S-W Chang, T. Tanaka, V. Tung, H-H Chou*, and Y-J Lu*, Plasmon-Enhanced Solar-Driven Hydrogen Evolution Using Titanium Nitride Metasurface Broadband Absorbers. ACS Photonics 8, 3125–3132 (2021).
[6] Z-Y Chiao, Y-C Chen, J-W Chen, Y-C Chu, J-W Yang, T-Y Peng, W-R Syong, H W H. Lee, S- W Chu, and Y-J Lu*, Full-Color Generation Enabled by Refractory Plasmonic Crystals. Nanophotonics (Accepted) (2022)

9:30 AM BREAK

10:15 AM EL16.06.07
Building Metastructures with Unconventional Plasmonic Material—Advances in Structural Colors and Active Tuning Potential Carlota Ruiz de Galarreta[1], Fernando Chacón[1], María Eva Nieto Piñero[1], Marina Garcia-Pardo[1], Nicolas Ramos[2], Jan Siegel[1] and Rosalia Serna[1]; [1]IO-CSIC, Spain; [2]University of the Basque Country UPV/EHU, Spain

In this work we explore a novel approach for the building of metasurfaces using a non-conventional plasmonic material (bismuth) with phase change potential. [1-3] Our choice is based in the excellent plasmonic response demonstrated by Bi-based nanostructures in the ultraviolet and visible promoted by interband transitions [2-3]. In addition, Bi exhibits a relatively low melting temperature (~270 C), with its solid-to-liquid phase transition being accompanied by significant changes in its optical response. Profiting from this property in previous works we have demonstrated the optical switching of Bi-nanocomposite films by hot-plate annealing (phase light switching) or under ns-laser irradiation (ultrafast response) [4-5].
In this work, we explore and experimentally validate two different approaches to high quality bismuth plasmonics for the realization of pure, pre-designed macroscopic colors. Both approaches are based on Al/oxide/Bi structures: one relies on the use of gap-plasmon metasurfaces where the top, 20 nm-thick Bi layer is structured in the form of nanodiscs arranged in a square lattice and supporting localized dipolar resonances. The second approach relies on more conventional and practicable Fabry-Perot cavities based on continuous 10 nm-thick Bi films lying on an oxide/aluminum thin film configuration. Both types of designs have been successfully fabricated employing e-beam lithography and pulsed laser deposition techniques for the case of structured devices, and pulsed laser deposition-only for the Fabry-Perot cavities. Characterization all the devices was carried out via angularly resolved reflectance measurements, showing excellent agreement with respect to simulations. We will discuss peculiarities, pros and cons of each approach in terms of color purity, fabricability and specific advantages for different applications. Finally for the case of the nanostructured Bi metasurfaces, we will show preliminary results of the tuning potential of the reflectance spectrum upon heating and melting of embedded Bi nanodisks, exploiting the solid-to-liquid optical contrast of Bi.

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10:30 AM EL16.06.08
Mapping Phonon Polaritons with Visible Light Kiernan E. Arledge[1], Michael A. Meeker[2,3], Chase Ellis[2], Nazli Rasouli Sarabi[1], Vincent R. Whiteside[1], Chul Soo Kim[2], Mijin Kim[2], Daniel Ratchford[2], Binbin Weng[1] and Joseph G. Tischler[1]; [1]University of Oklahoma, United States; [2]U.S. Naval Research Laboratory, United States; [3]The City University of New York, United States

Surface phonon polaritons (SPhPs) are surface electromagnetic modes resulting from the strong coupling of infrared light with optical phonons in polar materials. SPhPs show great promise for tailoring light-matter interactions at size-scales below the diffraction limit. Interrogating SPhP modes has mostly been pursued by measuring the far field behavior of resonant modes (i.e., eigenvalues), through which SPhPs can be investigated by looking at resonant frequencies and linewidths along with the strength of the resonances. In other instances, the study of SPhPs has been accomplished by mapping electromagnetic fields (i.e., eigenstates) solely at the surface of nanostructured resonators by atomic force microscopy assisted techniques and, in some limited cases, measuring the three-dimensional fields using electron scattering. Accurate knowledge of SPhPs has been hindered by the absence of experimental techniques to map eigenstates in three dimensions that are easy, cheap, and non-destructive.

Here, using Indium Phosphide (InP) nanopillars, we demonstrated direct three-dimensional measurements of SPhP modes. Confocal Raman microscopy is used to obtain the spatial distribution of phonon modes in the nanostructure. By comparing these maps with simulation results, we demonstrated that SPhPs couple to bulk Raman modes through the material's polarizability and, to a lesser extent, via electron-phonon coupling. These observations provide a new method for measuring SPhP modes in nanostructured materials and a novel way to investigate the physical phenomena involved in coupling bulk phonons to SPhPs.

10:45 AM EL16.06.09
Sodium Surface Plasmon Polaritons Ankun Yang; Oakland University, United States

Sodium (Na) is predicted to be an ideal plasmonic material with ultra-low optical loss across visible to near-infrared. However, there has been limited research on Na plasmonics due to its high reactivity. Here we develop a scalable fabrication method for Na nanostructures, by combining phase-shift photolithography and a thermo-assisted spin-coating process. Using this method, we fabricated Na nano-pit arrays with varying periodicities (300-600 nm) and with tunable surface plasmon polariton (SPP) modes spanning visible to near-infrared (NIR). We achieved SPP resonances with small linewidths as narrow as 10.2 nm. In addition, we observed linewidth narrowing of Na nanostructures from visible towards NIR, showing the prospect of high performance of Na nanostructures operating in the NIR. To address the challenges associated with the high reactivity of Na, we designed a simple encapsulation strategy and stabilized the Na nanostructures in ambient conditions for more than 2 months. As a low-cost and low-loss plasmonic material, Na offers a competitive option for nanophotonic devices and plasmon-enhanced applications.

11:00 AM *EL16.06.10
Polaritonic Metasurfaces Andrea Alu; City University of New York, United States

In this talk, I will discuss our recent progress in the area of polaritonics, and its role in advancing the field of metamaterials and metasurfaces. Tailored material resonances, based on excitons, phonons, or electronic transitions, can be strongly coupled to electromagnetic waves in engineered metasurfaces, unveiling new degrees of freedom for the control of light-matter interactions and enhancing optical nonlinearities. In particular, I will discuss how, as the degree of lattice symmetries in the involved materials and in optically engineered structures is reduced, new opportunities emerge in manipulating light and matter at the nanoscale.

SESSION EL16.07: Light Trapping and Absorber Designing with Metasurfaces and Metastructures
Session Chairs: Andrea Alu and Yu-Jung Lu
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3016

1:30 PM *EL16.07.01
All-Glass Metasurfaces for Durable and Large Aperture Laser Optics Eyal Feigenbaum; Lawrence Livermore National Laboratory, United States

The field of optical meta-surfaces is rapidly growing due to its great potential to enable thin optics implementation with relatively complex and flexible functions. Some of the anticipated key future optical technologies will require for its viability large optical apertures, durability to harsh environments, and robustness to laser powers and energies. These complex systems could benefit from thinner and more lightweight optics, and the improved phase-front control that metasurfaces could deliver. For example, high power and energy laser systems could benefit from optical meta-surfaces that implement beam shaping, e.g., for wave-front aberration correction, but with the advantages of smaller accumulation of nonlinearity and lighter weight. An additional benefit is the superior designs of antireflective layers that are enabled by such a technology.
We present an alternative approach, with far less limitations on scalability, and with inherent high durability. However, the main challenge for this approach is the attainable phase difference range and better understanding the underlying physics of this process. This process we recently presented and demonstrated [ACS AMI 11, 22684 (2019), Optica 7, 518 (2020), Adv. Opt. Mat. 10, 2200151 (2022)], utilizes a laser induced de-wetting of thin metal film on silica glass, followed by dry etching through the nanoparticles mask and removal of the residual metal mask, to result in an all-glass metasurface optics. In this approach the local laser induced heating, using a laser raster-scan, determines the local effective index. Alternatively, a large area and uniform antireflective layer could be generated using dewetting in a furnace. The process is relatively simple, scalable and results in an environmentally stable structure, and allows also for into-the-layer graded-index profile. However, the air-glass volumetric ratio mixing approach is limited by the depth of the layer, and so we have developed approaches to “boost” the attainable phase response and enhance the control over the nano-features shape.
In this talk we will detail the recent developments made in the controllability while preserving the scalability and durability, and the detail the recently demonstrated metasurfaces.
This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. We acknowledge LLNL LDRD support (21-ERD-002). LLNL-CONF-842487.

2:00 PM EL16.07.03
Large Photothermal Modulation of Dielectric Huygens' Metasurface Absorber Hao-Yu Cheng[1,2,2], Chi-Yin Yang[3], Min-Wen Yu[3], Wei-Ruei Chen[3], Shi-Wei Chu[1,4], Kuo-Ping Chen[3,4] and Kung-Hsuan Lin[2]; [1]National Taiwan University, Taiwan; [2]Academia Sinica, Taiwan; [3]National Yang Ming Chiao Tung University, Taiwan; [4]National Tsing Hua University, Taiwan

Mie-type resonators have been found to exhibit large nonlinearity of spectral responses under photoexcitation, which is applicable to all-optical modulation. The typical modulators, based on ring resonators are of size around 10-100 micrometers. To reduce the size of an optical modulator, one potential approach is to utilize Mie resonators. The state-of-the-art modulation depth of Mie resonators is 40-50%, which is still lower than the state-of-the-art all-optical modulator based on a silicon ring resonator. In this work, we demonstrate large modulation depth in Huygens‘ metasurface absorber. When multiple nanostructured resonators (units) are arranged periodically to form a metasurface, coupled electromagnetic interaction creates “lattice resonance” in addition to the resonances due to an individual unit itself. When the electric dipole lattice resonance (EDLR) matches with the magnetic dipole (MD) resonance and the materials possess moderate loss, each meta-atom (unit) could absorb most of the incoming electromagnetic wave due to the matched hybrid resonant modes, which is called Huygens‘ metasurface absorber. We used amorphous silicon-based Huygens’ metasurface absorber and ultrafast excitation to demonstrate two orders of magnitude enhancement of modulation depth, both theoretically and experimentally. We compared two sample structures with the EDLR matching and mismatching the MD of the single SiNB, respectively. At matched resonant condition, we found that the modulation depth was theoretically enhanced by two orders of magnitudes. Enhancement by an order of magnitudes and over 100% modulation depth were experimentally achieved at the matched resonant frequency. Since the optical spot covered tens of SiNBs in the array, our work manifested the feasibility to achieve a large modulation depth of a Mie-type all-optical modulator with size on the order of 1 micrometer. This work opens the avenue toward all-optical information processing via optimized modulation by careful spatiotemporal and spectral control over a metasurface.

3:30 PM EL16.07.06
Ultrathin Broadband Metasurface Superabsorbers from a van der Waals Semimetal Adam Alfieri[1], Michael Motala[2], Michael Snure[3], Jason Lynch[1], Pawan Kumar[1], Huiqin Zhang[1], Susanna Post[4], Christopher Muratore[4], Joshua R. Hendrickson[3], Nicholas Glavin[3] and Deep M. Jariwala[1]; [1]University of Pennsylvania, United States; [2]UES, Inc., United States; [3]Air Force Research Laboratory, United States; [4]University of Dayton, United States

Platinum diselenide ($PtSe_2$) is a novel van der Waals semimetal that exhibits extraordinarily strong interaction with light (a refractive index that exceeds 4 and an extinction coefficient over 2) over a broadband range from the visible to near infrared (NIR). We demonstrate cm-scale growth of 18 nm thick $PtSe_2$ layers with a solar-weighted absorption of 87.6% (from 400 nm – 900 nm) when transferred onto a 40 nm Al_2O_3/Ag reflector substrate[1]. By patterning the $PtSe_2$ layer into a periodic array of nanoresonators, the electric field can be localized in the $PtSe_2$, resulting in an average visible range absorption of 97.9% and a solar-weighted absorption of 97.0% (400 nm to 900 nm) in a total structure thickness of 158 nm and an active layer thickness of only 18 nm. Our $PtSe_2$ metasurfaces present a scalable approach to ultrathin broadband absorbers for photodetection and solar energy harvesting.

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2:30 PM BREAK

3:45 PM EL16.07.07
Transient Color Filters and Superabsorbers Based on Magnesium Peifen Lyu, Tao Gong and Marina S. Leite; University of California, Davis, United States

Photonic devices built upon ultrathin metal films have attracted rising research interest due to their structurally simple and mechanically stable design, which is highly scalable and time-efficient compared to the nanopatterning process, without compromising the superior optical performances. The current photonic thin film research depends heavily on conventional metals (e.g., Au, Ag and Cu) with limitations of high-cost, CMOS-incompatibility and bio-incompatibility, preventing their further usages in industrial applications. Here, we present Magnesium (Mg), the eighth most abundant material on the earth's crust, as a promising candidate for its competitive low-loss optical properties with additional compatibilities in CMOS and biological devices. The first device presented is a Mg-based transient broad-band reflective color filter made from a tandem stack structure of two metal-insulator-metal (MIM) stacks, Mg/MgO/Mg and Ag/Al_2O_3/Ag, interconnecting by a thin MgO layer [1]. Our devices can successfully achieve distinctive hues across the CMY reflective color gamut and are insensitive to incident angles up to 50 degrees, which are conducive for color displays. The transient process takes place while these first vivid colors can vanish within ~40 seconds after immersing in water [2]. It is beneficial that the hue fades quickly for the security and protection of optical information. Further etching ultimately removes away the Mg-contained layers, leaving bottom Ag/Al_2O_3/Ag MIM with another reflective color which is maintained stably under ambient conditions. In contrast, the second device incorporates an ultrathin a-Si absorbing layer and exhibits a spectrally selective and tunable near-unity resonant absorption [3]. By varying the thickness of the semiconductor layers (a-Si and SiO_2), it can generate characteristic colors which cover all the primary RGB and CMY color spaces. An exposure to water can dissolve the Mg back reflection layer and the remaining bilayer transmissive color filters are ready for reconfiguration. To summarize, we propose a novel platform for transient color filters and superabsorbers with Mg-based thin films, which can attain diverse structural colors by tuning the layer thickness. Its unique feature of the single-time and irreversible transient color change process in a zero-power consumption manner, provides new opportunities for next-generation CMOS compatible, biodegradable, and low-cost photonic devices.

[1] P. Lyu, et al. *Adv. Optical Mater*. 10, 2200159 (2022)
[2] T. G. Farinha, T. Gong, P. Lyu, et al, *Optical Materials Express*, 11(5), 1555-1565 (2021)
[3] T. Gong, P. Lyu, et al, In preparation (2022)

4:00 PM EL16.07.08
High Absorptivity Nanotextured Powders for Metal 3D Printing Ottman Tertuliano[1], Philip DePond[2], Jiho Hong[2], Andrew Lee[2], David Doan[2], Wendy Gu[2], Mark L. Brongersma[2], Manyalibo Matthews[3], Wei Cai[2] and Adrian Lew[2]; [1]University of Pennsylvania, United States; [2]Stanford University, United States; [3]Lawrence Livermore National Laboratory, United States

The widespread of application of metal additive manufacturing (AM) is limited by the ability to control the complex interactions between the energy source and the feedstock material. Here we develop a process to introduce nanoscale grooves to the surface of copper powders which increases the powder absorptivity by up to 70% during laser powder bed fusion. The absorptivity increase enables printing of pure copper structures with densities up to 92% using laser energy densities as low as 82 J/mm^3. Simulations show the enhanced powder absorptivity results from plasmonic resonances at nanoscale grooves features combined with multiple scattering events. The approach taken here demonstrates a generalized method to modifying the absorptivity and printability at low energy densities of reflective metal powders by changing the surface morphology and leveraging electric field localization in these self-evolving nanostructures.

4:15 PM EL16.07.09
Inverse Design Enables Large-Scale RGB-Achromatic Metalens and Metagrating Po-Cheng Yang[1], Lu-Yun Wang[1], Jhih-Hao Huang[1], Zhaoyi Li[2], Raphaël Pestourie[3], Steven Johnson[3], Federico Capasso[2] and Yao-Wei Huang[1]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]Harvard University, United States; [3]Massachusetts Institute of Technology, United States

Metalenses with forward dispersion engineering promotes the correction of chromatic aberration. However, forward design of achromatic metalenses find the limitation of scale with the limited dispersion range of meta-atoms. There are many inverse design strategies of metasurface design. However, Inverse design remains very challenging for aperiodic large-scale meta-optics because of limitation of computation time and memory capacity. In this study, we utilize inverse-design framework for aperiodic large-scale complex meta-optics in three dimensions, which alleviates computational cost for both simulation and optimization via a fast-approximate solver and an adjoint method, respectively. We demonstrate an RGB-achomatic metalens with diameter up to 1 centimeter. The focusing efficiency is ~24% in simulation and ~15% in experiment. Furthermore, we demonstrate a metagrating which effectively deflects the light to the 1st order diffraction by using inverse design method. The maximum efficiency of our metagrating achieves up to 67% at large deflection angle (~70°), which is 32% higher than that with forward design in the literature [2]. Moreover, we demonstrate a future virtual-reality platforms by using our meta-eyepieces with a laser back-illuminated micro liquid crystal display. The inverse-design framework can be extended to design large-scale high efficiency multifunctionality metasurfaces.
[1] Z. Li et al., Nature Communications 13, 2409 (2022).
[2] D. Sell et al., Nano Letters 17(6), 3752-3757 (2017).

4:30 PM EL16.07.10
SERS Chips Containing Internal Standard MoS_2 for Quantification of Analytes Seungkyun Lee, Seongdae Kwon, Kibum Kang and Yeon Sik Jung; KAIST, Korea (the Republic of)

Raman spectroscopy with Surface-enhanced Raman scattering (SERS) is one of the most selective, sensitive, and rapid methods for detecting target analytes. Recently, research for adjusting SERS to many fields such as food toxicity, biomolecules, and hazardous substances is being actively implemented. However, SERS has limitations for exact quantification, due to various factors such as spot variation, absence of standard, and reproducibility. Thus, research for integrating 'internal standard material' into the SERS chip has been conducted. It showed the possibility of calculating the ratio of 'Raman intensity of analyte' to the 'Raman intensity of internal standard material', which is supposed to be consistent within the controlled condition.
Here, we propose a 'MoS_2@Gold nanostructure SERS chip', in which the MoS_2 was used as the internal standard for the intrinsic Raman characteristic peak. Existing materials for the internal standard of SERS chips were mostly produced in form of particles or flakes, which may occur spot variation. By integrating the MoS_2 grown in film form, the uniformity and controllability of the substrate could be highly refined. Gold is located at both the top and bottom of the MoS2 in the form of film and nanogrid, which could increase the SERS effect on both MoS_2 and the analyte. This sandwiched structure resulted in a 10^{-9}M LOD of Rhodamine 6G (R6G) and a linear relationship between the Raman intensity and the concentrations of the analytes within the standard deviation of less than 4%, with the correction factors. Through the results of the linear relationship, the MoS_2@Gold nanostructure SERS chip developed in this research proposes future alternatives to the sensors on universal fields with a qualitative, quantitative, and quick method.

SESSION EL16.08: Poster Session: Nanostructure Design, Fabrication and Characterization
Session Chairs: Pin Chieh Wu and Yang Zhao
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL16.08.01
Optical Phenomena of Si@MoS_2 Core@Shell Architecture at the Nanoscale Yea-Shine Lee[1], Tatsuki Hinamoto[2], Sina A. Dereshgi[1], Shiqiang Hao[1], Matthew Cheng[1], Hiroshi Sugimoto[2], Minoru Fujii[2], Christopher Wolverton[1], Koray Aydin[1], Roberto d. Reis[1] and Vinayak P. Dravid[1]; [1]Northwestern University, United States; [2]Kobe University, Japan

Transition metal dichalcogenides (TMDs) are attractive for next-generation photonics due to their large exciton binding energy and exciton transition dipole moment. However, because of their few-atom-layered nature, observing nanoscale light-matter interaction through absorption and emission of the electromagnetic field in TMDs has been challenging. This unfortunately makes isolated TMDs inappropriate for use in optical-to-electrical conversion applications.

Recently, TMD-encapsulated nanospheres, or core@shells, have presented a potential avenue for strong light-matter interactions by leveraging the functionality of the nanoparticle core material. In a core@shell architecture, the dielectric nanosphere core acts as an optical cavity in the Mie regime while the encapsulating 2D material shell acts as a quantum emitter. When the two constituents couple, light-matter interaction is significantly improved and optical-to-electrical conversions such as lasers and quantum information processing that had been otherwise limited in 2D materials can be realized. This geometry has potential applications in nanophotonic devices such as all-optical switches, exciton−polariton lasers, and quantum information processing, as well as various optoelectronic applications such as ultrasensitive sensors, light-emitting devices, and solar cells. However, it is challenging to grow 2D materials on curved surfaces. Moreover, there is an urgent need to develop experimental techniques to probe complex systems that cannot be easily modelled computationally. In our work, we fabricate Si@MoS_2 and use valence electron energy loss spectroscopy (VEELS) to achieve enhanced light-matter interaction and understand the principles underlying this phenomenon.

We encapsulate silicon nanospheres with multilayers of MoS_2 via chemical vapor deposition. Using transmission electron microscopy (TEM) and single-particle scattering spectroscopy, we demonstrate energy coupling in this system with the silicon magnetic dipole mode undergoing Rabi splitting at the MoS_2 A-exciton wavelength in its scattering spectrum. The coupling constant is measured to be significantly higher than that of nanoparticle-on-TMD film geometries, and is an important validation of the Si@MoS_2 system for adoption in photodetection-based nanotechnology. Photoluminescence enhancement is also demonstrated by Si@MoS_2, effectively affirming that the core acts as an antenna to excite the TMD shell emitter.

We then extract the local dielectric functions of Si@MoS_2 with high spatial resolution via VEELS, which offers information on the valence electron excitations, to understand how the electronic structure of this heterostructure evolves from its two constituents. Using a cross-sectioned Si@MoS_2, the evolution of the electronic structure from uncovered silicon to the core-shell interface is evaluated. Notably, the resulting dielectric function of Si@MoS_2 demonstrates features attributed to heterostructuring semiconductors with different band gaps. As dielectric functions embed valence electron excitation, plasmonic excitation, and intra/inter-band transitions, they directly relate to optical parameters such as absorption, reflectance, and transmissivity of the material. The presentation will explain how optical properties of core@shells can be understood and provide a platform to improve their property-performance relationship.

5:00 PM EL16.08.02
Active Modulation of Vivid Color Enabled by Functional Materials Soo-Jung Kim, Chohyeon Park and Sung-Hoon Hong; Electronics and Telecommunications Research Institute, Korea (the Republic of)

Artificial structural color possesses many advantages over pigments or dyes, such as long-term stability, low energy consumption, color diversity, and environmental friendliness. Structural colors based on Fabry-Perot (F-P) cavity do not require the complex nanofabrication and is simply a thin film stacked structure. It is an easy way to generate various colors with thickness of cavity layer in large-scale. Because of these advantages, researchers have carried out color generation using F-P cavity for many applications such as high-resolution display, color printing, anti-counterfeiting technology, and millitary application. However, there are some issues that need to be addressed: such as active modulaion, durability, and portability for practical use.
In this study, we propose a tunable vivid structural coloration based on F-P cavity by using a unique nanocrystal (NP)-based metamaterial and functional materials. Our reconstructed F-P structure consists of top porous Ag NP metamaterial layer, bottotm metallic layer, and a functional material medium layer. The Ag NP layer as an upper metal forms a porous structure with controlled NP spacing through ligand exchange of NP. Application of the porous upper metal is a key factor to detemine the vivid and marked reflective color. The functional material (phase change material, functional polymer, etc.) can control the resonant frequency by changing the index properties or structural system with an external factor (electrical force, environmental conditions).

Acknowledgements
This work was partially supported by an ETRI internal grant (22ZB1130).

5:00 PM EL16.08.03
Solvent Dependent Swelling of a PDMS Mold for Accurate Replication of Metasurfaces Nara Jeon, Dong Kyo Oh and Junsuk Rho; Pohang University of Science and Technology, Korea (the Republic of)

A metasurface is composed of two-dimensionally arrayed subwavelength nanostructures, whose electromagnetic (EM) responses can be designed artificially to realize holography, optical cloaking, structural color printing, etc. Nanoimprint lithography (NIL) has overcome conventional nanofabrication limitations such as high cost and low throughput, which have been principal obstacles preventing the practical application of metasurfaces. A one-step fabrication method, however, is required to open the door to a way for the commercialization of metasurfaces. For this reason, a single-step fabrication of metasurfaces using high-refractive-index nanoparticle embedded resin (PER) has been implemented.
Methyl isobutyl ketone (MIBK) is mainly used in industrial coating solvents because resins used in paints, lacquers, inks, and other forms of surface coatings can be effectively dissolved by MIBK. In consideration of future industrialization, MIBK is chosen as an industry-compatible solvent to mix a monomer, photo-initiator, and nanoparticles for PER. However, it makes polydimethylsiloxane (PDMS), used as a soft mold, swell. Such fabrication imperfections from the swollen mold can cause undesired EM responses, or significant reduction in structures performance and Q factor of bound states in the continuum (BIC)-based metasurfaces, designed numerically to have higher resonance sharpness. Especially, since a dielectric metasurface that supported BIC used in ultrasensitive hyperspectral imaging for bio-detection requires extremely high-quality fabrication, limited fabrication tolerance has a significant impact on performance.
So far, how the swollen mold by a solvent affects the shape of replicated nanostructures is not still being considered. Here, we investigate the effects of different solvents on replicated metasurfaces to increase accuracy. By selecting appropriate solvents, the replication accuracy was increased up to 77%.

5:00 PM EL16.08.04
Direct Measurement of Ballistic and Diffusive Electron Transport in Gold Pravin Karna and Ashutosh Giri; University of Rhode Island, United States

Gold thin films are one of the most widely used thin films in plasmonic devices, where the hot electrons traverse in ballistic motion to transfer their energy to the underlying semiconductor layer used for applications in solar energy harvesting. Therefore, for efficient operation of these devices, the proper understanding of ballistic motion of electrons is of paramount necessity. However, the understanding of diffusive and ballistic electron mean-free paths in metals remains elusive, partly due to limitations of the experimental methods such as pump-probe measurements to accurately resolve the dynamics with high spatiotemporal resolution, limiting the efficient application of these thin films in plasmonic devices. For example, pump-probe measurements from prior studies have inferred the ballistic length of electrons in gold thin films to be around 100 nm, which has been accepted for over 30 years. However, a direct measurement of the ballistic (along with diffusive) mean-free paths of electrons in gold films with nanometric precision has still been lacking so far. To fill this void, in this work, we carry out an extensive experimental and first principles study to describe the characteristic scattering length scales of electron in laser heated gold thin films. Specifically, we use our homebuilt ultrafast super-resolution thermo-reflectance technique to track the evolution and scattering of electrons in gold. We find the ballistic length of these hot electrons to be in excess of 150 nm, around 50% higher than the previously accepted value of 100 nm. We also measure the diffusive length of hot electrons to be ~45 nm at peak electron temperature. Our parameter free density functional perturbation theory calculation predicts an average diffusive length scale of ~35 nm when the electrons and phonons are in thermal equilibrium. However, at elevated temperatures the reduction in electron-phonon coupling factor due to lattice stiffening arising from inter-band transition of electrons leads to a drastically enhanced mean-free paths of electrons in gold. Our results lend insights into the dynamic behavior of electrons in laser heated metals and significantly improves our understanding of warm dense matter in general.

5:00 PM EL16.08.05
Redirecting Light Propagation at the Nanoscale in Molybdenum Trioxide (MoO3) Nanobelts Mingze He[1], Levi Hoogendoorn[2,1], Saurabh Dixit[1], Zhiliang Pan[1], Deyu Li[1] and Joshua D. Caldwell[1,1]; [1]Vanderbilt University, United States; [2]Northwestern University, United States

Due to the long free-space wavelengths associated with radiation in the infrared (IR) to terahertz spectral domains, the realization of flat and subdiffractional optical components promise advances in imaging, communications, sensing, and IR sources. One approach to compress light into deeply subdiffractional length scales is to use polaritons, which are hybrid excitations in materials resulting from the interaction of light and oscillating charges. One type of particular interest is hyperbolic polaritons, which in principle allow infinitely small polaritonic wavelengths. Hyperbolic polaritons are supported in materials that are optically metallic along one crystal axis and optically dielectric along the other. Therefore, the resultant isofrequency curves indicate theoretically infinitely large wavevectors within these materials and so they have acquired an increasing interest in the past decade for applications such as super-resolution imaging and sub-diffractional on-chip waveguiding. Molybdenum trioxide (MoO3) is one of the materials that support these hyperbolic polaritons and, due to the orthorhombic crystal structure, its optical properties are different along all three crystal axes. In one frequency range (821 – 956 cm-1), only the [100] crystal direction behaves as a metal, leading to an in-plane dispersion with a hyperbolic isofrequency curve, which has allowed wavevectors in only certain directions. The fact that propagation is forbidden along the [001] within this spectral range restricts the ability to direct polariton motion, thereby limiting many applications.

In this work, we experimentally and theoretically demonstrated the topological transition of hyperbolic phonon polaritons in MoO3. This topological transition is characterized by an inversion of the polariton propagation direction in a certain subset of this frequency range and a change in behavior from type-II to type-I hyperbolic. To achieve this, we first theoretically analyzed that the topological transition can be realized in geometric confinement along the [100] direction. Due to the geometric confinement in the [100] direction, a Fabry-Perot mode can be formed. As a consequence of the in-plane hyperbolic isofrequency curve, the mode still possesses a wavevector component in the [001] direction, forming a propagating polariton in the [001] direction. This was done by controlling the nanobelt width, whereby a variation in the Fabry-Perot condition can be induced, thus forming a net wavevector along [001] direction. Next, we experimentally imaged the inverted polariton propagation using scattering-type scanning near-field optical microscopy (s-SNOM). Further, we demonstrated the criteria of this topological transition in both the frequency and geometric parameter domains. Our results open possibilities for the manipulation of hyperbolic polaritons and pave the way for promising applications in metamaterials, nanophotonics, and quantum optics based on natural vdW materials.

5:00 PM EL16.08.06
Novel Design Approach of Tri-Channel Image Display with Single-Cell and Single-Size Strategy Junhwa Seong, Joohoon Kim and Junsuk Rho; Pohang University of Science and Technology, Korea (the Republic of)

Multi-functional meta-devices have been intensively studied owing to the great potential for highly integrated and ultra-compact meta-devices. Currently, multi-functional meta-devices have relied on layer staking and interleaving of nanostructures to increase the information encoding capacity. However, these approaches are limited to low efficiency, design complication, and fabrication complexity. Thus, a high-capacity meta-display that can contain a lot of information in a simple structure has been required for practical applications. Here, we propose a single nanostructure-based tri-channel meta-display by merging the geometric phase spin-decoupling and Malus's law intensity control. This device displays two far-field helicity-dependent holographic information and one near-field nano-printing image. To increase the efficiency, we have employed low-loss hydrogenated amorphous silicon (a-Si:H) which supports high transmission efficiency in the whole visible frequencies. Low-loss a-Si:H has also an advantage of CMOS compatible and cost-effective plasma-enhanced chemical vapor deposition process. We believe that our novel approach opens new avenues in multi-funcional meta-devices.

5:00 PM EL16.08.07
Fabrication of Plasmonic Nanohole Array-based Hybrid Plasmonic Structures by a Sacrificial Layer Combined Tip-based Lithography Jeong-Sik S. Jo and Jae-Won Jang; Dongguk University, Korea (the Republic of)

The subwavelength-scale metallic nanostructures fabricated by nano-fabrication methods are extremely important structures in subwavelength optics due to physical phenomena based on plasmonic resonance. In particular, a subwavelength hole can focus and amplify electromagnetic waves; thus metal nanohole arrays can be used in various fields including nanophotonics, highly sensitive sensing, and highly efficient energy harvesting. Here, we demonstrate tip-based lithography utilizing a sacrificial layer that can fabricate subwavelength metallic nanohole arrays in room conditions. The size of the nanoholes is controlled by changing the contact force of the tips onto the sacrificial layer, and nanoholes of a diameter of 40 nm can be obtained. The distance between nanoholes can be precisely controlled by using the piezo-based tip-based lithography system equipped with a general AFM, with which plasmonic antennas with a nanogap of the scale of several tens of nanometers can be fabricated. In addition, the hybrid plasmonic structures are also fabricated by placing metallic nanoparticles inside the nanoholes. These hybrid plasmonic structures show strong field enhancement compared to the existing plasmonic structures and have the potential for surface-enhanced Raman spectroscopy applications. The developed fabrication method will be useful for plasmonic applications and the developed hybrid plasmonic systems will provide various research opportunities related to plasmonic coupling.

5:00 PM EL16.08.08
Deep Active Learning for Metamaterials Yang Deng[1], Simiao Ren[1], Jordan M. Malof[2] and Willie J. Padilla[1]; [1]Duke University, United States; [2]University of Montana, United States

Deep learning has recently shown great potential in accelerating the forward and inverse design of metamaterials. A wide range of model architectures, inverse modeling, and hybrid algorithms was explored recently, aiming to expedite the creation of more exotic metamaterials. Without exception, all the above deep learning techniques rely on their data-driven nature, which makes the neural networks always hungry for more data. Despite deep neural networks' orders of magnitude faster inference time, applying deep neural networks demands an initial cost of data collection, posing a considerable data bottleneck that delays the rapid prototyping of next-generation metamaterials. In this work, we explore active learning techniques to advance the data efficiency of the deep learning design of AEMs compared to random sampling. We carefully compare the performance of all deep active learning algorithms and the random sampling baseline to examine the generality of active learning methods to AEM problems. It is shown that deep active learning algorithms can save as much as 40% of data compared to random sampling. However, the limited generality and additional optimization requirements pose a significant challenge to applying active learning to metamaterial design in practice.

5:00 PM EL16.08.09
Rare Earth Ion Crystal Growth Investigations Ashleigh K. Wilson, Violet Macauley and Natalia Noginova; Norfolk State University, United States

Rare earth ions in organic matrices are of interest for a variety of applications, including optical sources and displays. To generate luminous crystals using rare earth ions and organic ligands such as dipyridyl and phenanthroline, a solution growth approach can be used. Under UV light, the ions in the crystals may be activated and become effectively luminous. We are now investigating the best regime for the crystal development of phenanthroline-based crystals containing various Ln ions utilizing varying chemical concentrations and substrates such as flat glass, gold, nanostructured alumina membrane, and gold nanomesh systems. We also investigated the possibility of controlling crystal formation and development using a nanostructured environment and extra light stimulation.

5:00 PM EL16.08.10
Helical Plasmonic Meta-Arrays Sculpted by Circularly Polarized Light Ji-Young Kim, Connor McGlothin, Minjeong Cha, Zechariah Pfaffenberger, Emine Emre, Kody Whisnant, Sanghyun Lee, Wonjin Choi and Nicholas A. Kotov; University of Michigan, United States

Chiral metasurfaces from nanoscale helicoids aligned perpendicularly to substrates display unique optical, catalytic, biological and mechanical properties but are difficult to produce. Currently, subwavelength chiral geometries on substrates are created primarily by two-photon lithography followed by electroplating of metals and etching by plasma. Other top-down patterning methods include ion/electron beam induced deposition and glancing angle deposition; All of them involve time-consuming process with multi-step treatment and demand high vacuum and temperature condition. Bottom-up self-assembly of nanoparticles (NPs) could be a simpler and faster pathway to chiral metasurfaces but there are several fundamental constraints. Compared to helical molecules, the spontaneous out-of-plane alignment of nanohelices is particularly hard due to prohibitively high energy penalties. Here, we show that the unfavorable thermodynamics can be overcome for light-guided synthesis and assembly of plasmonic NPs, producing stand-up arrays of helicoids sculpted by the circularly polarized light. The handedness of the silver helicoids and their polarization spectrum are controlled solely by the ellipticity and wavelength of the incident photons. Using a programmable motorized stage, millimetre- to centimeter-scale metasurface patterns with on-the-fly control of polarization effects are printed within seconds to minutes on various substrates. Substrate versatility, high optical asymmetry, and efficiency of light-to-matter chirality transfer enable rapid printing of metasurfaces for multiple applications including but not limited to photonic, optoelectronic, and electromechanical devices, as well as enantioselective catalytic and sensing systems.

5:00 PM EL16.08.11
Transfer Learning For Multitasks In Large-scale Metasurface Simulations Rixi Peng, Jordan M. Malof, Simiao Ren and Willie J. Padilla; Duke University, United States

Deep learning has successfully demonstrated the capability of learning the electromagnetic response of various metamaterials with a sufficiently large dataset. A neural network can work as an accurate and fast proxy model for applications such as design optimization and dynamic control. However, each new problem requires a new dataset to train a neural network, including those with slight modifications to the original problem. In this work, we integrate the underlying physics of metamaterials into transfer learning and obtain the neural network that can be reused for variations of the original problem.

This work focuses on the scattering problem of large-area random metasurfaces. It is a well-known challenging problem due to the limitation of computational resources. Solving this scattering problem in a reasonable timeframe is highly desirable in many applications, such as disordered metamaterials and metamaterial focusing lenses. We benchmark the transfer learning scheme on various single-factor changes from the original problem, including material choices, metamaterial element shapes, substrates, and incident fields. We demonstrate that tuning the original problem's neural network using transfer learning can significantly reduce the required data size to reach a certain level of accuracy for the new problem compared to a model trained from scratch.

This study also compares the efficiency of transfer learning among different changes from the original problem and analyzes the task distance between the original problem and the target problem. The task distance provides a performance prediction on which type of changes in the problem have higher gains by using transfer learning.

Our work provides the scheme to use a neural network trained for one metamaterial problem to flexibly train another neural network for a modified problem with reduced data requirement, representing an enhanced application of deep learning in the fast-changing metamaterial area.

5:00 PM EL16.08.12
Fast and Rigorous Optical Simulation of Periodically Corrugated Light-Emitting Diodes Based on a Diffraction Matrix Method Chanhyung Park, Jeongmin Shin, Sanmun Kim, Juho Park and Min Seok Jang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Organic light-emitting diodes (OLEDs) have become one of the major light sources for display applications due to their high luminosity, high color purity, and flexibility. The light emission of an OLED can be divided into two processes, which are the internal quantum efficiency and the light extraction efficiency (LEE). The internal quantum efficiency has approached almost 100%, while LEE is still limited to around 20% due to the total internal reflection. The remaining light is coupled to the bound modes such as substrate-confined modes, waveguide modes in the organic layers, and surface plasmon polaritons (SPP) modes. Adding periodic corrugation can increase LEE by extracting energies from these modes by diffraction. However, analyzing the effect of periodic corrugation quantitatively is quite challenging. To calculate the LEE of a periodically corrugated OLED, conventional electromagnetic simulation methods such as the finite-difference time-domain (FDTD) method or the finite element method (FEM) are mainly used. However, these numerical methods require huge computational power and take hours to compute. Therefore, fast calculation of corrugated OLEDs based on theoretical calculation is needed. Delbeke et al. made some progress in calculating far-field emission patterns of a periodically corrugated OLED theoretically [1]. However, a theoretical method doesn't exist that can calculate the LEE of a periodically corrugated OLED and be verified by comparison with other conventional methods.
In this work, we demonstrate how the light emission in a periodically corrugated OLED structure can be rigorously calculated. Our method, which we call the diffraction matrix method (DMM), tracks the mode conversion via diffraction matrices, which elements are calculated by rigorous coupled-wave analysis method (RCWA) [2]. We first compared DMM with the conventional FDTD method by calculating the optical properties of a periodic corrugated OLED with a single emitter. The far-field emission patterns of the model device calculated using DMM and FDTD agree well with the diffraction arcs and the emission peaks appearing at the same position in the reciprocal space. LEE and Purcell factor calculation results using DMM and FDTD agreed within error smaller than 2%, while DMM runs over 60 times faster. Also, DMM can perform optimization over 10,000 times faster than FDTD by analytical integration and reusing diffraction matrices. By DMM, we could also conduct a power dissipation analysis that helps identify the loss channel by resolving power dissipation channels into the unbound, waveguide, and SPP modes, which is impossible in FDTD. We also implemented the DMM of 2D periodically corrugated OLEDs within errors smaller than 3%.
We expect that DMM will help to find an optimal corrugated OLED structure with a higher LEE value than that of optimized planar OLED. We also expect that DMM can be applied to any photonic device that involves a wide-angle incidence within periodic geometry such as perovskite LED and QD display.

References
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2. J.P.Hugonin, et al, *arXiv*:2101.00901

5:00 PM EL16.08.13
High-Yield Plasma-Dependent Fabrication of Undulated Gold Nanoplates as SERS Substrates Mary Sajini Devadas, Dariush Aligholizadeh and Wilson Turner; Towson University, United States

Anisotropic Au nanostructures have been heavily pursued in recent years due to the energetic and optical phenomena which they generate. Generally, increasing anisotropy yields greater intensities of such events, e.g. Surface-Enhanced Raman Scattering (SERS). SERS is an energetic phenomenon that enables the detection of analytes in Raman spectroscopy at pico- and nano-molar concentrations by adsorbing an analyte to the surface of a metallic nanoparticle, such a method being used in the detection of molecules that are extremely potent in low quantities, such as environmental toxins or early detection of diseases through biomarkers. It thus becomes of great value to gain the most anisotropy with minimal resources used to create practical and powerful aides in molecular spectroscopy. Herein, we propose the fabrication of highly anisotropic Au nanostructures from a simple smooth Au nanoplate through quick plasma-dependent reshaping of the Au {111} surface to create pyramidal undulations. The differences between N2 and Ar will be presented. Due to a large number of theoretical hotspots now present at the surface of the plasmonic nanostructure, the SERS enhancement must greatly increase. We further provide an in-depth SERS analysis in both liquid and solid phases with a model analyte p-NTP to determine the strength of these SERS substrates, as well as various characterizations to further elucidate the properties of these substrates.

5:00 PM EL16.08.14
Light Scattering Optical Color Filters for Enhancing the Absorption in Colorful Semitransparent Solar Cells Minji Kim[1], Jongdeok Park[2], Jun Yeong Ryu[2], Jae-Joon Lee[2] and Jerome Hyun[1]; [1]Ewha Womans University, Korea (the Republic of); [2]Dongguk University, Korea (the Republic of)

Light scattering can be useful when applied to solar cells as it can increase the optical pathlength of light within the active medium via light trapping or multiple scattering events. Early studies demonstrated such concepts by incorporating metallic or dielectric particles inside or on top of various solar cells. The solar cells were opaque, prepared on reflective substrates, while the particles were, in many cases, placed on top to promote scattering in the forward direction. Recently, semitransparent solar cells imbued with colors have been gaining increased attention due to their applicability in colorful building integrated photovoltaics (BIPVs). By replacing the back-electrode of a semitransparent solar cell with a Fabry-Perot (FP) cavity, the transmitted colors can be tuned independent of the inherent color of the active material. In this work, we show that by preparing close-packed metal coated silica particles arrays on a metal film in place of the FP cavity, we can backscatter non-resonant light to high angles, promoting light trapping and enhancing the overall absorption while maintaining the same color rendering properties. This behavior is distinct from conventional bare scatterers, which tend to scatter light in the forward direction and a planar FP cavity which backscatters nonresonant light in the normal direction. Experimental results confirm that semitransparent solar cells with Ag coated silica particles outperform planar FP-cavity integrated solar cells in terms of the power conversion efficiency. These results suggest a simple strategy to enhance backscattering of light to high angles and further show promise in increasing the performance of semitransparent solar cells.

5:00 PM EL16.08.15
Boosting Photoelectrochemical Water Oxidation via Au Nanocluster Pattern Arrays with Amplified Localized Surface Plasmon Resonance Effect Seung Hun Roh, Jaekyum Kim and Jung Kyu Kim; Sungkyunkwan University, Korea (the Republic of)

Photoelectrochemical (PEC) water splitting is a promising method for producing renewable energy, the hydrogen fuel. The n-type metal-oxide based semiconductors have been widely researched for potential PEC photoanode due to their earth-abundant, high stability in aqueous electrolyte, and suitable band gap properties. Especially, $BiVO_4$ has been attracted the attention because of the low band gap (~2.4 eV) property that can effectively harvesting the light. However, the high recombination rates problem of $BiVO_4$, which originated by poor electrical conductance and short minority carrier diffusion length, hinders to reach high PEC performance. And the intrinsic defect causes the trade-off with light harvesting from photoanode thickness. To overcome above-mentioned bottlenecks, various strategies such as doping, morphology control, facet engineering, heterojunction, and plasmonic enhancement methods have been studied. Among them, utilizing localized surface plasmon resonance (LSPR) effect via plasmonic enhancement is regarded as effective strategy in PEC system as it has light-driven property.

LSPR phenomenon is collective charge oscillation from plasmonic metal nanoparticle which cause by incident electromagnetic wave, the light. Those charge oscillation induces the strongly localized electromagnetic field between plasmonic metal nanoparticles. From these unique properties, the device performance can be improved by two mechanisms: direct electron transfer (DET) and plasmon induced resonance energy transfer (PIRET). In DET process, the hot electrons, which are generated by LSPR, are directly injected to conduction band in neighbor semiconductor overcoming the schottky barrier. It can be preferable mechanism for enhancing light harvesting efficiency with improved the device performance from increased current. PIRET is the phenomenon of energy transfer from plasmonic metal to semiconductor which can generated electron-hole pairs without charge injection. With advantages of each mechanism, various research of enhanced device performance has been reported, and those reports are mainly focused on coupling effect between plasmonic nanoparticles, not groups. However, the LSPR phenomenon is sensitively affected by variables such as dielectric constant, shape, and size of plasmonic metal. Hence, it is reasonable that considering the configuration of plasmonic metal nanoparticles to effectively utilize LSPR phenomenon.

In this study, the highly ordered Au nanocluster (AuC) pattern arrays in Mo-doped $BiVO_4$ (BVO) is introduced to investigate the group-group coupling effect. We designed AuC hexagonal pattern structure to readily modify the configuration of Au nanoparticle. Also, the thin SnO_2 passivation layer was deposited between AuC and BVO that can induce PIRET effect rather than DET. To effectively suppress the charge recombination, DET process should be avoided. As a result, the LSPR effect was amplified by AuC configuration which is generated by particle-particle and group-group coupling effect. The photocurrent density of AuC/BVO was improved to 1.87 mA/cm^2 (~1.7 fold) at 1.23V (vs. RHE) with efficient light harvesting. Moreover, we found that the AuC pattern arrays efficiently enhanced charge transport and transfer efficiency and suppressed the overall charge recombination. From our report, we expect that the designing the configuration of plasmonic metal is essential for utilizing dense LSPR effect.

SESSION EL16.09: Photonics Resonance Designs and Imagining, Sensing and Spectroscopy Applications
Session Chairs: Yao-Wei Huang and Ho Wai (Howard) Lee
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3016

8:00 AM *EL16.09.01
Time-Resolved Microscopy of Plasmonic Spin Quasiparticles Chen-Bin Huang; National Tsing Hua University, Taiwan

Skyrmions and merons are stable quasiparticles of interest to fundamental physics, and with potential applications to data storage and quantum computing. Here in this talk, I will demonstrate orbital angular momenta contributed purely through the geometrical chirality leads to the generation of plasmonic spin merons. I will also address various other spin quasiparticles. The experiments are carried out through time-resolved two-photon photoemission electron microscopy.

8:30 AM EL16.09.02
Optical Suppression of Energy Barriers in Single Molecule-Metal Binding Ivana Qianqi Lin[1,2], Shu Hu[2], Tamás Földes[3], Junyang Huang[2], Demelza Wright[2], Jack Griffiths[2], Eoin Elliott[2], Bart de Nijs[2], Edina Rosta[3] and Jeremy J. Baumberg[2]; [1]University of Twente, Netherlands; [2]University of Cambridge, United Kingdom; [3]University College London, United Kingdom

Understanding the interactions between molecules and metal surfaces is of widespread importance in electrochemistry, sensing, medical imaging/targeting, molecular electronics and spintronics. Although many techniques have characterized the molecule-metal transient bonds, **conflicting conclusions arise from their buried location and heterogeneity, while single-molecule probes are scarce**. Confinement of optical fields to picometre length-scales around adatoms (termed *picocavities* [1]) has enabled tip-enhanced and surface enhanced Raman spectroscopies (TERS and SERS) of single-molecules. However how adatoms change with molecule-metal interactions, with light (both key ingredients in photocatalysis), and how they link to picocavity formation in plasmonic nanogaps is not understood.

In this work [2], we demonstrate how the light-molecule-metal interaction influences the formation and stabilisation of adatoms yielding picocavities. Through **statistics from over a million spectra** and modelling by density functional theory (DFT), **we show how the local polarisation of molecule-metal electrons is amplified by illumination, gradually eliminating the energy barrier for adatom extraction and subsequently binding molecule-to-metal**, instead of photothermal heating at the surface. We find rates $\propto \{-U_f(I) / k_B T\}$ where intensity I suppresses the barrier, scaling as $U_f(I) \propto U_f^0 / I$.

Interactions between a polarizable molecule and metallic atom create extremely powerful optical forces (>nN) capable of rearranging the material interface. This work provides not only a vital intuition for utilising light-molecule-metal systems to **control single-atom optical switches and next generation photonic devices**, but also a strong spur to develop new theories capable of combining electromagnetism with quantum mechanics.

References
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8:45 AM EL16.09.03
Deeply Subwavelength Exciton-Polariton Integrated Nanophotonics with van der Waals Materials Haonan Ling[1], Arnab Manna[2], Jialiang Shen[3], Siyuan Dai[3], Arka Majumdar[2] and Artur Davoyan[1]; [1]UCLA, United States; [2]University of Washington, United States; [3]Auburn University, United States

One of the challenges in today's integrated nanophotonics technology is that the size of optical elements has always been limited by the diffraction limit, $\lambda/2n$ [1]. This has set constraints on the individual device footprint, leading to relatively low photonic device integration density. Compared with conventional 3D covalent semiconductors at the backbone of today's integrated photonics industry such as Si and InP, bulk transition metal dichalcogenide materials (TMDCs), an emerging type of layered van der Waals materials, offer ~25% higher refractive index in the telecom frequency band. Due to their unique material properties, the high permittivity resulting from sharp exciton-polariton resonance in the visible range is preserved in the TMDC sub-bandgap (i.e., low-loss) regime [1], thus making them an ideal and promising material platform for deeply subwavelength integrated nanophotonic systems [2].

Here, for the first time to our knowledge, we demonstrate deeply subwavelength (thickness < λ/10) integrated nano-waveguiding devices made of bulk TMDCs and characterize their performances in the near-infrared bands, where loss is small. We first discuss the fabrication process of waveguides with grating couplers at both sides on exfoliated MoS_2 flakes with pre-selected thickness. Then we perform optical transmission measurement with wavelength ranging from 750 nm to 1000 nm. We find that despite the strong optical absorption close to material exciton resonance (~ 680 nm), light can be efficiently transmitted through over 20 μm long structures while operating at 910 nm and above. Moreover, we also perform polarization dependent study to show that only TE fundamental waveguide mode can be sustained in such deeply subwavelength devices.

Next we also study more complex waveguiding structures such as Y-splitters made of bulk MoS_2. By shining the light onto input coupler, the light can be coupled into and propagate along the structure get split into two arms. We can clearly observe two distinct emission spots during the measurement. By reading the transmission spectrum at each emission spot, we find a close to 50:50 power splitting is achieved. These results add the promise of using such material platform for creating deeply subwavelength integrated nanophotonic systems.

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9:00 AM EL16.09.04
Plasmonic Lattice Resonances in Highly Asymmetric Dielectric Environments Brandon K. Durant[1], Igor Vurgaftman[2], Joseph A. Christodoulides[2], Marc Christophersen[2], Nicholas Proscia[1], Paul D. Cunningham[2], Adam E. Colbert[2], Janice E. Boercker[2], Chase Ellis[2] and Stanislav D. Tsoi[2]; [1]NRC Postdoc residing at the US Naval Research Laboratory, United States; [2]U.S. Naval Research Laboratory, United States

Metal-based Surface Plasmon Polariton resonances have garnered attention for their ability to confine light to sub-diffraction dimensions and enhance light-matter interactions at the nm scale across the visible and infrared (IR) spectra regime. However, these enhancements are limited by optical losses that arise from radiative coupling and absorption, which limits the quality factor (Q = λ/Δλ) of resonances. Here, we report on the narrowing of the plasmonic resonances observed experimentally in reflectance measurements of Au nanodisc lattices fabricated on a GaAs substrate when the lattice periodicity matches the wavelength for the Rayleigh anomaly in the substrate. We attribute this narrowing to the diffractive coupling of the resonators, which results in surface lattice resonances (SLRs). While SLRs are typically observed for systems with homogeneous optical environments (closely matched indices of refraction for the substrate and superstrate), our system is highly inhomogeneous ($n_{air} = \sim 1$, $n_{GaAs} = \sim 3.4$) and still supports lattice resonances. The experimental reflectivity spectra are accurately reproduced in numerical simulations. Furthermore, we couple lead chalcogenide quantum dot emitters to the nanodisc lattices and demonstrate a 3-fold increase in their photoluminescence intensity and a significant alteration of the emission line shape, in correlation with the narrow SLR. Our findings highlight the optical properties of Au nanodisc resonator arrays within a heterogeneous environment, opening new possibilities in sensing and enhanced light emission applications.

9:15 AM EL16.09.05
Introducing Coupling between Surface Plasmon Resonance and Nanophotonic Modes Wen-Hui (Sophia) Cheng; National Cheng Kung University, Taiwan

Localized surface plasmon resonances (LSPR) can harvest sunlight and generate non-equivalent hot carriers, paving a new approach for photocatalysis. However, the inefficient light matter interaction limits the efficiency. We propose strategies to realize strong coupling condition between plasmonic and other nanophotonic modes. With proper design of Si nanodisk and Au antenna, Rabi splitting greater than the average of dephasing is demonstrated through coupling between the magnetic dipole and LSPR. We found that a low index spacer is critical in the hybrid structure. In addition, coupling between Au antenna and Si cavity mode can also be achieved. For a device made of an Au-NP/p-NiO/Au film, we theoretically examine the effect of nanoparticle size and surface coverage to the coupling condition between the plasmon and Fabry-Pérot (FP) cavity mode. Greater particle sizes result in higher splitting energies at the same surface coverage, while increased surface coverage results in higher splitting energy at the same particle size. The above results as an outlook show the possibility and design principle to incorporate strong light matter interaction in the field of plasmonic photocatalysis.

9:30 AM BREAK

10:00 AM *EL16.09.06
Meta-optic Accelerators for Image Processing and Object Classification Jason G. Valentine[1], Hanyu Zheng[1], Quan Liu[1], Ivan I. Kravchenko[2] and Yuankai Huo[1]; [1]Vanderbilt University, United States; [2]Oak Ridge National Laboratory, United States

We demonstrate meta-optic based accelerators that can off-load computationally expensive operations into high-speed and low-power optics. The key to these architectures are the new freedoms afforded by metasurfaces such as optical edge isolation, polarization discrimination, and the ability to spatially multiplex, and demultiplex, information channels. I will discuss how these freedoms can be utilized for accelerating optical segmentation networks and objection classifiers, both based on incoherent illumination. This approach could enable compact, high-speed, and low-power image and information processing systems for a wide range of applications in machine-vision and artificial intelligence.

10:30 AM EL16.09.07
Surface Energy-Modified and SERS-Based Plasmonic Sensing of Urine for the Diagnosis of High-Mortality Rate Illnesses Minjoon Kim, Sejoon Huh, Sungho Jo and Yeon Sik Jung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

High mortality-rate illnesses such as lung cancer and prostate cancer with survival rates of less than 20% and 10%, respectively, require rapid diagnosis to significantly decrease the number of deaths. However, conventional medical imaging diagnosis methods such as endoscopic ultrasound and computed tomography have limited practicability for early detection as the test process may not only be inconvenient for the patient but also be incapable of detecting fine changes in metabolism. Then, the analysis of metabolites can be suggested as a facile method for detecting biomarker changes in patients. Metabolites are promising early-stage cancer biomarkers because they are produced in different types or concentrations in normal and cancer cells and are excreted in body fluids including blood and urine. Urine is a suitable medium for metabolite analysis because it is easy to collect, and surface-enhanced Raman spectroscopy (SERS) is an outstanding option for the detection of low-concentration metabolites by rapidly collecting molecular-specific signals with high sensitivity. However, urine analytes do not adsorb well on hydrophobic nanostructured surfaces, creating thick buildups of urine components that are not delivered to Raman “hot spot” regions and cause Raman signal damping issues. Moreover, there are signal variation issues due to overlapping of numerous peak sources as well as urine composition differences by samples within the same patient group.

Here, we propose a surface energy-modified SERS sensing platform for enhanced adherence of urine analytes on the measuring substrate and for rapid Raman spectra collection of multiple samples that are analyzed with the aid of deep learning. Via a thermally-assisted nanotransfer printing (T-nTP) technique, a large-area superhydrophobic Ag nanowire substrate is fabricated, on which superhydrophilic data collection point arrays are marked for easy location of SERS measurement points. An efficient fabrication method is applied as the T-nTP technique allows uniform printing of nanowires over large areas whose surface energy is lowered via hydrophobic self-assembled monolayer functionalization, while multiple circular superhydrophilic areas are simultaneously formed on selected areas via roughness control and SiO_2 evaporation through a shadow mask. When urine is dropped on a data collection point, the large difference in surface energy guides the droplet to be spread and dried within the selected surface energy boundary while the high surface energy of the data collection point allows strong adhesion of analytes for clear and intensified Raman signals. In contrast to previous research on utilizing SERS for urine analysis that often require tedious nanoparticle size and concentration control, compactly located regular nanogaps are formed over large areas via T-nTP for enhanced plasmonic effects and regular signal intensification. Moreover, multiple samples of different patient groups are dried simultaneously on separate hydrophilic points for a high-throughput data collection system with reduced measurement preparation time. Signals of multiple samples are detected rapidly for deep learning-based analysis to detect and classify minor differences between normal and cancer patient groups. Overall, a plasmonic sensing platform is proposed for cancer diagnosis via rapid collection of enhanced Raman signals and classification of complex signals, which can be extended to rapid diagnosis of other diseases by analyzing water-based biological samples.

10:45 AM EL16.09.09

A Multifunctional Plasmonic Sensor for Excellent UV Photodetection and NO_2 Gas Sensing by an Array of Al Nanocaps on GaN Truncated Nanocones YuPing Kuang, Abhishek Dubey and Ta-Jen Yen; National Tsing Hua University, Taiwan

Plasmonic resonance has unique subwavelength properties, strong local field enhancement, and ultrafast decay time of carriers. Based on these advantages mentioned above, plasmons have recently attracted great attention in electromagnetic, optoelectronic, and photovoltaic applications such as photodetection, gas sensing, surface-enhanced Raman scattering, water splitting, solar cells, nonlinear optics, plasmonics lasing, metalens, etc. To support plasmonic resonance, the most commonly used metals are gold (Au) and silver (Ag), mainly because of their low intrinsic losses. However, Au and Ag suffer from low plasmonic frequencies and interband transitions at 500 nm and 300 nm, respectively, so these two noble metals can be used in the infrared (IR) and visible regions, but hardly in the ultraviolet region. There are increasing demands for UV applications such as UV light detection, advanced communications, environmental and biological monitoring, air purification, high-temperature flame detection, missile tracking, and more. Therefore, there is an urgent need to obtain a high-quality plasmonic metal to facilitate electromagnetic and optoelectronic applications under UV conditions.
Among metals with higher plasma frequencies for UV applications, aluminum (Al) offers several advantages such as low cost, low intrinsic losses in the UV region, native oxide protection, and Complementary Metal Oxide Semiconductor (CMOS) compatibility and other advantages. In this work, we design a heterogeneous Al nanocap (Al-NC) array on a wide-bandgap semiconductor of GaN truncated nanocones (GaN-TNCs), and then demonstrate a versatile plasmonic sensor that enables excellent UV photodetection and air quality index (AQI) gas sensing. Therefore, for UV detection, we exhibit an ultra-high responsivity (1.8 × 108 AW^{-1}), which, to our knowledge, is the highest detection rate (1.2 × 1018 cm $Hz^{1/2}W^{-1}$) for GaN-based UV detection device. In addition, this UV photodetector also exhibits ultrafast rise time (78.3 ms) and fall time (303.5 ms) responses, respectively. For gas detection, we measure NO_2, a key AQI gas used as an indicator for the larger group of nitrogen oxides (AQI). Our results showed an excellent response of 28% and a detection limit of 500 ppb.

11:00 AM EL16.09.10

Metal Oxides Metasurfaces with Controlled Refractive Index from 1.2 to 2.7, Elaboration by Direct High Throughput NIL and Applications in Optics, Photonic and Gas Sensing Victor Malgras[1], David Grosso[1], Magali Putero[1], Marco Abbarchi[1], Martin O'Byrne[1], Badre Kerzabi[2] and Zeinab Chehadi[1]; [1]IM2NP, CNRS AMU, France; [2]SOLNIL, France

Metal oxide (MO_X) nanopatterns have been prepared from Soft-Nano-Imprint-Lithography (soft-NIL) combined with sol-gel formulations. A careful adjustment of the chemical parameters and processing conditions are used to obtain faithful replicas with high vertical aspect ratios up to 3 and refractive index up to for instance 2.7@520 nm with TiO_2, on glass, silicon wafers, fused silica. This method is CMOS-compatible, cost-effective and easy to scale-up. [2,13]

As-deposited sol-gel layers are rather difficult to imprint as a result of the fast evaporation-induced stiffening of the precursors that prevents efficient mass transfer within the cavities of the soft mould. Nonetheless, by adjusting the processing conditions to the pure inorganic sol-gel chemistry we demonstrate that the process can be highly simplified while improving the quality of the replicas and avoiding the use of sacrificial, stabilising, organic agents that is always accompanied by a high shrinkage. A compromise can be found for all sol-gel materials to reduce the xerogel viscosity necessary for capillary filling, while limiting the shrinkage upon final thermal curing. Metasurfaces bearing arrays of high aspect-ratio 3D features of different shapes and composed of hard ceramics with controlled functionalities are directly available with such a one-step process. Besides, this method is compatible with high-throughput on 200 mm glass and silicon wafers (limited only by the machine in use) and conventional production constraints. It also benefits from the countless chemical compositions available from sol-gel chemistry and has been demonstrated with many metal oxides.

In this presentation, we will focus on Silica (SiO_2), Titania (TiO_2), Alumina (Al_2O_3), and Europium-doped Zirconia (ZrO_2:Eu^{3+}) as pristine, hybrid, or mesoporous materials. They have been patterned with different designs and bearing different motif dimension (down to 100 nm) and aspect ratio (up to 3), to address different functionalities such as controlled-wetting surfaces, light harvesting coatings, diffraction gratings for light extraction, multispectral filters, enhanced spectrally and spatially controlled emitting surfaces, wave guides, structural color coatings, anti-reflection coatings, photonic VOC sensors, or flow cells for DNA sequencing. [3-15]

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11:15 AM *EL16.09.11
High-Performance and Cost-Effective Liquid Metal Nanophotonic (LIMEN) Sensors Based on Surface-Enhanced Spectroscopy Peter Qiang Liu; State University of New York at Buffalo, United States

Gallium and several gallium-rich alloys are metals in the liquid phase near room temperature and possess unique and appealing material properties for various device applications, including nanophotonic sensors. Nanoscale photonic cavities supporting high field confinement and enhancement can be conveniently formed by utilizing these liquid metals. Employing such liquid-metal-based nanophotonic structures for sensor applications allows the efficient delivery of analytes into the desired hot spot locations to be completed before cost-effectively forming the nanophotonic cavities, hence resolving the fundamental dilemma of trading off analyte delivery efficiency against field confinement/enhancement which limits the performance of conventional nanophotonic sensors based on solid metals. Here, we present our recent developments of high-performance liquid metal nanophotonic (LIMEN) sensors for both surface-enhanced infrared absorption (SEIRA) and surface-enhanced Raman scattering (SERS) sensing applications.

SESSION EL16.10: Advanced Nanostructure Design with Machine Learning I
Session Chairs: Jason Valentine and Yang Zhao
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3016

1:30 PM *EL16.10.01
Physics-Informed Reinforcement Learning for Nanophotonic Device Design Min Seok Jang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The increasing demand on a high-performance metasurface requires a freeform design method that can handle a huge design space. Accordingly, various nanophotonic device design schemes have been investigated including the ones based on machine learning. In this presentation, I discuss design approaches based on deep reinforcement learning, which have achieved great success in many different fields spanning video games, the game of Go, protein folding problems, to matrix multiplication algorithms. Reinforcement learning has not yet been actively explored in the field of nanophotonics compared to other machine learning methods such as generative or discriminative models. I will introduce how to apply deep reinforcement learning to design a metasurface beam deflector with large degrees of freedom, and discuss how to increase the sample efficiency by informing the agent of the reinforcement learning using physical constraints that govern the electromagnetic system.

2:00 PM EL16.10.02
Phonon Polaritons in Hexagonal Boron Nitride Heterostructures Mingyuan Chen[1], Yuhan Zhong[2], Eli Harris[3], Jiahan Li[4], Zhiren Zheng[5], Hongsheng Chen[2], Jhih-sheng Wu[6], Pablo Jarillo-Herrero[5], Qiong Ma[3], James H. Edgar[4], Xiao Lin[2] and Siyuan Dai[1]; [1]Auburn University, United States; [2]Zhejiang University, China; [3]Boston college, United States; [4]Kansas State University, United States; [5]Massachusetts Institute of Technology, United States; [6]National Chiao Tung University, Taiwan

Using scanning probe infrared nano-imaging, we investigated phonon polaritons in hBN heterostructures assembled from monoisotopic crystals. Our combined experimental and theoretical study reveals multiple branches of hyperbolic phonon polaritons in hBN heterostructures. We also show that wave dispersions for hyperbolic phonon polaritons can be delicately altered by engineering the heterostructures. These phonon polaritons can be interpreted by the geometric optics model of the hyperbolic rays in the heterostructures and are promising for nanophotonic and thermal applications. The method of building new forms of van der Waals heterostructures may be extended toward a range of materials and properties.

2:15 PM EL16.10.03
Pushing the Limits of Functionality Multiplexing Capability in Metasurface Design Based on Statistical Machine Learning Yihao Xu[1], Wei Ma[2], Bo Xiong[2], Lin Deng[1], Ruwen Peng[3] and Yongmin Liu[1]; [1]Northeastern University, United States; [2]Zhejiang University, China; [3]Nanjing University, China

Enabled by cleverly designed nanostructures, metasurfaces offer an unprecedented way to manipulate light on a completely planar platform. The versatility and unique optical responses of metasurfaces under different illumination conditions are beneficial to encode independent information. Typically, a top-down, two-step design process for multifunctional metasurfaces proceeds as follows: First, the design goals are decoupled to obtain the phase requirements for each illumination condition. Then, the metasurfaces are built by multiplexing single-responsive meta-atoms or assembling multiple phase-tuning techniques such as the geometric phase and resonant phase. However, with an ever increasing number of design channels, this empirical design intervention becomes infeasible.

In this study, we propose utilizing machine learning techniques to capture the statistical features in the high-dimensional joint distribution of meta-atoms in the unit cell and the corresponding optical responses, thereby supporting a quantitative evaluation of the severity of function crosstalk and an on-demand inverse design. We enhance the design capabilities for various meta-atom design frameworks with the assistance of such framework. To provide an automated end-to-end design loop for multifunctional metasurfaces, the developed machine learning model can be seamlessly integrated with the gradient-based and non-gradient optimization processes. We have successfully constructed metasurface focusing lenses and holograms operating in eight customizable channels in the near-infrared range utilizing a single metasurface, where each channel is a combination of different incident frequencies and polarizations. We have also researched free-form meta-atoms represented by binary images, which support more resonance modes and enhance the independence of each information channel.

Our results suggest that the data-driven optical design technique outperforms conventional physical-guided methods, which will expedite the development of novel optical display, communication, and computing devices and systems.

2:30 PM BREAK

SESSION EL16.11: Advanced Nanostructure Design with Machine Learning
Session Chairs: Yao-Wei Huang and Min Seok Jang
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3016

3:30 PM *EL16.11.01
Artificially Structured Electromagnetic Media Based on Freeform Metamaterials Jonathan Fan; Stanford University, United States

In this talk, I will discuss new concepts in wavefront engineering based on freeform metasurface and metamaterial systems. First, I will discuss how broadband arbitrary birefringence responses can be realized and tuned using sets of freeform metagratings, which utilize microscale motions to enable birefringence control. Second, I will discuss how volumetric freeform metamaterials can utilize strong multi-scattering and non-local interactions to enable arbitrary and multi-functional wavefront responses. Third, I will discuss how the design of artificial freeform electromagnetic media can be accelerated by three orders of magnitude using neural network-based surrogate solvers and optimizers.

4:00 PM EL16.11.02
Facile Quantification of Nanosized Bioparticles in Bright-field Micrograph via Deep Learning Jiwon Kang, Jin-Hwi Park, Young Jin Yoo, Joo Hwan Ko, Hae-Gon Jeon and Young Min Song; Gwangju Institute of Science and Technology, Korea (the Republic of)

The pathogen is considered a critical threat to public health, especially immunocompromised people such as babies, and the elderly. Initiating the apt therapy to the defected patients before turning into the peak viral load is significant to prevent their fatal damage. However, most point-of-care diagnostics are unsuitable for counting the concentration of the virus. Accordingly, various bioimaging techniques are suggested to visualize and/or count biological samples like histopathology. Despite their superb resolution and precise quantitation, the need for sophisticated equipment or professional manpower stunts the broad interest.
Explosive interest in artificial intelligence (AI) induces profuse interdisciplinary studies, especially in biomedical engineering and clinical medicine recently. Due to the property of pure convolution and superior object categorization skills, convolutional neural networks (CNNs) that model human vision has been demonstrated in comprehensive clinical data to predict patient diagnoses. Even though CNNs produce high capabilities for the assigned task, plenty of pre-processing and the requirement of expert interpretation are still mandated.
Tri-layer resonator is adopted as the optical solution to break through weak light-matter interaction in far-field optics. By harnessing thin-film interference, the modulated light produces a strong resonance in the bioparticles of low refractive index and nanoscale size and leads to the perception of targeted analytes. Additionally, the aggregation of biofunctionalized nanoparticles in drop-casted solution due to hydrodynamics of an evaporating droplet (e.g., the Marangoni flow) synergizes with the slow-light effect so that the invisible analytes can be discovered with definite chromatic information even through the usual optical microscope (OM). During the nanofabrication and surface-functionalizing, however, the residues and defects randomly exist on the surface of the designed biosensor. Hence, we introduce the CNN that establishes a correlation between the chromatic information of optical micrographs and the ground-truth of corresponding scanning electron microscope (SEM) images.
Here, we showcase the chromatic immunoassay system consisting of the biosensor that is optically optimized for general zoonotic virus and deep learning that is robustly constructed with 1596 pairs of OM images and matching SEM images. The hard negative samples of the fabrication fluctuation including the impurities and the defects are trained to identify the desired particles automatically, thus averting the false-positive and enabling accurate quantitative analysis. The image-driven biosensing system validates the limit of viral detection of 104 copies/mL which is lower than the rapid antigen test using lateral flow immunoassay (LFIA) and achieves high sensitivity and specificity for the diverse bioparticles modeling Zika virus, Monkeypox virus, and Mumps virus. The presented immunoassay platform may also be amenable to microscopic hazardous fragments such as metal oxide nanoparticles and microplastics.
In this study, we have shown that CNN-based bright-field micrograph analysis allows not only intuitive immunoassay but also quantification of minuscule subjects. Nanosized bioparticles are detected with a straightforward antibody-antigen reaction, which does not require either labeling or amplification. A single drop of the solution enables visceral recognition through the vision. Owing to the purity of the CNN, the various analytes whose diameters are below the diffraction limit can be estimated with the little training set. We also have confirmed that the presented immunoassay quantifies the concentration accurately within the average viral load from SARS-CoV-2-infected patients. We believe that the streamlined quantitative system is applicable to numerous nanoscale dicey particles.

4:15 PM EL16.11.03
Prediction of Light Extraction Efficiency Using a Transfer Learning Model Jeongmin Shin, Sanmun Kim, Wonwoo Lee, Chanhyung Park and Min Seok Jang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Calculation of optical efficiency in an organic light emitting diode works as a bottleneck for the device geometry optimization process. However, almost all commercial simulation tools obtain solutions based on physical rules. Therefore, the calculation speed of the simulation tools is governed by the simulation space. However, prediction based on artificial neural networks is independent of the simulation space size, hence the calculation speed can be boosted while maintaining the complexity of structure which requires a large number of equations under the physical rules. [1] Despite its advantage, replacing the numerical simulation with an artificial neural network is not always efficient due to the computational load required for the generation of training data. Transfer learning is a useful method for reducing the required number of training data. There are few papers that used transfer learning to calculate the optical properties [2, 3]. However, these studies have been conducted on a case where a plane wave, which is a relatively simple case, is incident from the outside. Furthermore, the previous papers do not consider training models with data that contains errors.
This paper focuses on the OLED system and presents a method to design a network even when there is not enough trainable data. In this paper, we will explain network structure design techniques in cases where experimental or theoretical data are insufficient. To apply the transfer learning, we pre-trained a 15-layers deep learning model to calculate the light extraction efficiency spectrum of a 6-parameter OLED structure with 200,000 trainable data sets.
First, we demonstrate a transfer learning method by predicting the light extraction efficiency of a six-layer OLED system (7-parameter model) based on a neural network trained for predicting the light extraction efficiency of a five-layer OLED device (6-parameter model). We reuse some layers from the five-layer OLED prediction network and re-train the network for a six-layer OLED device with only 4,000 data. Generating speed for the whole model is 100 times faster than the non-transfer case. Root mean squared error (RMSE) is used to mark the accuracy of each model. The RMSE of the 6-parameter model is 0.0029 and the RMSE of the 7-parameter model reaches 0.0085 with only 2,000 data. For the 8-parameter model system, the RMSE is 0.0098 when applying the part of the 6-parameter network
Second, this paper also generates the deep learning model that predicts the light extraction efficiency from the measured dataset which contains both functional error and random error. Measured data not only contains random errors but also functional errors. Deep learning models cannot predict random error intrinsically, but functional error can be predicted by the deep learning model. We apply both Gaussian random error and functional error at input data that represent the structural parameter and transfer the deep learning model that is trained with error-free data. With only 8,000 training data, the model can predict the functional error with an RMSE error of 0.005.

This paper suggests a method for generating the deep neural network with a small amount of additional training data.

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4:30 PM *EL16.11.04
Meta-Optics—Multifunctionality and Neural Computing Nanfang Yu; Columbia University, United States

In this invited talk, I would like to share with you two pieces of recent work from my lab on meta-optics. In the first part of the talk, I will show you passive multifunctional metasurface devices based on quasi-bound states in the continuum that can produce distinct wavefront shapes at different wavelengths, and active multifunctional metasurface devices made of conventional dielectric materials that can produce distinct wavefronts under different heating conditions. The second part of the talk is about a new class of optical neural networks based on metasurfaces that can transform complex binary and gray-scale images, such as handwritten digits and human facial photos, into “optical barcodes” to enable their identification.

SESSION EL16.12: Poster Session: Active Control Metasurfaces and Metamaterials
Session Chairs: Yao-Wei Huang and Yang Zhao
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL16.12.01
Diffraction Fields Optimization for Proximity-Field Nanopatterning—Toward High Contrast 3D Chihun Lee[1], Gunho Chang[2], Seokwoo Jeon[2] and Junsuk Rho[1]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The design and manufacturing of a three-dimensional (3D) nanostructure with high resolution and uniform patterns are crucial in nanoengineering. The proximity-field nanopatterning (PnP) is one of the promising candidates for high spatial resolution and large area fabrication. The proper phase mask design is required to modulate the coherent light for high contrast 3D design. currently, optimal designs are limited to intuitive methods focusing on reducing the 0th order diffraction efficiency by changing the height of mask. In this research, with the particle swarm optimization, we concurrently optimize the phase mask with the new figure of merit for controlling the electric field intensity. We inversely designed the specific 3D electric field intensity distribution and got the required phase mask design. The optimal phase mask can fabricate uniform 3D hexagonal nanoarray structures compared to 0th suppress design which cannot modify the field distribution owing to the direct electric field intensity control. Our concurrent optimization method using global optimization can improve both the degree of freedom and nanopattern quality. Furthermore, this concurrent optimization method demonstrated versatility by varying the pattern periods and materials. We expect that the inverse design method can tune the nanostructure to improve its properties, which can benefit each application field.

5:00 PM EL16.12.02
Facile Fabrication of Titanium Nitride Nanoring Broadband Absorbers in the Visible to Near-Infrared over a Large-Area via Shadow Sphere Lithography Myeongcheol Go[1], Dasol Lee[2], Junsuk Rho[1] and Jinkon Kim[1]; [1]POSTECH, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of)

Plasmonic broadband absorbers have potential applications such as thermophotovoltaics, solar energy harvesting, and thermal emitters. However, poor thermal durability and fabrication in a limited area remain as a challenges. Refractory materials such as titanium nitride (TiN), chromium, and tungsten have been suggested for plasmonic absorbers because of their thermal stability, chemical resistance, and relatively low price. Colloidal lithography (CL) has been widely applied to prepare periodic two-dimensional nano-sized patterns such as nanoholes, nanodisks, and nanocones on various substrates in a large area. Further complicated hierarchical nanostructures such as nanorings and nanotowers were fabricated by using multiple patterning CL, which uses nanospheres twice as a mask for etching and mask for the deposition. In addition, Because CL uses spherical beads as a mask, it can give a shadowing effect to the pattern, unlike photolithography and electron-beam (E-beam) lithography. Thus, shadow sphere lithography (SSL), which combines glancing angle deposition (GLAD) that controls incident angle, azimuthal angle, and substrate rotation during the deposition with CL, more diverse and complex nanostructures such as nanocrescent and nanorings are easily fabricated. Herein, we fabricated TiN nanorings using SSL in a much simpler way than the conventional multiple patterning CL over a large area (inch^2) and demonstrated characteristics as a broadband absorber in the visible and near-infrared region. The nanoring absorber showed a high absorption of over 95% in a broad wavelength range (400-900 nm). The nanoring absorber verified the high potential as a broadband absorber by comparison with other absorbers having nanoholes and nanodisks prepared by CL. The nanoring absorber also showed over 2.3 times higher temperature increases than flat film without nanoring structures under the irradiation of light. This TiN nanoring absorber can be used for various photothermal applications such as thermoelectric and steam generation using solar energy.

5:00 PM EL16.12.03
Raman Identification of Single Bacterial Cells Patterned Using Capillary Assembly on Reflective Topographical Templates Joong Bum Lee[1], Minjoon Kim[1], Stefan A. Maier[2,3,4], Emiliano Cortés[4], Yeon Sik Jung[1] and Yoon Sung Nam[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Monash University, Australia; [3]Imperial College London, United Kingdom; [4]Ludwig-Maximilians-Universität München, Germany

The development of early diagnostic tools based on rapid and reliable detection of pathogenic bacteria is an actively ongoing process. Among several existing techniques, Raman spectroscopy has received growing interest due to its fast and direct output of molecular fingerprint information. However, an open challenge remains in establishing a platform with high signal reproducibility when detecting single cells. Here, we utilize a highly reflective Ag/SiO_2 film that enhances the intrinsically weak Raman signals by reflecting the laser for re-excitation of the bacteria and the downward scattered photons back into the detector. The given configuration is simple and effectively provides reproducible signals for different bacteria namely *Escherichia coli*, *Staphylococcus aureus*, *Salmonella gallinarum*, and *Corynebacterium glutamicum*. Provided that Raman intensities can vary depending on the position of the excitation laser on the cell, we employ capillary-assisted particle assembly (CAPA) to pattern single bacterial cells into a topographical template to allow the their most Raman active regions to be regularly aligned according to the trap site geometry. Moreover, the capability of CAPA to selectively trap single bacteria is utilized to directly separate cells from a suspension of artificial urine, which helps eradicate any additional steps previously required to isolate bacteria from biological samples. The simple and reliable detection method provided in this work has positive implications for clinically relevant settings.

5:00 PM EL16.12.04
Approaching to a Nanolaser via Hyperbolic Metasurface Supporting Whispering Gallery Modes TsungYu Huang and Jia Hsin Bai; Ming Chi University of Technology, Taiwan

We employed coordination transformation and designed a hyperbolic metasurface composed of metallic stripes and air trenches that revealed hyperbolic dispersion curves in the cylindrical coordination. Due to the mismatch of k_q between hyperbolic metasurface and surface plasma polaritons, such metasurfaces could function as a good resonance cavity for surface waves. To validate this idea, we employed finite element method to simulate the designed metasurface composed of a quantum well on top of a GaAs substrate, functioning as an active material, a 100-nm-thick MgF_2 spacer (permittivity of 1.8) and a 100-nm-thick silver (permittivity of -42.495+i×Í0.52152). The calculated mode showed the nature of a whispering gallery mode of $TM_{9,2}$ with a quality factor of 66.33, a modal volume of 4×10^{-22}, the normalized mode volume of 5×10^{-3} $(\lambda/ 2n)^3$, and the Purcell factor of 4726. Then, to test the lasing ability of the calculated whispering gallery mode, we used finite difference time domain simulation to demonstrate indeed such a cavity could be lasing at a frequency of 326 THz when optically pumped. Finally, such metasurface could be realized by focus ion beam and we believe that this proposed hyperbolic metasurface could facilitate the development of integrated photonics.

5:00 PM EL16.12.05
Stealthy Hyperuniform Disordered Light Trapping Designs for Solar Applications Alexander Lambertz[1], Nasim Tavakoli[2], Richard Spalding[3], Stefan Tabernig[2], Marian Florescu[3], Jorik Van de Groep[4] and Esther Alarcon-Llado[2]; [1]NWO-i AMOLF / UvA Amsterdam, Netherlands; [2]AMOLF, Netherlands; [3]University of Surrey, United Kingdom; [4]University of Amsterdam, Netherlands

Ultra-thin crystalline silicon solar cells could, in contrast to their thick counterparts, simultaneously reduce levelized cost of electricity by a large factor and be deployed on curved or non-static surfaces, windows, as well as facilitate building integration. Silicon at micron-scale thickness, however, suffers from poor light absorption and conventional light trapping approaches such as random KOH texturing fails due to the feature sizes produced.
We present hyperuniform disordered (HUD) light-trapping structures applied to ultra-thin solar cells via substrate-conformal imprint lithography. This approach enables rapid patterning of large areas (m2) at the nanoscale and can be performed on virtually any substrate and for any type of functional layer, such as the absorber, back-reflector, anti-reflection coating or carrier transporting layers. Correlated-disorder structures were shown to outperform periodic as well as random light trapping approaches [1] and the hyperuniform platform in addition offers tailored scattering to engineer light coupling to guided modes of ultra-thin absorbing layers [2]. To this end, we developed a coupled-mode theory (CMT) approach for estimating absorption with HUD patterns of arbitrary power spectral density distributions, which affords optimizations at low computational effort. CMT predictions are validated by determining the in-coupling rates per guided mods for different HUD designs, which we achieve through FDTD simulations. Furthermore, we show experimentally measured absorption in ultra-thin, free-standing, hyperuniform-patterned silicon slabs of thicknesses ranging from 1-30µm and compare with simulations. Finally, we show the performance of ultra-thin Si solar cells before and after the application of HUD light trapping structures.
In conclusion, our work exploits stealthy hyperuniformity for exceptional light trapping and aims to further expand the success of earth-abundant silicon to ultra-thin, flexible and semi-transparent PV devices, which can be produced with kerfless bottom-up technologies at significantly reduced capex and accompanying CO2 emissions while maintaining high power conversion efficiencies – A type of device that could literally pave all roads, roofs, walls, and windows by 2050!

Publication
N. Tavakoli et al., “Over 65% Sunlight Absorption in a 1 µm Si Slab with Hyperuniform Texture”*, ACS Photonics 2022, 9, 4, 1206–1217*, DOI: 10.1021/acsphotonics.1c01668

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5:00 PM EL16.12.06
3D Micro Architectures Using Intrinsic Stress in SU-8 Photoresist Zihao Lin, Shehua Thor and Jeong-Hyun Cho; University of Minnesota, Twin Cities, United States

It is commonly acknowledged that for SU-8 photoresist, a thermal stress is generated during a post bake induced cross-linking process. For decades, numerous of literature considered it as a side effect and tried to diminish or even overcome this problem. Here, conversely, we use this heat induced intrinsic stress to make 3D micro architectures. SU-8 photoresist is patterned on a pre-deposited sacrificial layer on Si wafers. Then most of the sacrificial layer is etched away, with only a tiny part holding down the structure. The structure is subsequently immersed in water with heat energy. Then, the thermal-induced stress causes the SU-8 to curve from 2D patterns to 3D architectures, such as tubes, rings, books, springs, and out of plane structures with different patterns on them. By intentionally controlling the exposure energy at different positions on the SU-8 surface, more complicated 3D structures can be made. Taking advantage of photolithography techniques, thousands of 3D microstructures can be integrated on a wafer with a self-assembly process that takes less than 30 seconds. Moreover, this assembly process allows the integration of 2D materials into the 3D structures, which enables the realization of 2D material-based 3D microstructures. This fabrication technique may promote further development of complex micro robotics, 3D sensors, and 3D passive elements.

5:00 PM EL16.12.07
Design of Ring-Patch Pattern Based Microwave Frequency Selective and Infrared Camouflage Surface Juyeong Nam, Injoong Chang, Joon-Soo Lim and Hyung Hee Cho; Yonsei University, Korea (the Republic of)

The aircraft requiring microwave communication has a frequency-selective surface (FSS) that selectively transmits the electromagnetic waves of a specific frequency. However, an infrared (IR) signature is generated on the fuselage surface for reasons such as aerodynamic heating, and this infrared signature is directly related to the survivability of the aircraft. In addition, if the location where microwave transmission is required and the infrared signature reduction is required coincide, such as the radome (nose) and leading edges of an aircraft, the previously developed FSS pattern of infrared camouflage surface including metallic mirror can not be used. Therefore, we think that the coatings capable of selectively transmitting microwaves and controlling the infrared signature is needed. In general, a thin metal film cannot transmit microwaves because it acts as an electromagnetic mirror. For this reason, many researchers designed various FSS patterns so that only desired frequency can pass through, but the FSS surface they designed did not consider those infrared signature characteristics. Similarly, many researchers studying infrared emissivity control did not consider the selective transmission performance of microwave bands. For this reason, we first fabricated the aluminum (Al) thin films by thickness using sputter equipment (LSP-06, pressure 1mTorr, sputtering rate 3.4 nm/sec) to control the infrared emissivity. The thickness of the thin film we made was 5-500 nm, and we measured the infrared spectral emissivity in long-wavelength infrared (LWIR) band using FT-IR (Fourier Transform Infrared spectroscopy) and the infrared signature images using IR camera (FLIR a655sc). In addition, we designed an FSS pattern that includes the metal thin film and allows selective transmission in the X-band (8-12 GHz), which is mainly used for aerial vehicles communication. To this end, we designed the ring-patch patten based microwave FSS to have transmittance of 90% or more at a frequency of 10 GHz using numerical analysis (COMSOL Multiphysics, RF module). The ring-patch pattern FSS derived through numerical simulation was fabricated and the FSS performance in the X-band was experimentally verified using a lens horn antenna (X-band) and a vector network analyzer (Anritsu) device.

5:00 PM EL16.12.08
Effect of Fractal Nanostructure on Multispectral Optical Properties in Visible–IR Waveband Injoong Chang[1], Juyeong Nam[1], Joon-Soo Lim[1], Namkyu Lee[2] and Hyung Hee Cho[1]; [1]Yonsei University, Korea (the Republic of); [2]Forschungszentrum Jülich GmbH, Germany

Fractal is a type of mathematical concept that the shape has a detailed or complex structure regardless of the view scale. While this concept satisfies the exact definition when the shape shows an infinitely detailed structure, in reality, there are finite-fractal structures in which a finite level of morphological repetition occurs, and they also have inherent fractality. Recently, the random fractal patterns of nanoscale structures have been reported, and the fractality has a relationship with the optical properties. These fractal-like structures make the strong and broad resonance effect in the visible spectra range owing to the extraordinary light trapping effect. However, these structures are rarely studied in the multispectral range. First, the fractal nanostructures (FNS) are formed using the wet-etching method so that the structural characteristics can control the only variable: etching time. Also, the studies on submicron-scale structures fabricated by the wet-etching method prominently show the antireflective characteristics with a similar scale waveband. Herein, a relationship between the structural and optical properties of silicon-based fractal nanostructures (Si-FNSs) is demonstrated. The six types of Si-FNSs are fabricated by Metal-assisted Chemical Etching (MaCE) method by varying the etching time from 10 to 240 min. The fractal properties (i.e., Fractal dimension and Lacunarity), calculated by capturing the scanning electron microscope (SEM) image with different magnification levels (x10k, x50k), vary by aggregation phenomenon along the etching process. Depending on the structure variation, Optical properties in visible and infrared (8-12 μm), measured by UV-vis-NIR spectrophotometer (Cary 5000, Agilent) and Fourier Transform Infrared spectroscopy (FT-IR; Vertex 70, Bruker), are dramatically change, especially the emissivity in the infrared range. The measured data are compared with the numerical simulation (COMSOL Multiphysics software) result made by an effective medium model of nanostructures. Therefore, we confirm that the fractal nanostructure fabricated by only varying the etching time can also control the multispectral properties, and it was possible to design and manipulate the visible reflective color and infrared emissive color simultaneously by controlling the etching time.

5:00 PM EL16.12.09
Hyperbolic Phonon Polaritons in Suspended α-phase Molybdenum Trioxide Jialiang Shen[1], Zhiren Zheng[2], Thao Dinh[2], Chuanyu Wang[1], Mingyuan Chen[1], Pengyu Chen[1], Qiong Ma[3], Pablo Jarillo-Herrero[2], Lixing Kang[4] and Siyuan Dai[1]; [1]Auburn University, United States; [2]Massachusetts Institute of Technology, United States; [3]Boston college, United States; [4]Chinese Academy of Sciences, China

Sample suspension is a important method to improve the mechanical, thermal, electronic, and optical properties of 2D materials. Polariton - confined half-light-half-matter wave - can be elongated its wavelength in the Type II of Reststrahlen band by the sample suspension. Previous work reported a wavelength elongation of about 10% for hyperbolic phonon polaritons (HPPs) in hexagonal boron nitride. In this work, we imaged the alteration of HPPs in a suspended α-phase molybdenum trioxide (α-MoO_3) by scattering-type Scanning Near-field Optical Microscopy (s-SNOM). This infrared nano-imaging technique combining with electromagnetic theory reveal a wavelength elongation over 60% and a propagation length increase more than 140%, because of the simultaneous wavelength elongation and dissipation elimination in the suspended specimen. We have also examined HPPs in Type I of the α-MoO_3 Reststrahlen band. The HPP wavelength is shortened and the dissipation is simultaneously reduced due to the sample suspension. The HPPs with improved quality factor in the suspended specimen may be used in the fields of nano-polaritonic circuits, biochemical sensing, emission engineering, and energy transfer.

5:00 PM EL16.12.11
Birefringence Of Chiral Hedgehog Particles Prashant Kumar[1], Emanuele marino[2], Alexander Simon[1], Daniel Katz[1], Christopher B. Murray[2] and Nicholas A. Kotov[1]; [1]University of Michigan, United States; [2]University of Pennsylvania, United States

Spiky hedgehogs can be self-assembled from twisted ribbons formed by gold-copper-cysteine complexes.[1] Furthermore, chirality of these twisted ribbons can be controlled by the cysteine amino acid and their arrangement into supraparticles is dictated by the ratio of L- vs D-form during the initial stages of self-assembly. Here we report that the seemingly spherically symmetric arrangement of twisted ribbons displays a maltese cross pattern typical of spherulites and liquid crystals under cross-polarizers.[2] This optical effect is observed at the single particle level[3] with tunable diameters of 1-10 um. We investigate the optical effects in chiral hedgehogs using single particle methodology and find that the emergence of Maltese cross pattern is dependent on the sphericity of the supraparticle and the spacing between individual spikes. We understand the interaction of light with hierarchically self-assembled structures through finite-element based electromagnetic simulations and reconstruct the distribution of electromagnetic fields around the hedgehogs in three dimensions. These hedgehogs are omnidispersible in a variety of solvents and offset the limitations of commonly observed organic molecule based spherulitic arrangement for biomolecular sensing under harsh environments.[4]

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5:00 PM EL16.12.12
Nanostructured Photonic Hydrogels for Continuous Glucose Monitoring Israr Ahmed, Haider Butt and Amal AlGhaferi; Khalifa University, United Arab Emirates

Diabetes has become one of the top 10 causes worldwide, with ~6.7 million deaths recorded in 2021. The development of low-cost, simple, and reusable sensors can provide a potential platform for reducing diabetic complications, which can be fatal. Phenylboronic acid (PBA) based hydrogel sensors with imprinted Aztec nanostructures were demonstrated for rapid, real-time, and continuous glucose monitoring. A simple and rapid fabrication was carried out to imprint nanostructures. Aztecs are comprised of hexagonally packed ring shape pyramids with nano steps. Two sensor geometries were demonstrated: stand-alone (SA) and optical fiber (OF). The optical response of sensors was observed for the glucose concentration range of 0 – 50 mM in both transmission and reflection modes. Upon exposure to the glucose concentrations, the hydrogel matrix undergoes swelling. The swelling occurs due to cis-diol (present in glucose) binding with phenylboronic acid. A sensitivity of 3 and 1.5 μW/mM was documented for SA and OF sensors along with a fast response time of 20 s. The sensor response was also measured in the physiological glucose range for healthy and diabetic people. A smartphone readout was employed for practical use. The optical response of the sensor in different glucose concentrations was measured using a smartphone photodiode. The developed sensors may find their application for real-time, remote, and continuous glucose monitoring systems.

SESSION EL16.13: Active Control Metasurfaces and Metamaterials
Session Chairs: Yao-Wei Huang and Min Seok Jang
Friday Morning, April 14, 2023
Moscone West, Level 3, Room 3016

8:30 AM *EL16.13.01
Bottom-up Fabricated Tunable Metamaterials Exhibiting Broadband Enhanced Chirality Ufuk Kilic[1], Matthew Hilfiker[1], Shawn Wimer[1], Alexander Ruder[1], Eva Schubert[1], Mathias Schubert[1] and Christos Argyropoulos[1,2]; [1]University of Nebraska-Lincoln, United States; [2]The Pennsylvania State University, United States

Circular dichroism and optical activity are fundamental chiral processes to understand handedness in molecules and control the spin angular momentum of photons. However, chiral light-matter interactions have an extremely weak nature, are difficult to be controlled and enhanced, and cannot be made tunable or broadband. In addition, planar ultrathin nanophotonic structures to achieve extremely strong, broadband, and tunable chiral light-matter interactions at visible and ultraviolet (UV) frequencies are still difficult to be fabricated. In our presentation, we will demonstrate that we tackled these important problems by experimentally realizing and theoretically verifying spectrally tunable, extremely large, and broadband circular dichroism by designing new nanohelical metamaterial configurations operating at the technologically important visible to UV spectrum (U. Kilic et. al., Advanced Functional Materials 31(20), 2010329, 2021). Moreover, all-dielectric silicon-based L-shaped metamaterials will be presented that achieve tunable and strong broadband chirality with simplistic variations in their geometry. The reported novel designs of ultrathin bottom-up fabricated all-dielectric and dielectric-metallic (hybrid) plasmonic metamaterials permit wide tunability with one of the largest and broadest ever measured chiroptical response achieved by a large-scale nanophotonic structure. The demonstrated ultrathin optical metamaterials are expected to provide a substantial boost to the broad fields of classical and quantum optics leading to significantly enhanced chiral light-matter interactions at the nanoscale with applications in biosensing, topological photonics, quantum communications, and photonic circuits.

The presented new large-scale metamaterials are fabricated by using an emerging bottom-up nanofabrication approach, named glancing-angle deposition (GLAD), that is free of masks or templates and permits fast, simple, cost-effective, and scalable mass-production of nanoscale 3D structures. In addition, comprehensive and accurate experimental optical characterization and theoretical simulations are performed by using the generalized Mueller matrix spectroscopic ellipsometry in transmission and reflection mode and finite element modeling, respectively. The currently presented work sets new benchmarks in the assembly of ultrathin broadband chiral metamaterials which are poised to efficiently control and enhance the chiral light-matter interactions at the nanoscale. It provides a comprehensive road map for designing chiral metamaterials with unprecedentedly high and broadband chiroptical properties that can be used in a plethora of diverse emerging classical and quantum optical applications, such as in the design of ultrathin polarization filters, chiral sensors, circular polarized single- or multi-photon radiation sources, and directional spin-dependent nanophotonic waveguides.

9:00 AM EL16.13.02
Broadly Tunable Unidirectional Hyperbolic Metasurfaces of Ultrathin Periodically Aligned Carbon Nanotubes Igor Bondarev, Chandra Adhikari and Michael Pugh; North Carolina Central University, United States

Self-assembled quasiperiodic finite-thickness single-wall carbon nanotube (SWCN) films have been recently shown experimentally to exhibit extraordinary optoplasmonic properties [1-3], which is why they are getting more and more attention of experimental communities. Here, we study theoretically the intrinsic collective quasiparticle excitations responsible for the in-plane electro-magnetic (EM) response of ultrathin plane-parallel periodic SWCN arrays and weakly inhomogeneous SWCN films [4,5]. Using the low-energy plasmon response calculation technique along with the many-particle Green's function formalism in the Matsubara formulation, we derive the in-plane dynamical EM response tensor of the system in the broad spectral domain of IR to visible. We show that the EM response can be controlled by the volume fraction of constituent SWCNs, the active component of the film, and that this can be done not only by varying the parameters of the SWCN content (CN diameter and/or intertube distance) but also by merely varying the thickness of the CN embedding dielectric layer. For homogeneous single-type periodic SWCN arrays and weakly inhomogeneous multi-type quasi-periodic SWCN films, the real part of the EM response function in the CN alignment direction is negative for a sufficiently wide domain in the neighborhood of a quantum interband
transition of the constituent SWCN, to form a relatively broad negative refraction (NR) band. The system behaves as a unidirectional hyperbolic metamaterial at higher frequencies than those (typically in the IR) the classical intraband plasma oscillations have to offer. By decreasing the CN diameter it is quite possible to push this unidirectional NR band in the visible, and using weakly inhomogeneous multi-type SWCN films can make it even broader than the NR band of the single-type SWCN array. We also show that for a properly fabricated two-component SWCN film, by varying the relative weights of the two constituent CN array components, it is possible to tune the optical absorption profile to make the film transmit or absorb light in the neighborhood of an exciton absorption resonance on-demand [5].

Acknowledgements: U.S. National Science Foundation Award No. DMR-1830874 (I.V.B.)

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9:15 AM EL16.13.03
Single-Gate Electrically Tunable Multi-Level Beam Switching Device with High Directivities Juho Park and Min Seok Jang; KAIST, Korea (the Republic of)

Beam switching, or beam steering devices with high directivity and electrical tunability are crucial component for realizing successful commercialization of LIDAR. Particularly, single-gate tunability is highly preferred due to robustness, stability issues involved in on-chip integration of LIDAR. Also, high directivity is fundamental figure of merit for realization of power efficient and highly-accurate LIDAR device. In this paper, we propose free-form optimized single-gate electrically tunable beam switching metasurface consisting of silicon metagrating, unpatterned graphene, silicon substrate and Au backreflector. The silicon metagrating layer is optimized using shape derivative, obtained by adjoint method. The optimized metasurface is capable of tuning incident mid-infrared plane wavefront into 80° (+1 diffraction order) and -80° (-1 diffraction order), according to different graphene Fermi levels. The both diffracted waves show over 99% directivities and near 50% diffraction efficiencies. By analyzing the relationship between metagrating height, substrate thickness and diffraction efficiency, we report that the sum of metagrating height and substrate thickness should be long enough to exceed light path length required to form Fabry-Perot resonance, and that too long metagrating height induces lower diffraction efficiency when substrate thickness is held constant. Next, we report three-level and four-level beam switching metasurfaces which show high directivity but moderate diffraction efficiencies. Finally, we analyze the beam switching performance on different graphene carrier mobilities.

9:30 AM EL16.13.04
Enhancing Forbidden Transition in Molecules by Toroidal Dipole Metasurface for Novel Photochemical Reactions Hiroaki Hasebe[1], Hiroshi Sugimoto[1,2], Taniyuki Furuyama[3] and Minoru Fujii[1]; [1]Kobe University, Japan; [2]JST PRESTO, Japan; [3]Kanazawa University, Japan

A molecular triplet excited state (T_1) with a long lifetime is beneficial for a mid-state of upconversion, photosensitizer, and various photochemical reactions. Because the excitation from the ground singlet state (S_0) to T_1 is spin forbidden transition, T_1 is usually excited via an intersystem crossing from a singlet excited state, which results in an energy loss of a few hundred meV. In this presentation, we propose an approach to excite a T_1 directly from S_0 by exploiting an optical resonance of a dielectric metasurface. For this purpose, we focus on the magnetic dipole transition in molecules that allows a spin-flip transition. By exploiting the magnetic dipole transition, direct excitation of T_1 from S_0 becomes possible. However, in typical molecular systems, the magnetic dipole transition rate that depends on the square of the magnetic field intensity is much smaller than that of the electric dipole one. In this work, by developing the metasurface platform that enhances local magnetic field intensity at a molecular position, we aim direct excitation of T_1 from S_0.
To enhance the local optical magnetic field, high-refractive dielectric (e.g. silicon (Si), gallium phosphide (GaP)) nanoantennas are promising because they exhibit magnetic Mie resonances in optical frequency. However, the enhanced magnetic field by the Mie resonance is localized inside the nanoantenna, which makes it difficult to harness the field for molecular excitations. In the previous work, we have realized the accessible and strong electric and magnetic field in the hexagonal array of thin Si nanodisks (diameter/height ratio ~10) exhibiting the coupled toroidal dipole (TD) resonance [1-3]. In this work, we demonstrate the enhanced photochemical reaction by exploiting the magnetic field enhancement in Si nanodisks. We first show the enhancement of excitation rate of the magnetic dipole transition in ruthenium (Ru(II)) complex molecules placed on the Si nanodisk array by photoluminescence excitation measurements. The magnetic dipole transition of Ru(II) complex molecules is approximately 40 times enhanced at the TD resonance wavelength (825 nm) of the Si nanodisk array.To demonstrate the application to photochemical reactions, we study the photosensitizing activity of Ru(II) complexes on the Si nanodisk arrays by monitoring the generation of singlet oxygen molecules. From the excitation wavelength dependence of the amounts of singlet oxygen, we successfully demonstrate the enhanced photosensitizing activity of Ru(II) complexes due to the large magnetic field by the TD resonance. The results demonstrate the singlet oxygen generation by efficient excitation of the Ru(II) complexes with much lower energy photons (~825 nm) than that of main absorption band of ~630 nm. In the presentation, we will further discuss the mechanism quantitatively by comparing the experimental results with simulation results.
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9:45 AM BREAK

10:15 AM EL16.13.05
Strong Coupling of Excitons in Monolayer WS_2 and Surface Plasmon Polaritons of a Silver Film Sylke Blumstengel[1,2], Nicolas Zorn Morales[1,2], Daniel Steffen Rühl[1,2], Sergey Sadofev[3] and Emil J. List-Kratochvil[1,2]; [1]Humboldt-Universität zu Berlin, Germany; [2]IRIS Adlershof, Germany; [3]Leibniz-Institut für Kristallzüchtung, Germany

Monolayer (ML) transition metal dichalcogenides (TMDC) are currently of strong interest in nanophotonics due to their narrow-band intense excitonic transition which persist even up to room temperature. When brought into resonance with electromagnetic fields of a plasmonic nanostructure unique opportunities for studying and engineering strong light-matter coupling arise. This has motivated quite intense research efforts in the past years and indeed indications of strong coupling of TMDC excitons of ML flakes with localized surface plasmons hosted in a variety of metallic nanostructures have been found in scattering spectra. Here, we propose an alternative geometry as well as experimental method to study the exciton-plasmon coupling. We consider a most simple planar geometry comprised of a thin Ag film, an Al_2O_3 spacer layer and a ML of WS_2 and we employ total internal reflection ellipsometry which combines spectroscopic ellipsometry with the Kretschmann-Raether-type surface plasmon resonance configuration. The combined amplitude and phase response of the reflected light proves that despite the ML thinness of WS_2, the strong coupling regime between the A-excitonic resonance and the surface plasmon polariton propagating in the Ag film is achieved. We show that the presentation of the phasor r_p/r_s in the complex plane (r_p and r_s are the reflection coefficients in p- and s-polarization, respectively) provides a convenient means to verify the strong coupling regime. Furthermore, ellipsometry measurements at varying angle of incidence yield the dispersion plot. The observed anticrossing of the two polariton branches confirms that the strong coupling regime is achieved. Transfer matrix method simulations were performed to support the experimental findings. The present planar geometry can be regarded as a building block for the realization of all-optical or electro-optical plasmonic modulators. The tunability of the TMDC optical properties via external stimuli like electric fields and light, as well as the dielectric/chemical environment provides means of active control over the light matter interaction which paves the way for the construction of novel plasmonic devices.

10:30 AM EL16.13.06
Far-Field Analysis of Plasmon Temperature-Dependence in Graphene Nanoresonators Junhyung Kim, Geonwoo Lee, Sergey Menabde and Min Seok Jang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Doped graphene behaves like a two-dimensional metallic sheet by exhibiting a robust plasmonic response from THz to mid-infrared frequencies. The extremely confined graphene plasmons (GP) that are supported by these graphene sheets have effective wavelengths that are up to two orders of magnitude shorter than the free-space wavelength. Despite the rising popularity of graphene plasmonics, the majority of GP research has been done at room temperature, and the temperature dependence of GP characteristics has not yet received much attention.
We report on the far-field analysis of the temperature-dependent mid-IR plasmonic response of graphene nanoresonators. As the temperature decreases from 300 to 100K, we see that the intensities of the resonance peak in the extinction spectra increase by 10-76%. The observation has two main factors: First, temperature-induced hole doping of graphene strengthens its oscillator properties. Second, the enhanced quality factor of the resonances provides additional evidence that reduced plasmon damping caused by the suppression of temperature-dependent scattering mechanisms lengthens the graphene plasmon lifetime.

We analyze the DC electrical characteristics of graphene while changing its temperature from 300 to 100K. The charge neutrality point (CNP) of graphene modifies from $V_{\mathrm{CNP}} = 62$V at 300K to 76.5V at 100K. The additional hole doping, $\Delta p = 1.04\times10^{12}\mathrm{cm}^{-2}$, is what causes the shift of $\Delta V_{\mathrm{CNP}} = 14.5$V. The cooling of graphene alters the doping concentration in addition to lowering the carrier scattering rate, which increases carrier mobility. Additionally, the hole mobility exhibits a monotonic rise with lower temperatures.

By analyzing the temperature-dependent normalized extinction spectra, we comprehensively study the temperature-dependent plasmonic characteristics of the graphene nanoresonators. Reduced temperature causes all extinction peaks to be more intense and causes a slight blueshift. This tendency can be attributed to the increased carrier density and mobility in graphene. Similar to the electrical measurement, the additional hole doping $\Delta p = 1.37\times10^{12}\mathrm{cm}^{-2}$ associated with cooling from 300 to 100K is present.

By calculating the intensities of GP resonance for observed extinction spectra, it was possible to examine the temperature-dependent electrodynamic response of the nanoresonators. Most of the time, peak intensities rose as temperature decreased. The increase in the peak intensities ranged from 10 to 76% as the temperature was cooled from 300 to 100K. We attribute the rising peak intensities to the increased doping due to cooling.

When the fermi energy decreases, the temperature dependence of the peak intensities gets stronger. This is most likely due to the fact that at lower carrier densities, the temperature-induced doping becomes more important than the electrostatic doping level. At the maximum gate bias, we also evaluate how the peak intensity varies with temperature for different resonator widths. The peak intensity in this regime is predicted to be mostly dependent on the plasmon scattering rate. Narrower resonators are predicted to contribute more to the temperature-independent extrinsic scattering rate. Indeed, compared to a wider one, the normalized extinction peaks in the narrower resonators are substantially less temperature sensitive.

We have studied the far-field temperature-dependent plasmonic response of graphene nanoresonators. The graphene plasmon resonance intensifies when the temperature decreases from 300 to 100K. The increased *p* doping brought on by cooling and the inhibition of the phonon-mediated scattering mechanism are both responsible for the increase in GP peak intensity. Our findings pave the way for enhanced graphene plasmonic devices that operate at cryogenic temperatures by illuminating significant but previously unrecognized temperature effects on tunable plasmons in large-area graphene-SiO_2 systems.

10:45 AM EL16.13.07
Magnetically Tunable 1D Plasmonic Photonic Crystals Chaolumen Wu and Yadong Yin; University of California, Riverside, United States

Structurally colored materials have been attractive for many years due to their vivid colors, long stability, and easy tunability. Within them, plasmonic and photonic nanostructures are two powerful systems that generate structure colors with easy control of the photonic colors. Although promising, the combination of plasmonic resonance and photonic bandgap within a single system is challenging. In this work, 1D plasmonic photonic crystals with angular-dependent structural colors are fabricated by assembling magneto-plasmonic colloidal nanoparticles under an external magnetic field. Different from conventional 1D photonic crystals, the assembled 1D periodic structures show angular-dependent colors from the selective activation of photonic diffraction and plasmonic scattering. Furthermore, the magneto-plasmonic nanoparticle chains can be fixed in an elastic polymer matrix to produce a photonic film with angular-dependent as well as mechanically tunable optical properties. Thanks to the easy and precise modulation of magnetic assembly, the orientation of the nanochains within the polymer matrix can be precisely controlled to produce photonic films with desired patterns, showing versatile colors from the backward photonic diffraction and forward plasmonic scattering. This work demonstrates an easy way to combine plasmonic and photonic properties within a single system, showing synergetic optical properties and the potential for the development of programmable optical functions for applications in color display, optical devices, and information encryption.

11:00 AM EL16.13.08
Exciton-Enhanced Light Scattering in Atomically-Thin Metasurfaces Ludovica Guarneri[1], Qitong Li[2], Jung-Hwan Song[2], Thomas Bauer[1], Jorik Van de Groep[1] and Mark L. Brongersma[2]; [1]University of Amsterdam, Netherlands; [2]Stanford University, United States

Nanophotonic metasurfaces employ dense arrays of optically-resonant nanostructures to manipulate the properties of light in ultra-compact optical coatings. By harnessing plasmonic or Mie resonances in metallic or dielectric nanoparticles, the phase and amplitude of the scattered light can be controlled at the nanoscale. Based on rapid advances in metasurface design, metasurfaces are now widely applied in flat optical elements for beam steering, lensing, and holography. However, novel applications in dynamic holography and augmented reality require metasurfaces and metadevices with actively-tunable functionality. So far, the use of plasmonic and Mie-resonances in active metasurfaces is limited as their optical resonances are difficult to tune dynamically.

Monolayer transition metal dichalcogenides, such as WS_2 , exhibit strong exciton resonances in the visible spectral range that dominate their optical response. The excitonic light-matter interaction in these 2D quantum materials is inherently very strong and highly tunable, which can be leveraged to realize mutable flat optical elements. To unleash the full potential exciton-enhanced light scattering in atomically-thin metasurface elements, it is essential to first achieve detailed understanding of the role of the exciton's quantum mechanical properties in passive nanophotonic wavefront shaping.

Here, we employ atomically-thin metasurface lenses carved out of a monolayer of WS_2 to directly study the influence of exciton decay and dephasing on the metasurface functionality and spectral line shape. We fabricate 500 µm diameter zone plate lenses using electron-beam lithography and reactive-ion etching. At resonance, excitonic light scattering strongly enhances the focal intensity. We systematically characterize the focal shape and focusing efficiency as a function of wavelength using confocal microscopy. To study the influence of exciton-phonon scattering and dephasing on the optical functionality of the lens, we then characterize the efficiency spectrum as a function of temperature.

At ambient conditions, the spectrum shows a strong asymmetric line shape revealing that the scattered light fields are directly governed by the monolayer susceptibility. This enables an almost background-free measurement of the optical properties of the monolayer, and thereby the excitonic light-matter interaction. Careful analysis of the line shape shows that the relative contribution from resonant excitonic light scattering is comparable to the non-resonant monolayer scattering. For decreasing temperatures on the other hand, the exciton energy shows a blue-shift, non-radiative decay and dephasing are suppressed, and the exciton becomes fully radiative. As a result, the asymmetric line shape not only narrows and increases in amplitude, but also transitions into a more symmetric line shape. This directly shows the increasing prevalence of the exciton resonance in the focusing efficiency. By comparing the results to numerical simulations and an analytical model, we show that the efficiency of the metasurface lens directly scales with the excitonic oscillator strength.

The results give direct insight in the role of exciton dynamics in optical wavefront shaping using atomically-thin metasurfaces. A full understanding of the role of exciton resonances in metasurfaces paves the way for dynamic components, combining tunable effects in quantum materials with classical metasurface optics.

11:15 AM *EL16.13.10
Tunable Metasurfaces in III-V Materials—Design and Experiment Michelle Povinelli, Alok Ghanekar, Hyun Uk Chae, Bo Shrewsbury, Ragib Ahsan and Rehan Kapadia; University of Southern California, United States

We investigate the design of tunable metasurfaces using III-V materials as the insulator layer in metal-insulator-metal (MIM) designs. We first propose several designs for switchable and tuanble thermal emissivity in such structures. We consider the use of incorporated p-i-n junctions to tune the carrier concentration, and hence the refractive index, of the III-V structure. In one case, we introduce a perturbation to every other tooth of an MIM grating, doubling the effective periodicity. We show that this effect opens a photonic band gap, switching off the emissivity at the desired midwave infrared wavelength. In a second approach, we investigate index tuning in a slow light structure. Here, the slow light design magnifies the angular sensitivity with respect to index change. We further present our experimental progress toward such structures. In a first case, we demonstrate direct growth of InAs on a metallic substrate for realization of midwave infrared metamaterials. In a second case, we investigate epitaxial gransfer of GaAs on a metallic substrate for the same purpose.

SESSION EL16.14: Nanophotonics and Metasurfaces
Session Chairs: Yao-Wei Huang and Min Seok Jang
Friday Afternoon, April 14, 2023
Moscone West, Level 3, Room 3016

1:30 PM EL16.14.01
The Importance of Surface Roughness on The Reflection from Epsilon-Near-Zero Substrates David Navajas[1,2], José M. Pérez-Escudero[1,2] and Iñigo Liberal[1,2]; [1]Public University of Navarre, Spain; [2]Institute of Smart Cities (ISC), Spain

Recent multiple applications and characteristics related to epsilon-near-zero (ENZ) media at infrared, visible and even ultraviolet frequencies have positioned them as a very active field of research. The performance of ENZ technologies is ultimately limited to material loss, which has been studied in detail, and the impact of surface roughness, which has attracted much less attention. In this work, the reflectivities of several silicon carbide (SiC) samples with different levels of artificially-induced roughness have been investigated numerically and experimentally. Samples have been treated via deep reactive ion etching (DRIE), and subsequently measured with a Fourier transform infrared spectroscopy (FTIR) microscope. The posterior characterization of the surface roughness of the samples focuses on the measurements made via atomic force microscopy (AFM).

Due to the dispersion of SiC, our samples enable a direct comparison of the impact of surface roughness on ENZ media, plasmonic-like systems and dielectric media, all within the same sample. The smoothest samples reveal near-perfect reflective behaviours, while the samples with more level of roughness shows a heavy decrease of the reflectivity, especially in the region between 10.3 µm and 12.55 µm. As a polar dielectric, its response at infrared frequencies exhibits this reflection band defined by the longitudinal and transversal optical phonons and a negative permittivity, it has been named Reststrahlen Band. Roughly, lower negative permittivities allow plasmonic-type effects, such as surface phonon polaritons. In consequence, the reflection band is strongly affected by the roughness. As long as the permittivity reaches high negative values, which are related to smaller skin-depths leading to hard interaction, this influence of the surface wave phenomena is decreased. The dielectric zone and the ENZ point ($\varepsilon=0$) are affected as well. However, it is found that the ENZ range is particularly robust against surface roughness.

We numerically validate our conclusions by using the full-wave solver Comsol Multiphysics. In a first approximation, the surface roughness was characterized by the sum of three waves and subsequently averaged with different periods in transversal electric (TE) polarization. Secondly, 15 AFM profiles were introduced manually and later their reflectivities calculated and averaged. Both calculations show a very precise approach to the measured reflectivities.

1:45 PM EL16.14.02
Negative Refraction in a Photon-Magnon Hybrid Junyoung Kim, Bosung Kim, Bojong Kim, Biswanath Bhoi, Haechan Jeon and Sang-Koog Kim; Seoul National University, Korea (the Republic of)

Artificially fabricated negative-refractive-index (NRI) metamaterials have been realized based on the negative values of both the permittivity and permeability of a given structure, the so-called double negative-material criterion. Here, we experimentally demonstrated, through the single-negative material criterion, the occurrence of the NRI in a photon-magnon hybrid composed of an Yttrium Iron Garnet (YIG) film and an inverted split-ring resonator (ISRR). The NRI signature was found by extracting S21 and S11 parameters versus the frequency of microwave ac currents and the static field strength from the sample. In order to obtain the underlying NRI mechanism from the YIG/ISRR hybrid structure, we analytically derived the permittivity and permeability along with the refractive index using series impedance (Z_{se}) and shunt admittance (Y_{sh}) based on an appropriate circuit model. The analytical model, which was in quantitative agreement with the experimental NRI values, revealed that the single-negative-material criterion is met at/near the intersection of resonance frequencies of YIG and the ISRR under specific field conditions. The advantages of NRI established in the photon-magnon hybrid are the tunability of NRI magnitude as well as the magnetic-field-controllable on-off switching in a fabricated structure. This work can provide a new paradigm for the realization of magnetic-field-controllable NRI metamaterials.

2:00 PM EL16.14.03
***In Situ* Optical Analysis of the High-Temperature Behavior of Refractory Materials** Margaret A. Duncan[1], Landin Barney[2], Tao Gong[1,1], Stuart Ness[1], Scott J. McCormack[1], Jeremy N. Munday[1], Mariama Rebello Sousa Dias[2], Marina S. Leite[1] and Peifen Lyu[1]; [1]University of California, Davis, United States; [2]University of Richmond, United States

The degree of control we have over the electromagnetic spectrum *via* tailoring of optical material properties and geometries governs our ability to advance cutting-edge photonic devices ranging from structural color pixels to thermophotovoltaic emitters to high-temperature sensors. A crucial step of improving this control is understanding how the dielectric functions of different materials change at high temperatures. Though the field has recently been of great interest to the photonics community for a variety of applications, most research in materials under extreme conditions have focused on structural properties. To address the growing need for high-temperature optical material properties, we present an *in situ* optical analysis of three refractory metals (Ru, Ta, and W) at elevated temperatures in an oxidizing environment. These samples preferentially oxidize when held at high temperatures (>500°C) in an oxidizing environment: by employing *in situ* ellipsometry measurements during a controlled heating treatment, we gain very precise control over the thickness of the oxide layers. We consider the application of these thin films to a structural color system, given their vibrant coloration: with our initial heating treatments our three structures generated vibrant pink (RuO_2/Ru/Si), yellow (Ta_2O_5/Ta/Si), and teal (WO_3/W/Si) hues. These structural color devices have the added benefit of being stable up to 1,200°C in an inert environment, showing the capability of these materials for use in high-temperature optical systems. We extend our technique to carbides, where a quantitative analysis of high temperature effects on permittivity will also be presented. These two sets of data represent a crucial advance in the development of robust materials for applications in extreme environments.

2:15 PM EL16.14.04

Tailoring Diffraction Characteristics of Resonant, Large Area Metagratings Employing Mask-Free UV Laser Interference Patterning Carlota Ruiz de Galarreta[1,2], Rosalia Serna[1], Joe Shields[2], Miguel Alvarez-Alegria[1], Rocio Ariza[1], Jose Ramon Deop-Ruano[1], Alejandro Manjavacas[1], C. David Wright[2] and Jan Siegel[1]; [1]CSIC, Spain; [2]University of Exeter, United Kingdom

Over the past decade, metasurfaces comprising arrays of localised ultrathin resonant subwavelength resonators ("meta-atoms") have been successfully employed to engineer the wavefront characteristics of optical beams, resulting in several recent demonstrations of ultra-compact devices for focusing, beam mode conversion or beam steering. To date, for the particular case of beam steering metasurfaces (nowadays known as phase-gradient metasurfaces), reflection or transmission of light at pre-designed angles has been realized based on the ray optics approximation (generalized Snells' law), via forcing linearly varying, discrete transverse phase increments to impinging waves [1]. This is typically carried out via the design and engineering of periodic "supercells" made of various meta-atoms having different shapes, sizes and/or orientation, thus imposing abrupt, local phase jumps for a given excitation frequency, which in turn results in constructive interferences at pre-designed angles. However, phase-gradient metasurfaces exhibit fundamental limits in terms of maximum achievable steering efficiencies, especially at large angles of incidence.

Recently, it has been pointed out that metasurfaces based on periodic 1D identical plasmonic dipoles lying on ultrathin insulator/metal substrates exhibit beam steering capabilities at oblique incidence with near unit diffraction efficiency when operating in the (0th, -1st) diffractive regime. Therefore, such an approach offers clear benefits with respect to more conventional phase-gradient metasurfaces, both in terms of optical performance and in terms of ease-of-fabrication using current lithographic techniques. Nevertheless, the physical realization of such "metagratings" today still requires e-beam lithography with several steps involving spin coating of appropriate photoresist masks combined with thin film deposition and lift-off or etching techniques.

In this work, we propose and experimentally validate a single-step, mask-free, nanopatterning technique for a virtually instantaneous realization of high performance, large area, near-infrared metagratings consisting of 1D metallic nanostripes. Our method exploits controlled pattern ablation of continuous gold films deposited on a SiO_2/Al/Si substrate. Nanostripe structures were fabricated by making two in-plane pulsed top-hat UV laser beams interfere at a specific angle onto the sample surface ($\lambda = 193$ nm, $\tau_{pulse} = 23$ ns), resulting in a large area 1D sinusoidal intensity distribution. A systematic study of the effect of the laser fluence and number of pulses on the final topography has revealed that a wide range of nanobar geometries can be achieved using this approach, ranging from low aspect ratio, wide nanostripes, to high aspect ratio, narrow nanostripes, depending on the processing conditions. Finite element analysis of the m=0 and m=-1 diffraction orders against the angle of incidence have revealed that the high diffraction efficiency characteristics of the fabricated devices in terms of bandwidth and dispersion can significantly vary depending on the resulting nanostripe geometry. Finally, diffraction measurements of as-fabricated devices employing spectroscopic scatterometry have been performed, confirming that laser-processed metagratings behave as predicted by our calculations, thus validating the versatility of our fabrication approach. Based on these results, we believe that our work paves the way for the realization of low cost, single-step and large area metagratings, with exotic and on-demand diffraction properties, which may find applications in many exciting fields including holography or free-space optical communications.

2:30 PM BREAK

3:00 PM EL16.14.05

Toroidal Dipole-Induced Photocurrent Enhancement in Silicon Nanodisk Hexagonal Array beyond 1400 nm in Wavelength Keisuke Moriasa, Hiroaki Hasebe, Hiroshi Sugimoto and Minoru Fujii; Kobe University, Japan

A laser with the emission wavelength longer than 1400 nm is "eye safe", because light in the wavelength range is strongly absorbed in the cornea and lens and cannot reach more sensitive retina. The eye safe lasers have been used as a light source for LiDARs in atmospheric physics, autonomous driving, etc. For the development of low-cost LiDARs for autonomous driving, a silicon-based CMOS compatible photodetector operating beyond 1400 nm is crucial. Several methods have been proposed to extend the detection range of a silicon-based photodetector beyond the band gap wavelength. The most widely studied one is using internal photoemission at a Schottky junction between silicon and metal nanoantennas. Another approach is enhancing defect-mediated weak absorption of silicon by optical resonances.

In this work, we show that a hexagonal array of low-aspect-ratio silicon nanodisks formed on a silicon thin film has the sub-radiant high-Q toroidal dipole (TD) resonances that strongly enhance light absorption in the low material loss wavelength range, i.e., sub-band gap range. We also demonstrate that the absorption enhancement appears as a photocurrent enhancement at the resonance wavelength, and thus the metasurface can be used as a narrow-band photodetector operating in the silicon sub-band gap wavelength range [1-2]. To further boost the performance of that device, we design a structure having perfect absorption by introducing the concept of the bound states in the continuum (BICs) in the TD resonances of a silicon nanodisk hexagonal array. The idea is introducing a mirror below the metasurface via a silicon dioxide spacer. In proper spacer thicknesses, interference between a TD resonance in a nanodisk array and the image dipole in the mirror cancels the radiation perfectly and BICs emerge. Slight detuning of the BIC condition by controlling the spacer thickness makes the radiation loss finite and to be equal to the material loss. This results in perfect absorption at the TD resonance wavelengths. Since the absorption is predominantly in the silicon region, the photocurrent is expected to be strongly enhanced. In this structure, the absorption spectrum is relatively insensitive to the incident angle and is independent of the polarization direction. Furthermore, since the TD resonances are very narrow, the device can detect photons at specific wavelengths without a bandpass filter. The device is composed of silicon, silica and aluminum mirror and electrodes, and does not require narrow band gap semiconductors and noble metal nanostructures for the detection of long wavelength photons. Therefore, the device can be easily integrated in silicon-based electronic devices.

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3:15 PM EL16.14.06

Picoelectrodynamics in Silicon Sathwik Bharadwaj, Todd Van Mechelen and Zubin Jacob; Purdue University, United States

The concept of photonic frequency (ω) - momentum (q) dispersion has been extensively studied in artificial dielectric structures such as photonic crystals and metamaterials. However, the photonic dispersion of electrodynamic waves hosted in natural materials at the atomistic level is far less explored. Here, we develop an atomistic nonlocal electrodynamic theory of matter by combining the Maxwell Hamiltonian theory of matter with a quantum theory of atomistic polarization. We apply this theory to silicon and discover the existence of atomistic electrodynamic waves. Atomistic electrodynamic waves have sub-nano-meter effective wavelengths in the picoelectrodynamics regime. Further, we show that the atomistic optical conductivity in silicon lattice is highly anisotropic along different momentum directions due to atomistic electronic correlations. Our findings demonstrate that the natural materials such as silicon host variety of yet to be discovered electromagnetic phases of matter and provide a pathway for material design and engineering to discover rich atomic scale light-matter interaction phenomena.

Reference:

Sathwik Bharadwaj, Todd Van Mechelen, and Zubin Jacob, Phys. Rev. Applied **18**, 044065 (2022).

https://www.doi.org/10.1103/PhysRevApplied.18.044065

3:30 PM EL16.14.08

Near-Field Imaging and Spectroscopy of Optical Resonances in a Semiconductor Metasurface Alex M. Boehm[1], Sylvain Gennaro[1,2], Chloe Doiron[1], Thomas Beechem[3], Raktim Sarma[1] and Taisuke Ohta[1]; [1]Sandia National Labs, United States; [2]Meta Reality Labs, United States; [3]Purdue University, United States

Metasurfaces have emerged as a versatile platform to control light-matter interactions in sub-wavelength volumes, leading to "planar" optics with various potentially groundbreaking applications in bio-sensing, hyperspectral imaging, lasing, frequency mixing, and quantum information processing. Historically, metasurfaces tailored electromagnetic fields via localized surface plasmon resonances confined in metallic nanostructures. However, dielectric metasurfaces made of III-V semiconductors have recently garnered much interest owing to their low losses at optical wavelengths and the ability to support electromagnetic Mie-like resonances within individual resonator units. Recent efforts have further introduced symmetry breaking elements to individual resonator units lending access to high-Q symmetry-protected quasi bound states in the continuum (BICs) optical modes, that offer a promising avenue for enhanced light matter interactions. A technique capable of directly imaging the electromagnetic fields at nano-scale in these platforms is sought after to inform us on the origin and the spatial extent of these photonics processes and expand pathways to tailor nanostructures for chosen functionalities.

Imaging nanoscale optical phenomenon is non-trivial since light-matter interactions take place at length scales smaller than the wavelength of light, far below the resolution of traditional optical probes. Nonetheless, several techniques such as scanning probe-based near-field optical microscopy (SNOM), photo-induced force microscopy (PiFM), cathodoluminescence (CL), and electron energy loss spectroscopy (EELS) have begun to probe this space. An imaging technique that, despite broad applications in plasmonics research, has hitherto remained unexplored in the field of nanophotonics is photoemission electron microscopy (PEEM), a technique that capitalizes on a true optical excitation in a "photon in, electron out" approach to probe the near-field enhancement of the electric fields through photoelectron intensity. Here we employ PEEM to image broken-symmetry III-V semiconductor metasurfaces with high–quality factor, quasi-bound state in the continuum resonances. We find that through far-field optical excitation at normal incidence we can elicit highly selective mode excitation which enables high-resolution imaging of field profiles as a function of wavelength and polarization. These profiles are further used to corroborate finite difference time-domain (FDTD) simulations and develop a more complete understanding of the optical response of the metasurface. Additionally, the "electron out" portion of PEEM provides full-field spectroscopic imaging allowing us to collect near-field spectral responses at high spatial resolution. Through spectroscopic analysis of the field profiles, we reveal significant shifts in the excited resonances as a function of position within an individual resonator. Finally, we exhibit the ability of PEEM to image long range interactions among resonators as an entire array of structures can be excited and imaged simultaneously. This work highlights the powerful capabilities of PEEM for the investigation of semiconductor metasurfaces and sheds light on nature of the photonic processes occurring in this class of materials.

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3:45 PM EL16.14.09

Design Parameters of Free-Form Meta-Color Routers for Sub-Micron-Pixel Image Sensors Sanmun Kim, Chanhyung Park, Shinho Kim and Min Seok Jang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Meta color routers are emerging as a next generation color filter for complementary metal-oxide-semiconductor (CMOS) image sensors. In a classical image sensor, a micro-lens and a color filter is placed on top of a silicon photodetector. The micro-lens focuses the light into the photodiode area and the color filter absorbs or reflects the light of unwanted wavelength. Until now, the classical image sensor configuration has dominated the visible image sensor market, but the reduction in pixel size to sub-micron range is limiting its performance. The geometric-optics based configuration is no longer valid and reduction of pixel area leads to a smaller number of photons reaching the photodiode.

As most of the light incident on the image sensor is blocked by the color filter, the optical efficiency of the classical image sensor is limited to 25% for red/blue lights and 50% for green lights. The meta color routers break this limit by directing all the incident light into the corresponding subpixel area.

A typical meta color router is configured by allocating dielectrics of different refractive indices inside the design region, thus involves freeform optimization of high degrees of freedom (DoF). Due to the advantages that can be brought by the meta color router, optimization of the meta color router has been widely investigated, both theoretically [1, 2] and experimentally [3, 4]. However, those studies lack the investigation on the selection of design parameters. The design parameters of a meta color router are the parameters that define the geometry and the design space of the device, and have critical effects on final device performance.

In this work, we investigate how the optical efficiency of a meta device is affected by the choice of each design parameters. We classify the design parameter into two different types: physical parameters, and spatial resolution parameters. Design parameters such as pixel size, device thicknesses, and refractive indices are the physical parameters. Spatial resolution parameters are parameters that determine how the design area is gridded. Through parameter tuning, we report the existence of optical thickness of the device and optimal choice of dielectrics. Also, we report how the subpixel resolution parameters affect the optical efficiency.

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SESSION EL16.15: Virtual Session I
Session Chairs: Yao-Wei Huang and Pin Chieh Wu
Wednesday Morning, April 26, 2023
EL16-virtual

8:00 AM *EL16.15.02
Vacuum UV Nonlinear Meta-Devices Ming Lun Tseng[1], Michael Semmlinger[2,2], Ming Zhang[2,2,2], Catherine Arndt[2,2], Jian Yang[2,2,2], Mu Ku Chen[3], Din-Ping Tsai[3], Peter Nordlander[2,2,2] and Naomi Halas[2,2,2]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]Rice University, United States; [3]City University of Hong Kong, Hong Kong

Vacuum ultraviolet (VUV) light lies in the wavelength range from 100 nm to 200nm. It is of great importance to practical applications ranging from biomedical spectroscopy to material science. Due to the strong absorption of matter in this range, producing efficient and compact VUV devices is challenging. However, it is highly desired to realize miniaturized photonic devices to further advance and explore the applications of VUV light. In this talk, we will report nonlinear metasurfaces (1-3) capable of generating and controlling VUV light. By carefully choosing the nonlinear material, rotational symmetry, and resonance mode for their unit cells, the reported metasurfaces are able to efficiently convert the incident visible laser into VUV light and control the wave properties. Metasurfaces for VUV light focusing and beam steering were fabricated and experimentally characterized. Experimental results confirm the functionalities of metasurfaces. This work points out a promising route toward novel nanophotonic devices for this valuable wavelength range.

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8:30 AM *EL16.15.03
Electrically Tunable Metasurface for Light Detection and Ranging Junghyun Park, Byung Gil Jeong, Sun Il Kim, Minkyung Lee, Young Kim, Kanghee Won and Kyoungho Ha; Samsung Advanced Institute of Technology, Korea (the Republic of)

Tunable metasurfaces have facilitated novel spatial light modulation technologies with an unprecedentedly fast operation speed and an extreme shrinkage in pixel sizes. By exploring the optical response for given control stimulus from the Huygens' metasurfaces, we can establish the look-up table and achieve arbitrary wavefront shaping. Recent trends are focusing on how to harvest a large efficiency (power-in to power-out ratio) and a stark contrast between intended wavefront over undesirable background noise. To meet these goals, there have been various approaches; these include the adoption of materials with wide tunability such as phase change materials with low loss, the combination with nano-structured optical configuration with local control of liquid crystal, and the use of exciton manipulation in transition metal dichalcogenides. One may also consider utilizing highly sensitive resonance mechanism such as non-local metasurfaces, guided mode resonance, and dimerized gratings, to name a few. <div>In this presentation, we take a brief review on the recent progress and envision the future direction of the tunable metasurfaces. We also address potential applications that would become possible by use of electrically tunable metasurfaces, including light detection and ranging (LiDAR), free space optical communications, and holographic displays. We will present the experimental demonstration of the LiDAR by using the beam steering device based on the tunable metasurfaces, which features high reflectivity above 60% and the directivity (side mode suppression ratio) above 10 dB, as well as fast operation speed of 300 kHz.</div> <div> </div>

9:00 AM *EL16.15.04
Crossing of the Branch Cut in Topological Metasurfaces Patrice Genevet; CRHEA, France

Research on topological photonics has considerably grown, transferring condensed matter concepts of topological insulators with the discovery of the integer Quantum-Hall effect into the realm of photonics. Today, nanophotonics, which is related to light manipulation with subwavelength objects, offers new opportunities to address light properties. New degrees of freedom in the design of optical components are attained by considering the response of topological nanostructures. So far, optical metasurfaces, made of subwavelength arrangements of nanostructures, have relied on resonant phase scattering occurring in Mie resonators or ultrathin pillars. Full wavefront control requires finding sets of nanostructures that can provide 2π optical phase retardation on the incoming beam. Ultimately, and despite all the efforts in understanding the physical mechanisms leading to optimal designs, including powerful optimization methods, metasurface designs often require witless numerical parameter searches. Relying on symmetry-breaking arguments and topological properties of the associated non-Hermitian matrices representing the metasurfaces, we provide new guidelines for achieving 2π phase coverage in transmission and reflection. This framework allows us to unravel the physical principles underlying Huygens metasurfaces, showing that it exploits degeneracies of transmission- or reflection-matrices Zeros, so-called exceptional points, corresponding to transmissionless and reflectionless states. Overall, symmetry-breaking leading to a displacement of a Zero-Pole pair with its branch cut crossing the real axis, provides a very intuitive design approach for achieving full resonant phase scattering. Encircling EPs and/or zeros in the nanostructure parameter space to provide full 2π-phase are considered, entrusting metasurfaces and flat optics with additional light modulation schemes. Our results explain the importance of topological defects and how they can be manipulated for achieving realistic and insightful metasurface designs.

Acknowledgement

We acknowledge financial support by the French National Research Agency ANR Project DILEMMA (ANR-20-CE09-0027) and the French National Research Agency ANR Project Meta-On-Demand (ANR-20-CE24-0013).

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9:30 AM EL16.15.05
Ultrafast Reconfigurability of Circular Dichroism Using Bound-State-in-Continuum Dielectric Metasurfaces Prasad Iyer[1,2], Luis M. Martinez[3,4,1], Chloe Doiron[1,2], Wesley Mills[1,5], Christina Boyd[1,6], Michael B. Sinclair[2], Ting S. Luk[1,2], Prashant Padmanabhan[1,4], Alex Cerjan[1,2] and Igal Brener[1,2]; [1]Center for Integrated Nanotechnologies, United States; [2]Sandia National Labs, United States; [3]The University of Texas at El Paso, United States; [4]Los Alamos National Laboratory, United States; [5]Utah State University, United States; [6]Rensselaer Polytechnic Institute, United States

Reconfigurable dielectric metasurfaces have shown tremendous potential to actively control the fundamental (amplitude, phase and polarization) properties of light with minimal losses. Here we demonstrate ultrafast tuning of circular dichroism (CD) using dual degenerate bound-state-in-continuum (BIC) resonances in a Silicon metasurface. We design and fabricate tall (1.27um) Z-shaped amorphous Silicon resonators in a hexagonal lattice (700nm period) on glass with overlapping left (LCP) and right (RCP) circularly polarized quasi-BIC resonances at 1.22um in reflection. These high Q (180) metasurface resonances results in a giant change in CD (0.85) over a small wavelength range (10nm). We use ultrafast (80fs) pump (600nm)-probe (1200nm) spectroscopy to tune the refractive index of the resonators through Drude free-carrier refraction; demonstrating dynamic modulation of the circular dichroism from the metasurface by more than the full-width half max (FWHM) of the quasi-BIC resonances. This is one of the first experimental demonstrations of dynamic reconfigurability of CD in a dielectric metasurface through continuous index tuning in the ultrafast (ps) regime. We believe the results presented here will enable large area scalable CMOS metasurfaces with reconfigurable all-optical control of the polarization of light in the ultrafast timescales.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy. Sandia National Laboratories is a multi- mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. The views expressed in this article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

9:45 AM *EL16.15.06
Dynamic Light-Engineering with Flat Optical Devices Antonio Ambrosio; Fondazione Istituto Italiano di Tecnologia, Italy

We realized a shapeshifting diffractive optical element with reconfigurable surface relief geometry that provides different optical functionality: a grating can turn into a different grating or into a lens, and back to the original grating when and if needed; on-demand. For our approach, we used films (on glass substrates) of azobenzene-containing polymers (or simply azopolymers) that have the ability to develop surface reliefs directly on the free surface of the film when exposed to spatially structured UV\visible light. The photo-induced surface structuration arises from a light-fuelled microscopic motion involving cyclic isomerizations of the azobenzene molecules which drive a macroscopic transport of the entire polymeric matrix under illumination. The geometry of the resulting surface reliefs depends on both the intensity and on the polarization distribution of the irradiated light across the surface. Not involving any destructive or chemically altering process, the light-induced surface structuration of azopolymers is intrinsically reversible. Complete all-optical reconfigurability of the structured surfaces were then demonstrated through the irradiation of a second light beam that, acting as pattern erasing beam, restores the initial flat state, making the surface ready to be re-shaped at will in successive writing steps. We used our reconfigurable diffraction gratings to dynamically select the light wavelength from a white light source that is diffracted in a specific direction, realizing a prototype of monochromator operating without any mechanical moving part. Similarly, efficient and reconfigurable flat diffractive lenses, with reprogrammable focal lengths and optimized diffraction efficiency were then directly inscribed on the azopolymer film and used in dynamical imaging systems able to focus on objects placed at different depths and to provide different zoom levels of large scenes, without the movement of multiple optical components necessary in standard bulky systems to accomplish same functionalities.
We also developed a structured light laser capable of producing vortex laser arrays with actively tunable topologies and non-local coupling dictated by the array's topology. The gain medium of our laser has a large transverse cross-section supporting many transverse modes that we forced to organize and form a lattice of a hundred laser beams by inserting a metasurface mask that modulates the phase and amplitude of the field. More specifically, the phase profile was designed to produce vortex beams with an annular intensity profile, useful for communication, microscopy and lithography applications. Importantly, in our new laser arrays, the coupling network is not limited to the nearest neighbours as for arrays of Gaussian lasers with no topological charge, but instead can be tailored to mix vortices that are widely separated in the lattice. Although different schemes for generating a single vortex inside a resonator have been demonstrated, we demonstrated the conditions for generating vortex laser arrays in a single cavity, realizing a platform to explore complex topological transformations and collective vortex effects at the source. Furthermore, we demonstrated the robustness of the designed complex light distribution to defects in the metasurface mask. This opens up the possibility of iteratively manipulating structured light parameters and could be used to develop photonic simulators.

SESSION EL16.16: Virtual Session II
Session Chairs: Ho Wai (Howard) Lee and Yang Zhao
Wednesday Morning, April 26, 2023
EL16-virtual

10:30 AM *EL16.16.01
Critical Coupling for Enhanced Biosensing and Energy Conversion Enabled via Bound States in the Continuum Stefan A. Maier[1,2]; [1]Monash University, Australia; [2]Imperial College London, United Kingdom

Metasurfaces based on bound states in the continuum enable careful tuning of the radiative loss channel of surface modes via small changes of the asymmetry parameter of unit cell resonators. This enables exploring the regimes of under-coupling, critical coupling, and over-coupling for a variety of applications in metasurface photonics. Here we will focus on the exploration of surface enhanced infrared absorption spectorsocpy, and energy conversion in a context of photocatalysis, and examine how their efficiency varies with the coupling regime. Strikingly, criticial coupling does not in all circumstances lead to the highest sensitiviy for sensing.

11:00 AM EL16.16.02
Plasmon Enhanced Quantum Properties of Single Photon Emitters in Hexagonal Boron Nitride Flakes Mohammadjavad Dowran, Suvechhya Lamichhane, Adam Erickson, Andrew Butler, Sy-Hwang Liou, Christos Argyropoulos and Abdelghani Laraoui; University of Nebraska-Lincoln, United States

Two dimensional (2D) materials such as hexagonal born nitride (hBN) have emerged as promising hosts of single photon sources (SPEs) which exhibits promising optical properties (high brightness, optically accessible spin states, high quantum efficiency, *etc*.), making them highly desirable elements for integrated quantum photonics [1]. In this study, we create SPEs in thin (thickness ≤ 10 nm) hBN flakes deposited on a Si/SiO2 substrate by using a high-temperature (1100 °C) annealing method under O_2 flow and characterize their quantum properties using a home-built confocal fluorescence microscope. We demonstrate plasmonic enhancement of SPE properties by spin-coating of 100 nm Ag nanotubes on top of the hBN flake: a decrease of emission linewidth by 30% and quantum emitter lifetime decrease by 60% [2]. We expect > 2 order of magnitude enhancement of SPE fluorescence when integrating them to optical nanocavities. Such enhancement is supported using COMSOL numerical simulations where hBN flakes are integrated into a composite nanophotonic structure entailing plasmonic effects from silver nanocubes and the optical frequency resonance from the fabricated metallic nanocavity. J. D. Caldwell, et *al.*, Nat. Rev. Mat. 4, 552-567 (2019). M. Dowran, et *al.*, under preparation.

Acknowledgment: This material is based upon work supported by the National Science Foundation/EPSCoR RII Track-1: Emergent Quantum Materials

and Technologies (EQUATE), Award OIA-2044049. The research was partly performed in the Nebraska Nanoscale Facility: National Nanotechnology Coordinated Infrastructure and the Nebraska Center for Materials and Nanoscience (and/or NERCF), which are supported by the National Science Foundation under Award ECCS: 2025298, and the Nebraska Research Initiative.

11:15 AM EL16.16.03
Light Trapping and Directional Scattering in Hybrid Metasurfaces Dominic Bosomtwi and Viktoriia Babicheva; University of New Mexico, United States

We design and analyze the optical response of subwavelength layered disk nanoresonators. The hybrid plasmonic / high-index dielectric nanoresonators allow for efficient light trapping and directional scattering. We investigate the scattering response of the layered nanoresonators array, and we show that varying the nanoresonator height leads to the realization of strong electromagnetic mode confinement resulting in a high-quality (Q) factor. We then demonstrate that strongly coupled electromagnetic modes in the nanostructure can interfere destructively in the surrounding medium of the nanostructure, inducing bound states in the continuum (BIC) for the modes excited in the nanostructure. Finally, we report on the observation of overlapping of electric and magnetic dipole moments giving rise to the suppression of electromagnetic waves either in the forward or backward directions.
This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Los Alamos National Laboratory (Contract 89233218CNA000001) and Sandia National Laboratories (Contract DE-NA-0003525). The work is also supported by Contract DE-2375849.

11:30 AM EL16.16.04
Multipole Coupling in Nanoparticle Lattices with Quasi-Bound States Md Sakibul Islam and Viktoriia Babicheva; University of New Mexico, United States

Metasurfaces and periodic lattices have become promising candidates for numerous photonic applications due to their unique ability to manipulate, control, and confine electromagnetic waves at the nanoscale dimensions. Collective resonances are excited in the periodic lattices of nanoparticles at the wavelength close to the Rayleigh anomaly. Effectively, it occurs at the wavelength equal to the array period or the latter divided by the refractive index of the surrounding medium. In this work, we demonstrate the coupling of multipole modes and quasi-bound states in the continuum with the modes trapped and localized in the nanoparticle array. This behavior is observed due to the suppression of radiative losses and increase in quality factor due to the disappearance of the mode scattering. We show that the combination of different materials in the nanoparticle allows the tuning of electric and magnetic resonances of the nanoparticles and achieving broadband overlap.
This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Los Alamos National Laboratory (Contract 89233218CNA000001) and Sandia National Laboratories (Contract DE-NA-0003525). The work is also supported by Contract DE-2375849.

11:45 AM *EL16.16.06
Non-Local, Non-Linear and Non-Hermitian Nanophotonics Guru V. Naik and Ciril Samuel Prasad; Rice University, United States

Miniaturing optical resonators into meta-atoms and packing them together in meta-devices have revolutionized nanophotonics. Building various meta-atoms have been extensively studied in the past. However, packing them together into meta-devices remains less explored. Quantum many-body effects offer a novel direction in this regard. Here, we discuss two approaches – emulating and integrating quantum many-body systems – to deliver meta-devices exhibiting quantum many-body effects.

Emulating quantum many-body effects in nanophotonics is difficult because nanophotonic resonators only weakly confine light in them. Radiative and often non-radiative losses are not negligible in nanophotonics necessitating non-Hermitian physics. We demonstrated a non-Hermitian metasurface based on passive parity-time symmetry. We coupled a lossy plasmonic resonator with a lossless dielectric resonator to achieve the best of plasmonics and photonics, i.e., enhanced absorption as in plasmonics and high Q-factor as in dielectric photonics. Further, we demonstrated non-trivial topology in this system resulting in robust directional thermal emission. Here, we will discuss the directionality of thermal emission from such metasurfaces. We show that a highly asymmetric thermal emission is possible from a transparent metasurface held at 900 K. Such directional, bright, and spectrally selective thermal light sources could be revolutionary for thermal imaging and efficient thermophotovoltaic energy conversion.

In another approach, we combine quantum materials with nanophotonics to leverage powerful design tools. We study the optical properties of a layered charge-density-wave (CDW) material, 1T-TaS_2 under illumination and electrical bias. We observed a unity-order index change in 1T-TaS_2 under both stimuli. Our investigation showed that charge density wave (CDW) domains reorganize into a different stacking order under a stimulus. As a result, the optical response of this quantum material is not only non-linear but also non-local. We build a non-local model to capture the light-matter interaction in 1T-TaS_2 and other quantum materials and understand the energy landscape of strong correlations in this material. Measuring non-locality could be a non-invasive probe of the quality of a quantum material and thus could catalyze the discovery of functional quantum materials. Further, we demonstrate a tunable 1T-TaS_2-based metasurface with 100% modulation depth, MHz bandwidth, and ultralow-power operation. Such tunable optical devices could be disruptive for emerging imaging and display applications.

In summary, we demonstrate that quantum many-body effects in meta-devices lead to non-local, nonlinear, and non-Hermitian light-matter interaction. Understanding this unique regime of light-matter interaction would unlock novel nanophotonic phenomena leading to meta-devices with unprecedented functionalities.

12:15 PM *EL16.16.07
Intrinsic and Extrinsic Nonlinearities in Epsilon-Near-Zero Adam Ball[1], Dhruv Fomra[1], Samprity Saha[1], Jingwei Wu[1], Ray Secondo[1,2,3] and Nathaniel Kinsey[1]; [1]Virginia Commonwealth University, United States; [2]Azimuth Corporation, United States; [3]Air Force Research Laboratory, United States

Optical materials with a refractive index, and permittivity, that tend towards zero provide quite fascinating optical responses. From emission tailoring and perfect absorption to 'DC-light' and optical tunneling, epsilon-near-zero (ENZ) and near-zero-index (NZI) materials have provided new and interesting methods of manipulating light in a linear fashion. Perhaps to no surprise, the nonlinear properties of these materials are also quite intriguing, having recently been utilized to realize unity-order refractive index tuning, enhanced harmonic generation, and spatio-temporal control over light flow in sub-micron layers. In this talk, we will summarize the origins of the nonlinearities in homogeneous ENZ and NZI materials, focusing on the intrinsic and extrinsic factors on the response. Through this lens we will highlight avenues where such materials are less suited, where they provide unique advantages, and discuss techniques to push these advantages. We will overview our recent experimental works combining high-Q metastructures with ENZ materials as well as dual-pump tailoring of the index and loss profiles. Through this will aim to illustrate the unique benefits of ENZ materials for numerous nonlinear optical applications.

SYMPOSIUM

April 11 - April 25, 2023

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Himchan Cho, Korea Advanced Institute of Science and Technology
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SESSION EL17.01: Hybrid Perovskite Materials, Stability and Devices I
Session Chairs: Lina Quan and Barry Rand
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3006

10:30 AM *EL17.01.01
Heterointerface Materials Science for Perovskite Tandems and Triple-Junctions Edward H. Sargent; University of Toronto, Canada

I will discuss issues at the materials interface (e.g. between active layer, ETL/HBL and HTL/EBL) especially as these relate to constructing perovskite tandem and triple-junction solar cells.

11:00 AM EL17.01.03
Towards Injection Lasing: Intense Electrical & Optical Co-Pumping of Perovskite Light-Emitting Diode Structures Karim Elkhouly[1,2], Iakov Goldberg[1,2], Nirav Annavarapu[1,2], Robert Gehlhaar[1], Weiming Qiu[1], Jan Genoe[1,2] and Paul Heremans[1,2]; [1]imec, Belgium; [2]KU Leuven, Belgium

Metal halide perovskites are a promising candidate as gain medium for a thin-film electrically-pumped laser. This is owing to their excellent optoelectronic properties combining high carrier mobilities and near unity photoluminescence quantum yield. Furthermore, their high optical gain values lead to low amplified spontaneous emission (ASE) thresholds. Encouragingly, optically-pumped lasing has been routinely observed from perovskite-based active layers in different resonator structures, while continuous-wave lasing has been realized not only under cryogenic conditions, but also at room temperature. Moreover, perovskite light-emitting diodes (PeLEDs) show external quantum efficiencies (EQE) values above 1% at high current densities above 1 kA/cm^2. Despite this progress, an electrically-pumped perovskite laser has not been demonstrated so far.

In this work, we demonstrate a novel PeLED architecture that yields low ASE thresholds. At the same time, the device maintains excellent electrical injection properties up to kA/cm^2 current densities. Furthermore, we study the device performance under cryogenic conditions, where we show a 3-fold increase in EQE and more than an order of magnitude lower ASE threshold compared to room temperature operation. These interesting device features allow us to study the response of the PeLED to electrical and optical excitations at different temperatures. Moreover, we study the effect of simultaneous electrical and optical excitation on device performance. Finally, by comparing the device response to optical and electrical excitations, we estimate the threshold current density needed to achieve ASE in our structure. These results pave the way toward a proof-of-concept demonstration of an electrically-pumped perovskite laser.

SESSION EL17.02: Hybrid Perovskite Materials, Stability and Devices
Session Chairs: Tae-Hee Han and Seokhyoung Kim
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3006

2:15 PM EL17.02.02
The Trade-Off Between Efficiency and Electrical Stability in Green Mn^{2+} Doped Perovskite Light-Emitting Diodes Sebastian Fernandez[1], William Michaels[1], Manchen Hu[1], Pournima Narayanan[1], Natalia Murrietta[1], Arynn Gallegos[1], Ghada Ahmed[1], Mahesh Gangishetty[2] and Daniel Congreve[1]; [1]Stanford University, United States; [2]Mississippi State University, United States

While light-emitting diodes (LEDs) made from lead halide perovskites have demonstrated external quantum efficiencies (EQEs) well over 20%, their electrical stability must be addressed before they are seriously considered for commercial applications. In an effort to improve the optoelectronic properties of lead halide perovskites for light emission, many researchers have investigated introducing both alkaline-earth metal ions (e.g., Ba^{2+} and Sr^{2+}) and transition metal ions (e.g., Mn^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+}) into the B-site of the perovskite's ABX_3 structure. Additionally, the factors that limit the electrical stability of perovskite LEDs remain under investigation. In this work, we dope Mn^{2+} ions into an organic-inorganic hybrid quasi-bulk 3D perovskite resulting into $(PEABr)_{0.2}Cs_{0.4}MA_{0.6}Pb_{0.7}Mn_{0.3}Br_3$ thin films with the addition of tris(4-fluorophenyl)phosphine oxide (TFPPO) dissolved in a chloroform antisolvent to achieve an EQE of 13.4% and a peak luminance of 95,400 cd/m^2. While the inclusion of TFPPO into the chloroform antisolvent dramatically increases the EQE of perovskite LEDs, the electrical stability is severely compromised. At an electrical bias of 5 mA/cm^2, our perovskite LED fabricated with a pure chloroform antisolvent (2.5% EQE) decays to half of its initial luminance in 90.68 minutes. Alternatively, our perovskite LED fabricated with TFPPO (13.4% EQE) decays to half of its initial luminance in 2.07 min. In order to investigate this trade-off in EQE and electrical stability, we study both photophysical and electronic characteristics before and after electrical degradation of the perovskite LEDs. We find that given identical electrical degradation conditions, the TFPPO-based device's turn on voltage and overall electrical resistance increases in a much larger fashion as compared to the pure chloroform-based device. While the EQE characteristics of this Mn^{2+} doped perovskite LED show promise for B-site engineered perovskites, there is still large concern to simultaneously achieve both energy-efficient and electrically stable perovskite-enabled lighting. Uncovering the effects from the TFPPO additive on perovskite LEDs will reveal pathways on how to mitigate their negative consequences on electrical stability while retaining their energy-efficiency boosting properties.

2:30 PM *EL17.02.03

Comprehensive Strategies to Increase Electroluminescence Efficiency in Colloidal Metal-Halide Perovskite Nanocrystals Young-Hoon Kim[1], Sungjin Kim[2], Jinwoo Park[2] and Tae-Woo Lee[2]; [1]Hanyang University, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)

As the technology has advanced and the amount of information grows in an information society, display technology needs to show information more vividly and efficiently. In this sense of line, display technology has found a high color purity light emitter, metal halide perovskite, and tried to demonstrate high efficiency light-emitting diodes (LEDs). However, device efficiency of perovskite LEDs is limited by lack of comprehensive materials design strategies both to suppress formation of defects and to enhance charge carrier confinement inside perovskite nanocrystals (PNCs). Here, we report comprehensive strategies that generate smaller, monodisperse colloidal particles (confining electrons and holes and boosting radiative recombination) with fewer surface defects (reducing nonradiative recombination) to demonstrate high efficiency perovskite LEDs.

Firstly, we performed ligand engineerings during the PNC synthesis. We synthesized methylammonium lead bromide ($MAPbBr_3$) and formamidinium lead bromide ($FAPbBr_3$) PNCs with a dimension larger than exciton Bohr diameter (regime beyond quantum size), which have emitting light with size-insensitively high color-purity and constant wavelength, by controlling ligand concentration and ligand length, respectively. Ligand-engineered PNCs can increase photoluminescence quantum efficiency (PLQE) upto 70% by preventing non-radiative recombination of charge carriers and also improve the charge injection/transport capability in PNC films, resulting in external quantum efficiency (EQE) of 5.5% in PNC-LEDs.

Secondly, we conducted crystal engineering on the PNCs. We used substitutional doping of guanidinium (GA) into $FAPbBr_3$ PNCs to incorporate an optimal proportion of GA cations into the structure. The GA cations can reside in the bulk of the PNC in low concentrations (~10%). The surplus GA then accumulates on the surface of the PNC. Guanidinium incorporation provides bulk entropy stabilization, surface stabilization (by additional hydrogen bonding contributed by their extra amino group), and better electron–hole confinement, which results in high PLQE over 90%. A GA to FA ratio of 0.1 was shown to maximize the electroluminescence efficiency. Moreover, a 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (TBTB) overcoat was introduced to heal the residual halide vacancy defects in $FA_{1-x}GA_xPbBr_3$ PNCs and to improve the charge balance in PeLEDs. The result is highly efficient PNC-based LEDs that have current efficiency of 108 cd/A (EQE of 23.4%), which rises to 205 cd/A (EQE of 45.5%) with a hemispherical lens.

Furthermore, we report that highly efficient large-area perovskite LEDs with high uniformity can be realized through the use of colloidal PNCs which decouple the crystallization of perovskites from film formation. PNCs are precrystallized and surrounded by organic ligands, and thus they are not affected by the film formation process, in which a simple modified bar-coating method facilitates the evaporation of residual solvent to provide uniform large-area films. PeLEDs incorporating the uniform bar-coated PNC films achieve an external quantum efficiency (EQE) of 23.26% for a pixel size of 4mm^2 and EQE of 22.5% for a large pixel area of 102mm^2 with high reproducibility and EQE of 21.46% in 900mm^2.

3:00 PM BREAK

3:30 PM EL17.02.04

Enhancing the Performances of Blue Perovskite Light-Emitting Diodes by Controlling the Carrier Injection, Transfer and Confinement Wallace C. Choy; The University of Hong Kong, China

Recently, substantial efforts have been made in enhancing the performances of blue perovskite light-emitting diodes (PeLEDs), and efficiencies over 10% have been achieved. However, the performances still lag far behind with the efficient green, red, and near-infrared PeLED analogs. It is highly desirable to develop highly-performed and stable blue PeLEDs.

In this work, we will improve the performance from quasi-two dimensional (quasi-2D) blue PeLEDs by enhancing the carrier injection, transfer and confinement. To improve the carrier injection, we will suppress the trap states and improve the band alignment of device structure[1]. Then, we will modify introduce mixed quasi-2D perovskite structure to enhance the carrier transfer and narrow the n-phase of quasi-2D perovskites for improving the emission efficiency [2,3]. To further optimize the performance of quasi-2D blue PeLEDs, we systematically study the effects of organic passivating agents with different carbon chain lengths. Our results show that the appropriate carbon chain length of the organic agent simultaneously offer good carrier confinement for the massive radiative recombination within the perovskites, and efficient carrier transfer in quasi-2D perovskites for high emission efficiency. Benefitting from the good optical and electrical properties of TBPO incorporated perovskites, we achieve high-efficient blue PeLEDs with an EQE of 11.5 % and prolonged operational stability of 41.1 min [4]. Consequently, this work contributes the effective approaches to design high-quality perovskite films and efficient blue PeLEDs.

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3:45 PM EL17.02.05

Binary Phase Separation of Quasi-2D Perovskite Light-Emitting Diodes in Mixed-Halide System Seok Joo Yang and Letian Dou; Purdue university, United States

Quasi-two-dimensional (2D) perovskite material has been recently receiving a lot of attention as a light emitter due to its unique quantum-well properties. However, forming undesired multi-quantum-well, called as phase separation, spontaneously occurs in quasi-2D perovskite films since ions can be migrated during the crystallization process. The phase separation produces unexpected emission wavelength, decreases external quantum efficiency (EQE) and stability in light-emitting diode (LED) devices. Therefore, many research groups try to overcome the phase separation using a new design of organic ligands or crystallization kinetics.

In the LED fields, mixing halide ions such as iodide and bromide has widely been used since it can control energy bandgap of the perovskite films. However, mixing halide ions in quasi-2D perovskite films induces phase separation much more than pure halide ions because smaller halide ions in the mixed-halide system have faster ion migration than larger halide ions. In addition, halide segregation also appears in the quasi-2D perovskite film when mixing halide ions. In this work, we define the phase separation and halide segregation as binary phase separation. And our newly designed ligands can suppress the binary phase separations effectively compared to conventional ligands.

Heterogeneity and the phase separation of the mixed-halide quasi-2D perovskite films can be spatially demonstrated using a confocal-photoluminescence (PL) measurement with different ranges of PL wavelengths. The quasi-2D perovskite films using the conventional ligands are suffered from phase separation having small *n* phase and high *n* phase even to three-dimensional phase. Moreover, the halide distribution in mixed-halide quasi-2D perovskite LED devices is analyzed by *in-situ* X-ray fluorescence (XRF). In the *in-situ* XRF mapping, the halide ions in the quasi-2D perovskite film using the conventional ligand are observed to be migrated in operating LED devices, and already segregated before applying bias. On the other hand, well-suppressed the binary phase separation using our ligands can manufacture the quasi-2D perovskite LED have controllable emission wavelength by mixing halide ions and high EQE of over 26% and higher operational stability compared to other quasi-2D perovskite LED devices.

4:00 PM EL17.02.06

Wide-Bandgap Perovskite Quantum Dots in Perovskite Matrix for Sky-Blue Light-Emitting Diodes Ziliang Li[1], Yuan Liu[1], Jian Xu[1], Yitong Dong[1], Bin Chen[1], So Min Park[1], Dongxin Ma[1], Seungjin Lee[1], Jianan Erick Huang[1], Sam Teale[1] and Oleksandr Voznyy[2]; [1]University of Toronto, Canada; [2]University of Toronto, Scarborough, Canada

The emergence of perovskite quantum dots (QDs) has enabled light-emitting diodes (LEDs) with narrowband emission and high external quantum efficiencies (EQEs). Epitaxially growing a perovskite matrix onto perovskite QDs provides robust QD surface passivation and efficient charge transport, thus further boosting luminescence efficiency and operation stability.

Efficient and stable red LEDs have been developed based on $CsPbI_3$ QD-in-perovskite matrix solids[1]. However, the synthesis of this heterostructure has so far remained elusive for wide-bandgap (E_g) perovskite emitters relevant to blue photon sources. The chemical challenge has resided in the paucity of wide-E_g QD:matrix combinations: the identification of the rare pairings that implement type-I band alignment and lattice matching between QDs and matrix.

Here, we report a wide-E_g (>2.6 eV) $CsPbBr_3$ QD-in-perovskite matrix solid that enables efficient sky-blue LEDs[2]. We initiated a wide screen of prospective A-site and B-site alloying candidates and found promising for $CsPb_{1-x}Sr_xBr_3$ as a matrix: it was the sole candidate that minimized lattice mismatch with the blue-emitting perovskite QDs while allowing an E_g of the perovskite matrix larger than that of the QDs.

In light of the hygroscopic nature of Sr^{2+}, we then developed an approach to passivate the surface of the $CsPb_{1-x}Sr_xBr_3$ matrix. By uniting molecular dynamics simulations with experimental efforts, we found that bis(4-fluorophenyl)phenylphosphine oxide (DPPO) strongly coordinates with Sr^{2+} located on the matrix surface and offers sufficient steric hindrance to block H_2O from the atmosphere. As a result, the QD-in-matrix solids exhibit efficient charge transport with enhanced stability. Sky-blue LEDs using this material as the active layer exhibit an EQE of 13.8% and a brightness exceeding 6000 cd m^{-2}.

Reference:

[1] Y. Liu et al, *J. Am. Chem. Soc.* **2021**, 143 (38), 15606–15615
[2] Y. Liu, Z. Li et al, *J. Am. Chem. Soc.* **2022**, 144 (9), 4009–4016.

4:15 PM EL17.02.07

Enhanced Operational Stability of Perovskite Light-Emitting Devices Through Differentiated Ion Motion Jason D. Slinker; The University of Texas at Dallas, United States

Hybrid perovskites are emerging as highly efficient materials for optoelectronic applications. However, their operational lifetime has remained a limiting factor for their continued progress. In thin-film perovskite light-emitting devices, ionic redistribution may distort the perovskite crystal structure, lowering conductivity and light emission due to the formation of vacancies and other traps. Our strategy for enhanced lifetimes involves producing differentiated ion motion within a device with a rational materials blend. The materials selectively move additive ions while restricting the transport of perovskite ions. To accomplish differentiated ion transport with optimal thin-film morphology, we combine a perovskite, a polyelectrolyte such as poly(ethylene oxide), and a salt additive such as $LiPF_6$. The added mobile Li^+ and PF_6^- ions redistribute more favorably than the intrinsic ionic species and largely preserve the inherent structure of the perovskite film. At 0.5 wt% $LiPF_6$, $CsPbBr_3$ devices exhibit 100 h operation at more than 800 cd/m^2 under constant current driving, achieving a maximum luminance of 3260 cd/m^2. Incorporating zero-dimensional perovskite nanocrystals into these devices enhances the lifetime further to a luminance half-life of 129 h at 1530 cd/m^2. We rationalize these findings through optical spectroscopy, impedance spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, and X-ray diffraction.

4:30 PM EL17.02.09

Highly Luminescent Lead-free Cesium Copper Halide Perovskite Nanoplatelets for Luminescent Solar Concentrator Application Junyu Wang[1], Tong Cai[2] and Ou Chen[1]; [1]Brown University, United States; [2]Northwestern University, United States

Luminescent solar concentrators (LSCs) are light-managing devices capable of absorbing and concentrating solar energy to a specific wavelength range and the target region. By coupling with photovoltaic (PV) cells, a PV-LSC system can significantly reduce the total material consumption for solar panel fabrication and simplify the design of large-scale solar harvesting devices for practical utilization. In particular, halide perovskite nanocrystals have shown promising potential for LSC applications due to their excellent optical properties, such as high photoluminescent quantum yield (PLQY), large Stoke's shift, and tunable optical bandgaps. Here, we report the fabrication of high-performance luminescent solar concentrator devices using copper halide perovskite nanoplatelets (NPLs). The $Cs_3Cu_2Cl_5$ perovskite NPLs with high photoluminescence quantum yield (PLQY) and large stock shift are synthesized through a hot-injection method. The NPLs are then deposited onto a polydimethylsiloxane (PDMS) substrate through our recently reported ultrasonic nebulization spray method with a low scattering effect and high average visible transmittance. The obtained LSC devices show a high optical efficiency performance and high-power conversion efficiency for the photons in both UVB and UVC regions, making them an ideal LSC device for capturing and energy conversion of high-energy photons.

SESSION EL17.03: Poster Session I
Session Chairs: Himchan Cho and Tae-Hee Han
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL17.03.01
Controlling Phase Transitions in 2D Perovskites by Organic Cation Alloying Rand L. Kingsford and Connor G. Bischak; The University of Utah, United States

Two-dimensional perovskite quantum wells have emerged as promising materials for optoelectronics applications, including LEDs, nanoscale lasers, and phototransistors. Ruddlesden-Popper (RP) perovskites have monovalent cation spacers and often exhibit a solid-solid phase transition, in which the organic layer undergoes an order-to-disorder transition. This "melting" of the organic layers induces changes in the inorganic layers, impacting the emissive properties of the material. Here, we demonstrate control over the phase transition temperature of RP 2D perovskites by alloying two similar organic cations. Although halide alloying is used regularly to precisely tune electronic properties, cation alloying to control thermodynamic properties has not been explored. By blending hexylammonium (HA) and pentylammonium (PA) cations in different ratios, we can tune the phase transition temperature of 2D perovskites over a large temperature range. We demonstrate this tunability in single crystals and solution-processed thin films. By correlating temperature dependent grazing incidence wide angle X-ray scattering (GIWAXS) and photoluminescence (PL) measurements, we show that the phase transition has a direct impact on the PL intensity. We also directly image this phase transition with temperature-dependent PL imaging to show that the phase transition is highly heterogeneous at the microscale. Overall, our work provides the necessary design principles to control phase transitions in 2D perovskites with the potential to use these materials as dynamically switchable optoelectronic materials.

5:00 PM EL17.03.02
Rational Ligand Pair With Short and Long Ligands to Stable and Efficient Light-Emitting Diodes Ah-young Lee and Myoung Hoon Song; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Even if perovskite nanocrystals (PNCs) have been well known as the defect tolerance in as-synthesized conditions, the unplausible defects are easily formed during the washing procedures. It is because no deep level defect states are generated due to the formation of halide vacancies, while the loss of PbX_2 shell induces the severe degradation of PNCs. Therefore, in the colloidal solution states, only loss of PbX_2 shell visibly deteriorated the performance of PNCs. However, during light-emitting diodes (LEDs) operations, halide vacancies can provide the ion migration pathways, resulting in the rapid degradation of perovskite structures. Simultaneously, Pb^0 states, generated due to electron injection, have been reported as the deep level defect states. Therefore, the rational strategies toward all possible defects are important to enhance the optical properties of PNCs and the performance of PNCs LEDs. Recently, diverse defect passivation strategies have been reported to passivate all possible defect states. General approach toward defect passivation of PNCs might be treatment of surface ligands having suitable functional groups such as ammonium, carboxylate, sulfonate, and so on. However, there is another important consideration to apply the colloidal PNCs into thin films: the binding affinity of surface ligands. Since PNCs have ionic nature, the binding of surface ligands usually has ionic nature, leading ease detachment of surface ligands from the surface PNCs. The easier detachment of surface ligands in colloidal states may induce the surface ligands loss during thin film formation of PNCs, resulting in the severe loss of efficiency of PNCs LEDs. Therefore, there are lots of effort to understand the surface binding affinity of PNCs with DOSY. Several alternatives, such as quaternary ammonium bromide and sulfonate, to replace native ligands have been reported, having higher binding affinity than native ligands. Along with the tightly bound ligands, the optical properties of PNCs are maintained adding of PbX_2 into PNCs during washing process. The addition of PbX_2 during washing can mitigate the loss of PbX_2 shell, maintaining the original photoluminance quantum yield (PLQY).
Bodnarchuk et al. reported treatment of PbX_2 and DDAB improved the colloidal stability of PNCs. The PLQY of $PbBr_2$ and DDAB treated PNCs was maintained in 90% after polar solvent washing process, while PLQY of native ligands was reduced from 60% to 30% after washing. Moreover, perovskite has self-doping properties where the electronic band structure is tuned in the ratio control over the PbX_2 and AX. The band structure tuning is important to the charge injection of LEDs operation. Additionally, the stability of LEDs is one of the important issues in perovskite societies. One of the well-known approaches is B-site metal doping. The formation energy of B-site doped PNCs was enhanced, resulting in the stable PNCs.
In this study, the ratio control over Pb to DDA was conducted to tune the band structure of PNCs. The post-synthetic surface treatment with Pb-DDA was enhanced PLQY from 46% to near unity. Based on the ratio control, highest occupied molecular orbital (HOMO) became shallow with increasing DDA ratio. Further, the charge injection of PNCs with different ratio was measured in hole only devices. The charge injection was best at Pb-DDA2, implying trade-off between energy level and ligand density in charge injection ability. Consequently, the ratio control over Pb to DDA was resulted in highly efficient LEDs, optimizing charge injection. To further enhance the stability of PNCs, additional $NiBr_2$ was treated in PNCs, called Ni-DDA. There was no significant different in PLQY. Finally, LED devices were fabricated to compared Pb-DDA and Ni-DDA. Even if the device efficiencies were similar with each other, the device stability of Ni-DDA was enhanced compared to Pb-DDA.

5:00 PM EL17.03.03
Exploring the Design Rules for Efficient Metal Halide Perovskite Light Emitting Diodes Jiajun Qin, Jia Zhang and Feng Gao; Linkoping University, Sweden

Defect passivation, through decreasing nonradiative recombination rate, has long been considered as the key to efficient perovskite light emitting diodes (LEDs). Here, by revisiting the two commonly used defect passivation strategies, stochiometric ratio tuning and additive engineering, in various perovskite systems, we found its limitations in explaining the superior high performance in light emitting. Surprisingly, a different mechanism other than defect passivation is proved to be responsible for efficient perovskite LEDs. Our low-temperature photoluminescence and ultraviolet photoelectron spectroscopy (UPS) results indicate that these strategies lead to increment of shallow traps and thus p-dope the perovskites. Such p-doping largely enhances the photoluminescence quantum efficiency especially at low carrier density region and can even go beyond 90%. Through carrier dynamics analysis, we point out that the dominant factor responsible for high efficiency in perovskites is the enhancement of radiative recombination via doping rather than defect passivation. Furthermore, this p-doping effect is verified by special device design where poor hole injection results in high external quantum efficiency of perovskite light emitting diodes (PeLEDs). Our discoveries provide design rules to fabricate high-efficiency PeLEDs.

5:00 PM EL17.03.04
Photopatterning of Perovskite Nanocrystals with Photo-Crosslinkable Ligands Evon Ong and Zhi Kuang Tan; National University of Singapore, Singapore

Perovskite nanocrystals (NCs) have emerged as promising luminescent materials for full-colour display applications due to their strong optical properties, widely tunable emission, and narrow full-width half maximum. By precise tuning of their emission spectra, high-resolution full-colour light-emitting diode (LED) arrays can be achieved by micro-patterning red, green, and blue sub-pixels with perovskite NCs as emitters. Currently, photolithography is the most widely used patterning technique in the industry due to its capabilities to achieve high resolution, large area production, and low cost. However, due to the ionic nature of perovskite NCs, conventional photolithography techniques are incompatible as the use of polar solvents can damage underlying perovskite NC patterns, resulting in defect formation and luminescence quenching. Herein, we report a series of novel photo-crosslinkable ligands for the microscale patterning of perovskite NCs. We incorporated photosensitive acrylate groups in the ligands, which upon exposure to ultraviolet light, undergo polymerization and changes the solubility of the NC films. This enables the direct photo-patterning of perovskite NCs without the need for additional photoresist. Through a facile solution-phase ligand exchange process, we functionalized cesium lead halide ($CsPbX_3$) NCs with our photo-crosslinkable ligands. We also demonstrate the photopatterning of 10 µm features on the $CsPbX_3$ NC films via direct laser writing with a 405 nm laser. Our approach offers a versatile strategy for the patterning of perovskite NC films in a simple and cost-effective manner, thus enabling the integration of perovskite NCs in various display applications.

5:00 PM EL17.03.05

External Distributed Feedback Halide Perovskite Lasers Fabricated by High-Throughput UV Nanoimprint Lithography Iakov Goldberg[1,2], Nirav Annavarapu[1,2], Simon Leitner[3], Robert Gehlhaar[1], Karim Elkhouly[1,2], Cedric Rolin[1], Jan Genoe[1,2] and Paul Heremans[1,2]; [1]imec, Belgium; [2]KU Leuven, Belgium; [3]University of Leoben, Austria

Metal-halide perovskites have emerged as promising gain media for lasing applications. In the state-of-the-art, perovskite gain media can be deposited atop a pre-patterned substrate. Alternatively, a negative mould pattern can be directly embedded into the perovskite to form desirable photonic nanostructures. However, conventional thin-film deposition techniques such as spin-coating, vacuum evaporation, etc., exhibit poor conformality and are only marginally compatible with the deposition on textured substrates or above high-aspect-ratio features.

In this work, we present an all-solution fabrication approach of external second-order one-dimensional distributed feedback (1D DFB) gratings by means of soft UV-nanoimprint lithography (UV-NIL). This high-throughput fabrication method can be carried out in the ambient environment, and it requires mild temperatures as low as 70 °C, gentle imprint pressure, and the use of compatible UV-NIL resin that does not attack the chemically fragile methylammonium lead iodide ($MAPbI_3$) perovskite film used in this work. The UV-NIL gratings are isolated from the perovskite layer and are limited to the UV-NIL resin deposited above the perovskite, thus preserving perovskite morphology and low roughness. We show that commercially available UV-NIL products are suitable for a high-fidelity pattern transfer to perovskite-based optical lasers without affecting perovskite optoelectronic properties.

As a result, we reproducibly achieve a single-mode, low-threshold (below 100 $\mu J/cm^2$), narrow linewidth (below 0.2 nm), and strongly polarized (extinction ratio above 50) optically pumped lasing. In addition, we explore characteristic lasing far-field and mode patterns of these 1D DFB gratings. We believe that the proposed resonator integration approach can be extended towards the complete electrically active devices, enabling an alternative integration route towards perovskite injection-lasing.

5:00 PM EL17.03.07

Surface Metallic Lead Passivation of 2D Ruddlesden-Popper Perovskite via Molecular Acceptor Deposition Kitae Kim[1,2], Donghee Kang[1], Sylke Blumstengel[3], Nicolas Zorn Morales[3], Emil J. List-Kratochvil[3,4], Soohyung Park[2], Hyunbok Lee[5] and Yeonjin Yi[1]; [1]Yonsei University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of); [3]Humboldt-Universität zu Berlin, Germany; [4]Helmholtz-Zentrum für Materialien und Energie GmbH, Germany; [5]Kangwon National University, Korea (the Republic of)

Two-dimensional Ruddlesden-Popper (2D RP) perovskites have emerged as promising materials in optoelectronics. The 2D RP perovskites possess significantly improved stability against oxygen, moisture, heat, and ion migration while they still have novel properties such as large exciton binding energies and tunable band gaps. However, 2D RP perovskites suffer significantly from photostability. Photodegradation induces various defects in 2D RP perovskites, such as undercoordinated halide or metal ions like 3D perovskites. The photodegradation of 2D RP eventually leads to the metallic lead (Pb^0), a critical defect for all kinds of lead-based perovskite. The Pb^0 not only plays a role as a deep trap for carrier and exciton transport but also accelerates the degradation process. We employed a strong organic molecular acceptor 2,2′-(perfluoronaphthalene-2, 6-diylidene) dimalononitrile (F6-TCNNQ), to suppress such Pb^0 formed on phenylethylammonium lead iodide (PEA_2PbI_4). We systematically derived the Pb^0 with a blue laser (405 nm) irradiation on PEA_2PbI_4, then deposited the F6-TCNNQ molecules on its surface. *In-situ* X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) measurements showed the changes in Pb^0 states with F6-TCNNQ deposition. Pb^0 on the surface was completely suppressed after the deposition of F6-TCNNQ. It reduced the non-radiative recombination and consequently recovered the photoluminescence slightly. Interestingly, the recovered film showed much-improved photostability by preventing the formation of photoinduced Pb^0. UPS measurements revealed that the Pb^0 is passivated into Pb^{2+} due to the electron transfer from Pb^0 states into F6-TCNNQ, which is the only possible route. Our results provide a new efficient passivation strategy to improve the performance and stability of 2D RP perovskites, suggesting the importance of understanding the charge transfer at the interface.

5:00 PM EL17.03.08

High-Throughput Exploration on the Phase Growth Behaviors in Quasi-2D Formamidinium-Based Perovskites Jonghee Yang and Mahshid Ahmadi; University of Tennessee, United States

Low-dimensional quasi-two-dimensional (2D) perovskites – a mixed structure of 2D and three-dimensional (3D) perovskite lattice – are now the leading materials platform for the demonstration of functional optoelectronics. The dimensional confinements of perovskite lattice by molecular spacer cations and the resulting quantum-well structures bestow their unique functionalities including chemical robustness and strong light-emission properties. Despite its versatility, little has been known on the principle of phase control in quasi-2D perovskites. Herein, by using a robot-based high-throughput automated synthesis platform, we explore the phase formation behaviors of quasi-2D phenethylammonium-formamidinium perovskite system in a wide range of 2D (PEA_2PbI_4):3D ($FAPbI_3$) compositions. We observe that, in contrast to the stoichiometric consideration, incorporation of only 1% of the 3D component provides substantial emergence of n=2 2D phase, which is prominent up to the 3D ratio of 92%; after this composition, 3D-like phases that are more stable than the pristine 3D $FAPbI_3$ mainly emerge. Coupled with hyperspectral cathodoluminescence microscopy, we uncover that thermal annealing is necessary for thin film fabrication of quasi-2D perovskites, but concurrently involves the emergence of PbI_2. Our work provides practical insights into the fundamental principles in 2D perovskite phase control, further benefitting the functionalities of novel materials systems towards sustainable device applications.

5:00 PM EL17.03.09

Transport Layer Engineering Towards Lower Threshold for Perovskite Lasers Jia Zhang, Jiajun Qin, Xiao-Ke Liu and Feng Gao; Linköping University, Sweden

Lead halide perovskites are promising candidates for future lasers as they are proven good gain medium, low-cost solution processable, and exhibit bandgap-tunable luminescence with high color purity and photoluminescence quantum yields. Sandwiching the perovskite layer into transport layers is inevitable during the integration of electrical devices for electrically pumped perovskite lasers. However, the appearance of perovskite/transport layer interfaces is absent in most reported optically pumped perovskite lasers, and is usually considered as detrimental factors to lasing actions. This is why the electrically pumped perovskite lasers are still not realized even with the realization of high injection current densities ($> 1\ \text{kA/cm}^2$) and achievement of optically pumped continuous wave (CW) perovskite lasers at room temperature. Here we report the treatment of perovskite polycrystal thin films with different transport layers effect of transport layers, and the amplified spontaneous emission (ASE) threshold are studied to investigate the influence of perovskite/transport interfaces on lasing actions. We demonstrate largely reduced ASE threshold (22.0%) and enhanced ASE intensity (18.6%) with introducing an additional hole transport layer poly(triaryl amine) (PTAA) on top of perovskite layer. We show that the key role of PTAA layer is to accelerate the hot carrier cooling process from 488 fs to 422 fs by extracting the excess hot holes of perovskites. With suppressed hot holes, the Auger recombination loss is largely reduced, which in turn reduces the ASE threshold. Our work for the first time exemplifies how to further reduce ASE threshold with transport layer engineering. This is critical to maintain the good gain medium properties of perovskites when integrating perovskites into electrical devices and could also have a broader impact on paving the way for future electrically pumped laser fabrication.

5:00 PM EL17.03.12
High-resolution Direct Optical Patterning of Perovskite Nanocrystals Using Photo-induced Ligand Exchange Sun Jae Park, Seongkyu Maeng, Jaehwan Lee and Himchan Cho; KAIST, Korea (the Republic of)

Metal halide perovskite (MHP) nanocrystals have been recognized as a promising material class for next-generation realistic displays, owing to their excellent color purity. To adopt MHP nanocrystals to the next-generation displays (*e.g.*, augmented reality displays) with high-resolution, precise patterning method should be developed to fabricate RGB pixel arrays. However, the traditional photolithography is not suitable for patterning colloidal MHP nanocrystals since the solvent in photoresist often results in the degradation of the emissive properties of MHP nanocrystals. Direct optical patterning is a photoresist-fee method to pattern MHP nanocrystals, which uses the change in solubility due to a chemical reaction upon light source irradiation. However, the photo-induced chemical reaction often affects the passivation of MHP nanocrystals which is critical in maintaining the photoluminescence quantum yield throughout the patterning process. Herein, we propose a nondestructive photo-induced in-situ ligand exchange mechanism for direct optical patterning of colloidal MHP nanocrystals. The MHP nanocrystals became photosensitive with thiol additives; high-resolution 2-µm line patterns of MHP nanocrystals were achieved without compensating the emissive properties, which is due to the effective passivation of in-situ-exchanged thiolate ligands. The patterning mechanism was in-depth investigated by analyzing the surface properties of MHP nanocrystals at each patterning step.

5:00 PM EL17.03.13
Direct Optical Patterning of Colloidal InP-based Quantum Dots Using Photoacid Generators Jaehwan Lee and Himchan Cho; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Direct optical patterning of colloidal nanomaterials has recently received a lot of attention because of photoresist-free simple patterning procedure. The use of photoacid generator (PAG) additive has been studied as one of the promising approaches for direct optical patterning of colloidal quantum dots (QDs). With PAG, high-resolution QD patterning without complete ligand exchange is enabled. However, direct optical patterning of QDs with PAG may result in decrease in photoluminescence quantum yield (PLQY) in case of insufficient surface passivation of patterned QDs. Furthermore, such PLQY decrease could be enhanced for colloidal InP-based QD, which has high oxophilicity. Therefore, systematic and fundamental studies to achieve high-resolution InP-based QD patterns while minimizing the surface damage are required. Here, we show high-resolution direct optical patterning of InP-based core/shell QDs using a triazine-based photoacid generator. We investigate the changes in optical and structural properties of the core/shell QDs with each patterning step. Also, our study involves ligand post-treatment for the PLQY recovery of patterned InP QDs. The post-treatment passivated the surface defects and thereby increased the PLQY of InP QDs by ~90%. We believe our study suggests a facile way of patterning air-sensitive colloidal nanomaterials for various electronic and optoelectronic applications.

5:00 PM EL17.03.14
Methoxy Functionalized Conjugated Passivation Ligand for Efficient Perovskite Light Emitting Diodes Xinwen Sun[1], Kwan Ho Ngai[1], Jianbin Xu[1] and Mingzhu Long[2]; [1]The Chinese University of Hong Kong, Hong Kong; [2]South China Normal University, China

Due to the advantages such as exceptional optoelectronic properties, readily tunable emission, high photoluminescence quantum efficiency (PLQE), narrow emission bandwidth, and solution processability, metal halide perovskites are attractive for applications in light-emitting diodes (LEDs). Despite the halide perovskite LEDs (PeLEDs) have achieved high external quantum efficiency (EQE) of above 20%, there are still many issues to be further investigated in the process of promoting the industrialization of PeLEDs. Unfortunately, the solution-processed polycrystalline perovskite films suffer from severe trap-mediated non-radiative recombination and ion migration. A tremendous amount of effort has been carried out to improve the performance of PeLEDs, including blocking iodide ion migration by strengthening the space restriction on carriers, preparing high-quality crystalline perovskites, and forming interface engineering between the ETL and the perovskite light-emitting layer. Since both ion migration and non-radiative recombination are highly related to the defects in perovskites, defect passivation is essential to achieve efficient and stable PeLEDs. Although ligand-assisted mediation has proven to be a useful method for passivating the imperfections of PeLEDs, the control strategy of alkyl chain length and the electron donating ability of the ligands bring great challenge to rational passivation. Herein, by considering the electron donating ability for the defect passivation efficiency and steric hindrance for the crystallization process, we find that methoxy group can be introduced to phenethylammonium molecular served as an efficient additive, namely 4-methoxy-phenethylammonium (4-MeO-PEA) to facilitate defect passivation process in perovskite light-emitting materials. We have demonstrated that the 4-MeO-PEA agent can substantially increase the crystal orientation, enlarge the crystalline grain size and mitigate the defect centers through strong bonding between the methoxy group with Pb ions. The external quantum efficiency (EQE) value of the PeLEDs with optimized passivation reaches to a maximum of 21.57%, which is one of the best records in the near infrared PeLEDs (~790 nm emission peak) to date. In addition, a threefold increase in the T_{50} operational time of the devices is observed, compared to the control samples. The findings provide a simple and effective strategy to produce highly efficient perovskite films and to devise the high-performance optoelectronics devices.

The work is in part supported by Research Grants Council of Hong Kong, particularly, via Grant Nos. N_CUHK438/18, and CUHK Group Research Scheme.

5:00 PM EL17.03.15
Optimizing the Quasi-Equilibrium State of Hot Carriers in All-Inorganic Lead Halide Perovskite Nanocrystals Through Mn Doping—Fundamental Dynamics and Device Perspectives Jie Meng and Kaibo Zheng; Lund University, Sweden

Hot carrier (HC) cooling accounts for the significant energy loss in lead halide perovskite (LHP) solar cells. Here, we study HC relaxation dynamics in

Mn-doped LHP $CsPbI_3$ nanocrystals (NCs), combining transient absorption spectroscopy and density functional theory (DFT) calculations. We demonstrate that Mn^{2+} doping (1) enlarges the longitudinal optical (LO)–acoustic phonon bandgap, (2) enhances the electron–LO phonon coupling strength, and (3) adds HC relaxation pathways via Mn orbitals within the bands. The spectroscopic study shows that the HC cooling process is decelerated after doping under band-edge excitation due to the dominant phonon bandgap enlargement. When the excitation photon energy is larger than the optical bandgap and the Mn^{2+} transition gap, the doping accelerates the cooling rate owing to the dominant effect of enhanced carrier–phonon coupling and relaxation pathways. We demonstrate that such a phenomenon is optimal for the application of hot carrier solar cells. The enhanced electron–LO phonon coupling and accelerated cooling of high-temperature hot carriers efficiently establish a high-temperature thermal quasi-equilibrium where the excessive energy of the hot carriers is transferred to heat the cold carriers. On the other hand, the enlarged phononic band-gap prevents further cooling of such a quasi-equilibrium, which facilitates the energy conversion process. Our results manifest a straightforward methodology to optimize the HC dynamics for hot carrier solar cells by element doping.

SESSION EL17.04: Colloidal Quantum Dots, Patterning and Devices I
Session Chairs: Himchan Cho and Young-Hoon Kim
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3006

8:00 AM *EL17.04.01
Colloidal Quantum Dot Laser Diodes Victor I. Klimov; Los Alamos National Laboratory, United States

Electrically pumped lasers or laser diodes based on solution-processable materials have been long-desired devices for their compatibility with virtually any substrate, scalability, and ease of integration with on-chip photonics and electronics. Such devices have been pursued across a wide range of materials including polymers, small molecules, perovskites, and colloidal quantum dots (QDs). The latter materials are especially attractive for implementing laser diodes as in addition to being compatible with inexpensive and easily scalable chemical techniques, they offer multiple advantages derived from a zero-dimensional character of their electronic states. These include a size-tunable emission wavelength, a low optical-gain threshold, and high temperature stability of lasing characteristics stemming from a wide energy separation between their atomic-like discrete energy levels.

Several challenges complicate the realization of colloidal QD laser diodes (QLDs). These include extremely fast nonradiative Auger recombination of optical-gain-active multicarrier states, poor stability of QD solids under high current densities required to achieve lasing, and unfavorable balance between optical gain and optical losses in electroluminescent (EL) devices wherein a gain-active QD medium is a small fraction of the overall device stack comprising multiple optically-lossy charge-transport layers.

Here we resolve these challenges and achieve electrically driven laser action due to amplified spontaneous emission (ASE) in a colloidal-QD optical-gain medium. To demonstrate this effect, we employ compact, continuously graded QDs with strongly suppressed Auger recombination incorporated into a low-loss photonic waveguide integrated into a pulsed, high-current density light-emitting diode. These prototype QLDs exhibit strong, broad-band optical gain and demonstrate low-threshold, room-temperature laser action which leads to intense edge-emitted EL with intensity of more than 100 microwatts.

8:30 AM *EL17.04.02
Synthesis of Novel Quantum Dot Emitters in Molten Inorganic Salts Aritrajit Gupta, Wooje Cho, Ruiming Lin, Zirui Zhou, Justin Ondry and Dmitri V. Talapin; University of Chicago, United States

Many functional nanomaterials used for catalysis, healthcare, solid-state lighting, and displays are synthesized by colloidal techniques. The scope of chemical transformations accessible to colloidal chemists is determined by the stability and compatibility of solvents and surfactants used as a reaction medium. For example, very few traditional solvents can handle temperatures above 400C, while many inorganic phases require even higher temperatures to form. We are developing comprehensive understanding of a novel class of colloidal systems, colloids in molten inorganic salts. Nanoparticles of different transition metals, semiconductors, oxides, and magnetic materials can form true colloids in molten inorganic salts. The colloidal stability of nanoparticles in molten salts could not be explained by traditional electrostatic and steric stabilization mechanisms. Our experimental and computational studies point to the importance of the long-range ion correlations in the molten salt near the nanocrystal interface.
In addition to the fundamental exploration of new colloidal systems, molten salts expand the boundaries for solution synthesis of many nanomaterials that have been out of reach for colloidal chemists. We have used molten salts to synthesize colloidal GaAs, $In_xGa_{1-x}As$, $In_xGa_{1-x}P$ and GaN quantum dots, which resisted numerous synthetic attempts for over two decades. By further developing colloidal chemistry in molten salts, we hope to enable synthetic routes toward various functional nanomaterials previously considered unsynthesizable by colloidal methods.

9:00 AM DISCUSSION TIME

9:30 AM EL17.04.04
The Dynamics of Reversible Hole Trapping in InP/ZnSe/ZnS Quantum Dots Paul Cavanaugh[1], Anne Myers Kelley[1], Christian Ippen[2], Haochen Sun[1], Ilan Jen-La Plante[2], Maria Bautista[2], Ruiqing MA[2], Xudong Wang[2] and David F. Kelley[1]; [1]University of California Merced, United States; [2]Nanosys Inc, United States

The presence of impurities or defects in most quantum dots leads to irreversible carrier trapping. However, high quality InP/ZnSe/ZnS quantum dots (QDs) behave very differently. In this case, excess indium in the ZnSe shell of gives rise to hole traps that are transiently populated following photoexcitation. This leads to a slow (hundreds of picoseconds to nanoseconds) photoluminescence (PL) risetime.[1] Equilibrium between these traps, which are optically dark, and the emissive valence-band state also results in delayed emission and therefore longer PL lifetimes. The radiative lifetime can be varied from 32 to 48 ns, depending on the density of traps. Transiently trapped holes also affect the biexciton kinetics, allowing for variation of the electron versus hole Auger excitation ratios under high flux. In addition, the amplitude and time scale of the slow PL rise and the delayed emission time can be varied by different treatments of the InP cores prior to shell deposition, as indicated by resonance Raman spectroscopy. The Raman spectra are interpreted in terms of different radial distributions of the indium-based hole traps which can be related to differences in the interfacial lattice strain. Modulating the core/shell interface can also create interfacial dipoles varying the trap depth, in extreme cases leading to 10% of the photoluminescence coming from repopulation of the band edge by deep traps that occurs on the microsecond timescale.[2]
Several possible chemical and structural assignments of the traps are considered, and a substitutional indium adjacent to a zinc vacancy, In^{3+}/VZn^{2-} , is found to be the most likely.[3] This assignment is consistent with the observation that trapping occurs only when the QD has excess indium and is supported

by experiments showing that the addition of zinc oleate or acetate decreases the extent of trapping, presumably by filling some of the vacancy traps. We also show that addition of alkyl carboxylic acids causes increased trapping, presumably by creation of additional zinc vacancies.
This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Award Number DE-EE0009164 and NSF CHE-1506803.

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9:45 AM EL17.04.05
Origins of Red Emission from ZnS:Cu Colloidal Nanocrystals and Potential Applications for Quantum Information Science Sarah M. Thompson[1], Cuneyt Sahin[2], Shengsong Yang[1], Michael Flatté[3], Christopher B. Murray[1], Lee Bassett[1] and Cherie R. Kagan[1]; [1]University of Pennsylvania, United States; [2]Bilkent University, Turkey; [3]The University of Iowa, United States

Colloidal ZnS:Cu nanocrystals (NCs) are prototypical colloidal nanophosphors in bio-imaging and optoelectronic applications thanks to their bio-compatibility and broadly tunable luminescence properties. Visible luminescence from ZnS:Cu colloidal NCs is typically dominated by green and blue peaks (denoted G-Cu and B-Cu), with observations of red (R-Cu) luminescence from nanocrystalline ZnS:Cu remaining extremely limited. Here, we present a synthetic method for obtaining colloidal ZnS:Cu NCs that emit primarily R-Cu. We use time- and temperature-resolved luminescence spectroscopies to study the emission mechanism, which provides advanced knowledge of the electronic structure produced by defects in ZnS:Cu that is critical for controlling the luminescence properties of this material. We also discuss the applicability of colloidal nanocrystals containing color centers to quantum information science, where electronically isolated defect states can serve as optically addressable spin qubits.

10:00 AM BREAK

10:30 AM *EL17.04.06
Semiconductor Nanocrystal Optoelectronics Using Colloidal Quantum Wells for Lighting and Displays Hilmi Volkan Demir[1,2]; [1]Nanyang Technological University, Singapore; [2]Bilkent University, Turkey

Lighting and displays are integral parts of human activities and economic development. Semiconductor nanocrystals, now offering a market volume exceeding 1 Billion Euros annually, have attracted great interest in quality lighting and displays in the last decade. Such colloidal semiconductors enable enriched color conversion essential to superior lighting and displays. These colloids span different types and heterostructures of semiconductors, starting in the form of colloidal quantum dots and most recently extending to the latest sub–family of nanocrystals, the colloidal quantum wells. In this talk, we will present most recent examples of photonic structures and device architectures using the colloidal quantum wells for lighting and displays. Also, we will present a powerful, large–area self–assembly technique for orienting these colloidal quantum wells either all face down or all edge up. We will demonstrate three–dimensional constructs of their oriented self–assemblies with monolayer precision. Finally, we will show record high–efficiency colloidal LEDs of these quantum wells employed as the electrically–driven emitter layer. Given their current accelerating progress, these solution–processed quantum wells hold great promise to challenge their epitaxial thin–film counterparts in semiconductor optoelectronics in the near future.

11:00 AM EL17.04.07
Tuning Phonon Energies in Nanocrystals for Enhanced Nonlinearity and Upconversion Emory Chan, Artiom Skripka and Zhuolei Zhang; Lawrence Berkeley National Laboratory, United States

Optical applications of lanthanide-doped nanoparticles require materials with low phonon energies to minimize nonradiative relaxation and promote nonlinear processes like upconversion. Heavy halide hosts offer low phonon energies but are challenging to synthesize as nanocrystals. Here, we demonstrate size-controlled synthesis of low-phonon-energy potassium lead halide nanoparticles and the ability to tune nanocrystal phonon energies. These nanoparticles are moisture resistant and can be efficiently doped with lighter lanthanides. The low phonon energies of these nanoparticles promote upconversion emission from higher lanthanide excited states and enable highly nonlinear, avalanche-like emission when doped with neodymium ions. The realization of nanoparticles with tunable, ultra-low phonon energies facilitates the discovery of nanomaterials with phonon-dependent properties, precisely engineered for applications in nanoscale imaging, sensing, luminescence thermometry and energy conversion.

11:15 AM EL17.04.08
Low Dimensional Perovskite for Wearable Optoelectronics Xiwen Gong; University of Michigan, United States

Multifunctional skin-interfaced electronics is one of the most anticipated medial Internet of Things (IoT) technologies that enables non-invasive collection of high-quality data on biological activity. This is realized thanks to their wearability and conformal coverage of our body. Building on these data and recent advances in deep learning, artificial intelligence-based bioimaging, diagnosis, and therapy will be performed with higher accuracy and speed than ever before. Furthermore, skin-like multifunctional sensors are revolutionizing the technologies and applications of soft robotics. This talk will first focus on the current knowledge gap in designing intrinsically deformable optoelectronic materials using low dimensioal perovskite. We will then discuss new material design strategies to achieve mechanical deformability in perovskite optoelectronic material and devices.

11:30 AM EL17.04.09
Room-Temperature Distributed Feedback $CsPbBr_3$ Perovskite Lasers Integrated on Silicon Nitride Waveguide Platform Federico Fabrizi[1,2], Piotr Cegielski[1], Manuel Runkel[3], Saaed Goudarzi[2], Cedric Kreusel[3], Bartos Chmielak[1], Stephan Suckow[1], Thomas Riedl[3], Surendra B. Anantharaman[1] and Max C. Lemme[2,1]; [1]AMO GmbH, Germany; [2]RWTH Aachen University, Germany; [3]Bergische Universität Wuppertal, Germany

Lead halide perovskites are solution processable semiconductors, which have shown promise for applications in solar cells and light emitting diodes. Further, the feasibility of device fabrication at low- temperature (100 °C) opens the door to explore new opportunities on integrated lasers on-chip, waveguide lasers on the silicon nitride (Si_3N_4) platform [1] and other electro-optical modulators [2]. However, perovskites have much higher refractive indices ($n = 2.3$-2.6) than that of a typical Si_3N_4 waveguide ($n = 2$). Such a contrasting refractive index at the perovskite/Si_3N_4 interface makes it challenging to extract light from the perovskite lasers. In this work, we address this challenge by using the perovskite as the emission medium and the Si_3N_4 as the cavity medium. Upon optical pumping, photons emitted from the perovskite couple to the cavity via the evanescent field for light amplification leading towards lasing on-chip ([1], [2]).

In this study, the cesium lead bromide ($CsPbBr_3$) thin film (90 nm) is used as a laser gain medium and Si_3N_4 as a distributed feedback (DFB) medium. The DFB constitutes of a 200 nm thick Si_3N_4 rib waveguide with a quarter-wavelength shifted first-order grating structure etched directly into the Si_3N_4 waveguide. Using a finite difference time domain simulation (Lumerical software), the grating dimensions and the cross-section of the Si_3N_4 waveguide was optimised to maximize the effective refractive index of the waveguide mode. The mode overlap between the perovskite film and Si_3N_4 waveguide mode was identified to be ~24%. Using the optimised configuration obtained from the simulation studies, our experiments were designed to realise the perovskite DFB lasers on a 6” Si wafer with 2.3 µm of thermally grown SiO_2. The experimental workflow to achieve a high-quality DFB system will be presented. 90 nm thick $CsPbBr_3$ film was spin coated on the DFB structure followed by a planar hot process to reduce the grain boundary defects [3]. The perovskite film was patterned as reported previously ([1], [3]) and encapsulated with a 1 µm thick PMMA protective layer. The device was optically pumped using a 300 nm pulsed excitation source with 300 ps pulse width and 1 kHz repetition rate at room temperature. At low excitation fluence, the weak photoluminescence signal showed a broad linewidth (16 nm). With increasing pump fluence, a single peak with ultranarrow linewidth (0.24 nm) was observed. An S-shaped curve for the emission intensity vs pump fluence confirming a clear sign of lasing with a threshold power density of 775 $\mu J/cm^2$ will be presented. Further, the change in the emission wavelength upon varying the grating periodicity and etch depth will be presented. Our work demonstrates a DFB $CsPbBr_3$ laser on a silicon nitride waveguide platform operating at room temperature, which opens new avenues for integrated optoelectronics.

Acknowledgments: This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 956270 and NRW project PEROVSKET funding code No EFRE-0801508.

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11:45 AM EL17.04.10
Lasing Threshold Overestimation in Optical Pumping of Metal Halide Perovskites Jiajun Qin, Jia Zhang and Feng Gao; Linkoping University, Sweden

The threshold carrier density, conventionally evaluated from optical pumping, is a key reference parameter towards electrically pumped lasers, with the widely acknowledged assumption that optically excited charge carriers relax to the band edge through an ultrafast process. However, characteristically slow carrier cooling in perovskites challenges this assumption. Here, we investigate the optical pumping of state-of-the-art bromide- and iodine-based perovskites. We find that the threshold decreases by one order of magnitude with decreasing the excitation energy from 3.10 eV to 2.48 eV for methylammonium lead bromide perovskite ($MAPbBr_3$), indicating that the low-energy photon excitation facilitates faster cooling and hence enables efficient carrier accumulation for population inversion. Our results are then interpreted due to coupling of phonon scattering in connection to the band structure of perovskites. This effect is further verified in two-photon pumping process, where the carriers relax to the band edge with a smaller difference in phonon momentum that speeds up the carrier cooling process. Furthermore, by extrapolating the optical pumping threshold to the band edge excitation as an analog of electrical carrier injection to the perovskite, we obtain a critical threshold carrier density of $\sim 1.9 \times 10^{17}$ cm^{-3}, which is one order of magnitude lower than that estimated from the conventional approach. Our work thus highlights the feasibility of metal halide perovskites for electrically pumped lasers.

SESSION EL17.05: Colloidal Quantum Dots, Patterning and Devices II
Session Chairs: Wallace Choy and Xiwen Gong
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3006

1:30 PM *EL17.05.01
Toward Halide Perovskite Laser Diodes Noel C. Giebink; The Pennsylvania State University, United States

Metal halide perovskites have emerged as promising gain media with the potential to realize wavelength-tunable, non-epitaxial laser diodes. This talk will focus on recent progress toward this goal, including continuous-wave optically-pumped lasing from methylammonium lead iodide ($MAPbI_3$), the operation of $MAPbI_3$ LEDs at ~kA/cm^2 current densities, distributed feedback $MAPbI_3$ LEDs that lase under optical pumping, and combined electrical+optical pumping experiments that demonstrate a reduction in the optical threshold for amplified spontaneous emission when the optical pulse overlaps in time with a 3 ns electrical pulse injecting >1 kA/cm^2 at low temperature.

2:00 PM EL17.05.02
Morphology-Controlled Synthesis of Ruddlesden-Popper Nanowires of Monolayered Lead Bromide Perovskite Seokhyoung Kim; Michigan State University, United States

Layered two-dimensional organic-inorganic hybrid perovskites (OIHPs) are promising materials for light emitting purposes owing to their higher exciton binding energies compared to the three-dimensional lattices. Stacking of the 2D layers into ordered phases such as Ruddlesden-Popper phase with well-formed external morphologies is expected to create nanostructures that will bring in nano-confined optical properties while maintaining the quantum-confined electronic nature of layered perovskite sheets. Coupling band excitons with optical cavity modes, for example, has been exploited in nanowires (NWs) and nanoplatelets of 3D perovskites to enable ultra-small, low-threshold lasers. The cavity-coupled light emission is expected to experience a substantial enhancement if the nanostructures are made of layered 2D perovskite sheets. In this presentation, I will show the morphology-controlled synthesis of NWs of monolayered butylammonium lead bromide, $(C_4H_9NH_3)PbBr_4$, via chemical vapor deposition (CVD). We have systematically investigated the morphological outcomes with independent growth parameters including source temperatures, reactor pressure, and gas flow rates, which is well-summarized in a morphology phase diagram. Structural, elemental, crystallographic analyses will be presented to validate the quality of our NWs. We have observed a sharp, quantized absorption around 400 nm and strong photoluminescence at 405 nm, an indication of the presence of layered $(C_4H_9NH_3)PbBr_4$ sheets. I will present time-resolved photoluminescence and variable-temperature measurements to show stronger exciton binding characteristics in NWs of 2D $(C_4H_9NH_3)PbBr_4$ than of 3D CsPbBr3. Lastly, I will share the amplified light emission behaviors of the NWs upon pulsed excitation. Our NWs of layered OIHPs present potential to develop ultra-compact, coherent ultraviolet and visible light sources.

2:15 PM EL17.05.03
Spin-Exchange Carrier Multiplication in Manganese-Doped Colloidal Quantum Dots Ho Jin[1,2], Clement Livache[1], Whi Dong Kim[1] and Victor I. Klimov[1]; [1]Los Alamos National Laboratory, United States; [2]The University of New Mexico, United States

During carrier multiplication (CM) a high-energy, 'hot' electron or hole relaxes within the same band by creating new electron-hole (e-h) pairs.[1] This occurs via one or more impact ionization events whereby a pre-existing valence-band electron is excited to the conduction band after an Auger-type collision with a high-energy carrier. In principle, CM could improve the performance of a variety of optoelectronic, photovoltaic (PV) and photocatalytic devices because due to this process, the quantum efficiency of photon to e-h pair conversion (*Q*eh) becomes greater than one.[2,3] However, practically realized CM efficiencies are still not sufficiently high to achieve an appreciable boost in device performance, suffering from the high CM threshold ($h\nu_{th}$) and the high e-h pair creation energy (e_{eh}).
The use of engineered colloidal quantum dots (QDs) allows one to reduce $h\nu_{th}$ down to the energy-conservation-defined value of $2E_g$.[4] However, e_{eh} is not appreciably decreased compared to bulk solids. To reduce e_{eh}, one needs to increase the energy-gain rate associated with Coulomb collisions versus the phonon-related energy-loss rate. Here, to accomplish this objective, we exploit not 'direct' but ultrafast 'spin-exchange' Coulomb interactions in magnetically doped QDs.[5,6] For this purpose, we synthesize Mn-doped core/shell PbSe/CdSe QDs wherein the dopants exhibit strong spin-exchange coupling to both CdSe and PbSe QD components. By applying transient photoluminescence measurements, we observe a highly efficient excitation transfer from the light-harvesting CdSe shell to the Mn dopants, which is followed by a CM-like spin-exchange process which leads to generation of two core excitons. Due to spin conservation, the biexciton produced via relaxation of the excited Mn ion is a combination of a dark and a bright exciton (spins 1 and 0, respectively) in two different L-valleys of PbSe. The corresponding quantum efficiency measured at $2.5E_g$ is ~140%, almost three-fold enhancement versus undoped QDs, implying that the e-h pair creation energy is less than $1.25E_g$. This is near the fundamental one-bandgap limit and is also considerably smaller (a factor of >2.5) than for the reference undoped QDs. These results suggest that the use of spin-exchange interactions represents a viable approach for realizing highly efficient CM-enhanced solar-photoconversion schemes.

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2:30 PM BREAK

3:00 PM *EL17.05.04
Photostable Wide Bandgap Metal Halide Perovskites Annamaria Petrozza; Istituto Italiano di Tecnologia, Italy

Bandgap tuning is a crucial characteristic of metal-halide perovskite, with benchmark lead-iodide compounds having a bandgap of 1.6 eV. To increase the bandgap up to 2.0 eV a straightforward strategy is to partially substitute iodine with bromine in so-called mixed-halide lead perovskites. Such compounds are prone, however, to defect-induced halide segregation resulting in bandgap instabilities, which limits their application in tandem solar cells and a variety of optoelectronic devices. The optimization of the perovskite composition and surface passivating agents can effectively slow down, but not completely stop, such light-induced instabilities. Here we identify the defect and the intra-gap electronic state that triggers the material transformation and bandgap shift. It allows us to engineer the perovskite band edge energetics to radically deactivate the photo-activity of such defects and stabilize the perovskite bandgap over the entire spectral range above 1.6 eV. Then, I will discuss how the generation of I2 in mixed-halide perovskites under illumination has a crucial role in halide segregation. In fact, I2 reacts with bromide (Br−) in the lattice to form a trihalide ion I2Br-, which mediates a Br−/I− ion exchange reaction and the formation of an I-rich phase. Importantly, we observe that the efficiency of the process is highly dependent on the binding strength of the bromide within the crystalline structure. Based on this, we propose a general paradigm where an iodine redox based model rationalizes the initiation and growth of halide photo-segregation. Thus, we show how the design of the chemical composition of the metal-halide perovskite crystalline unit can stabilize the semiconductor bandgap, and eventually the performance of related solar cells, not only acting on the reduction of the density of native defects, but stabilizing the elemental composition of the perovskite crystalline unit. This is demonstrated by the fabrication of photo-stable purely inorganic CsPbI1.5Br1.5 solar cells.

3:30 PM *EL17.05.05
Circularly Polarized Photoluminescence with Spin Selectivity Through Rashba Band Structures and Chiral Structures in Hybrid Perovskites Bin Hu; University of Tennessee, United States

Circularly polarized photoluminescence (CPL) have been observed in organic-inorganic hybrid perovskites. In general, CPL require the orbital momentum in light-emitting states that can be circularly polarized by a photoexcitation and substantially conserved within PL lifetime. Both chiral structures and Rashba band structures can fulfill this requirement: generating circularly polarizable orbitals with sufficient conservation time constant to develop CPL. In chiral structures, our experimental studies found that light-emitting states establish chirality dynamics with ultrafast response (< picoseconds) and then conserve their circular polarization up to nanoseconds, enabling CPL. This provides a circular polarizer functionality in light emission shown in chiral structures. Furthermore, spin scattering between circularly polarized light-emitting states can shorten the conservation time constant of circularly polarized orbitals, decreasing CPL. This indicates that spin interaction between circularly polarized orbitals plays an important role in developing CPL. In Rashba band structures, we found that left-hand and right-hand circularly polarized orbitals can be optically operated between spin-up and spin-down bands to generate selective CPL by using circularly polarized photoexcitation. Moreover, we found that spin polarizations can directly interact with circularly polarized orbitals in Rashba band structures through spin-exchange coupling, generating spin-switchable phenomena in 2D-superlattice perovskites. This demonstrates switchable CPL between left-hand and right-hand circular polarizations when changing spin polarizations between positive and negative magnetic field directions. This indicates that the spin-exchange coupling functions as the key parameter towards developing CPL in Rashba band structures in hybrid perovskites.

4:00 PM EL17.05.06
Optical Properties of Binary Nanocrystal Superlattices Produced by Assemblies of Strongly and Weakly Confined $CsPbBr_3$ Perovskite Nanocrystals Grigorios Itskos[1], Modestos Athanasiou[1], Andreas Manoli[1], Marios Sergides[1], Taras Sekh[2,3], Etsuki Kobiyama[4], Rainer Mahrt[4], Maryna Bodnarchuk[2,3], Thilo Stoeferle[4], Maksym V. Kovalenko[2,3] and Andreas Othonos[1]; [1]University of Cyprus, Cyprus; [2]ETH Zürich, Switzerland; [3]Empa–Swiss

Federal Laboratories for Materials Science and Technology, Switzerland; [4]IBM Research Europe – Zurich, Switzerland

Periodicity in long range-ordered nanocrystal superlattices (NC SLs) can be exploited to alter or even tailor the properties of the individual NC building blocks while generating new collective electronic and optical phenomena as a result of the enhanced interactions between NCs. Perovskite NCs have emerged as highly attractive building blocks for SLs, based on their facile fabrication as sharp, monodisperse cubes as well as due to the observation of superfluorescence from single and multi-component perovskite NC superstructures.
Binary superlattices of the ABO$_6$ type, produced via self-assemblies of CsPbBr$_3$ NCs with sizes in the strong (~5 nm) and weak (~18 nm) confinement regime are being demonstrated for the first time. We discuss the optical properties of such binary SLs, focusing on the electronic interactions between the strongly and weakly-confined NC excitons. Transient photoluminescence and absorption measurements indicate efficient depletion of the small NC exciton population at the few to tens of ps scale; a concomitant delay of the transient absorption rise time signal of the large NC exciton bleaching is also observed. Such results are consistent with a highly efficient energy transfer process from the small to the large NCs within the binary superstructure. On-going experiments are investigating whether the fast energy funneling into the weakly confined NC excitons can compete and influence the characteristics and dynamics of the superfluorescence observed in such binary perovskite SLs.

4:15 PM EL17.05.07
Direct Optical Patterning of Colloidal Nanocrystals Jia-Ahn Pan[1,2], Emory Chan[1] and Dmitri V. Talapin[2]; [1]Lawrence Berkeley National Laboratory, United States; [2]The University of Chicago, United States

Colloidal nanocrystals (NCs) have emerged as a diverse class of materials with tunable composition, size, shape, and surface chemistry. From their facile syntheses to their unique optoelectronic properties, these solution-processed NCs are a promising alternative to materials grown as bulk crystals or by vapor-phase methods. However, the use of NCs in real-world devices is often held back by challenges in depositing them as a patterned two-dimensional layer. Alternative approaches to patterning colloidal NCs need to be established to aid the transition from individual devices to integrated optoelectronic circuits, multi-color NC displays, and nanophotonic devices. This talk will focus on the development of photo-chemical methods that enable direct optical lithography of colloidal nanocrystals. We will discuss various light-sensitive ligands and their suitability for patterning various NCs including lead halide perovskite NCs, semiconducting quantum dots, metal oxide nanoparticles, and lanthanide-doped upconverting NCs. We will show that this patterning approach preserves many of the desirable properties of the NCs, such as high photoluminescence, good charge transport, and high refractive index. Ultimately, this work aims to expediate the implementation of colloidal NCs in a broader range of functional devices.

4:30 PM EL17.05.09
***In Situ* Core/Shell Perovskites for Ultra-Bright, Efficient and Stable Light-Emitting Diodes** Joo Sung Kim[1], Jung-Min Heo[1], Gyeong-Su park[1], Seung-Je Woo[1], Changsoon Cho[2], Hyung Joong yun[3], Dong-Hyeok Kim[1], Jinwoo Park[1], Seung-Chul lee[1], Sang-Hwan Park[1], Eojin Yoon[1], Neil Greenham[2] and Tae-Woo Lee[1]; [1]Seoul National University, Korea (the Republic of); [2]University of Cambridge, United Kingdom; [3]Korea Basic Science Institute, Korea (the Republic of)

Metal halide perovskites (MHPs) have been considered next-generation light-emitting materials due to their excellent emission property of narrowband emission. Still, even after various material types of perovskites including 3D, low-dimensional quasi-2D, and colloidal nanocrystal structures were studied, perovskite light-emitting diodes (PeLEDs) have not realized high luminance, high efficiency, and long lifetime simultaneously, because of the intrinsic limitations related to the trade-off properties between charge transport and confinement in each type of perovskite materials. Here, we report an ultra-bright, efficient, and stable PeLEDs made of core/shell perovskite nanocrystals with a size of ~10 nm obtained using a simple in situ reaction of benzylphosphonic acid (BPA) additive with 3D polycrystalline perovskite films without separate synthesis process. During the reaction, large 3D crystals are split into nanocrystals and the BPA surrounds the nanocrystals, achieving strong carrier confinement while maintaining good charge-transport properties of 3D perovskites. We demonstrate simultaneously efficient, bright, and stable PeLEDs that have maximum brightness of ~470,000 cd m^{-2}, maximum external quantum efficiency of 28.9% (maximum current efficiency of 151 cd A^{-1}), and half-lifetime of 520 h at 1,000 cd m^{-2} (estimated half-lifetime >30,000 h at 100 cd m^{-2}). These results suggest that PeLEDs are not only laboratory-level high-efficiency devices but also promising candidates for commercial self-emissive displays and lighting applications.

SESSION EL17.06: Poster Session II
Session Chairs: Lina Quan and Barry Rand
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL17.06.01
Excited State Dynamics and Transport of Self-trapped Excitons in Lead-Free Double Perovskites Hui Fang[1,2], Yanfeng Yin[2], Yang Yang[3], Haiming Zhu[3] and Shengye Jin[2]; [1]University of Pennsylvania, United States; [2]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China; [3]Zhejiang University, China

Understanding the excited state and transport dynamics of self-trapped excitons (STEs) in lead-free double perovskites (DPs) is essential for popularizing their optoelectronic applications. Herein, we apply a series of spectroscopies and microscopies techniques to systematically investigate the formation, transport, and relaxation dynamics of SETs in Bi-doped double perovskites (Bi-DPs). The PLQY, consistent with the STEs activation energy of Bi-DPs shows an increasing and then decreasing trend as a function of Bi^{3+} content, suggesting tiny Bi^{3+} can passive the defects and more Bi could generate more non-radiative decay channels. Moreover, we find the Bi-DPs exhibit dual white emission, originating from the intrinsic STEs (i-STE) and Bi^{3+} induced STEs (Bi-STEs), respectively. The STEs formation and relaxation timescale will be detailed discussed in as well. Finally, we will present the temperature-active transport behavior. The fundamental mechanism understanding of the doping engineering established in this work will provide helpful guidance about how to improve the performance of DPs optoelectronic devices.

5:00 PM EL17.06.02
Chiral CsPbBr$_3$ Perovskite Nanoplatelets Synthesized Using Phosphaste-based Anionic Ligands Thi Kim Tran Tran and Jing Zhao; University of Connecticut, United States

Perovskite nanocrystals functionalized with chiral molecular ligands exhibit unique optical activity, making them promising materials for optoelectronic applications. However, the ligand type has been limited to cationic chiral amines in majority of the studies. In order to expand the ligand selection, chiral anionic binaphthyl molecules with phosphate functional groups have been introduced to synthesize CsPbBr$_3$ nanocrystals. Tramission electron microscopy, X-ray diffraction, together with UV-vis spectroscopy revealed that the nanocrystals are plateletes, with a thickness of five unit cells. The nanoplates show distinct circular dichroism signal and maintain their chiral properties after purification using anti-solvent. They also exhibited linearly polarized emission in solution due to the anistropy in their geometry.

5:00 PM EL17.06.03
Amino Acid-Passivated Pure Red $CsPbI_3$ Quantum Dot LEDs Dezhang Chen and Jonathan E. Halpert; The Hong Kong University of Science and Technology, Hong Kong

$CsPbI_3$ quantum dots (QDs) are promising light-emitting materials for pure-red display applications. Several methods have been tried for perovskite to obtain the red-light emission in the range 620-650 nm, including mixed-halide perovskite $CsPbI_xBr_{3-x}$, quazi-2D perovskite, and quantum-confined $CsPbI_3$. Among those methods, quantum-confined $CsPbI_3$ is the most exciting material as it is not subject to ion migration effects or contains organic cations that lead to spectral instability. Unfortunately, small colloidal quantum dots contain excess resistive ligands, negatively affecting the efficiency and stability of the resulting light-emitting diodes (LEDs). Here we developed a facile ligand-exchange method using amino acids to reduce native long-chain ligands on $CsPbI_3$ quantum dots. As a molecule with amine and carboxylate groups, amino acids can mildly exchange the oleate ligands and oleylammonium ligands on the surface of quantum dots. We also assessed a variety of related amino acids on their side-chain effects on LED performance. We found that in cysteine-exchanged QDs, both thiol and amino acid groups passivated the surface of quantum dots and led to the best LED performance. The optimized LEDs achieved an external quantum efficiency (EQE) of 18.0% and a T_{50} of 87 minutes, comparable with many of the best-reported perovskite pure red LEDs.

5:00 PM EL17.06.04
Enhancement of Photoluminescence in Two-Dimensional Tin Perovskite by van der Waals Contact with Low Work Function Metal Jun-Ho Park, Youjin Reo, Ju-Hyun Jung, Yong-Young Noh and Cheoljoo Kim; POSTECH, Korea (the Republic of)

Halide perovskites have attracted great attentions for optoelectronic elements with excellent quantum efficiency. Recent studies have focused on lead-free, tin halide perovskites with low-toxicity, but the low oxidation barrier of tin induces substantial in-gap states, which are responsible for non-radiative recombination. Previous reports show that addition of reducing agents during the material syntheses can enhance their photoluminescence (PL) quantum efficiency, however it is still unclear if the PL intensities are simply enhanced by reducing the oxidation states or changes in the electrochemical potential of the material also play a key role. Here, we show that van der Waals (vdW) contacts of aluminum (Al) onto two-dimensional $(PEA)_2SnI_4$ (PEA = phenylethylammonium) films after the material synthesis can still enhance its PL intensity by 4 times, reaching a record high quantum yield of 10 % for $(PEA)_2SnI_4$. The PL intensities do not increase in the cases of vdW contacts of copper and gold. Ultraviolet photoelectron spectroscopy measurements show that the energy level of electronic bands for $(PEA)_2SnI_4$ are shifted by 0.6 eV with the Al contact, compared to that of the as-grown sample, indicating a significant n-type doping by Al. Our results suggest that electron doping can effectively suppress the PL quenching in tin-based perovskites, mediated by defect-states.

5:00 PM EL17.06.07
Organo-metallic Halide Perovskite Thin Film/Quantum Dot Heterostructures for Novel Applications Jorge Arteaga[1], William; Delmas[1], Melissa Guarino-Hotz[2], Jin Zhang[2] and Sayantani Ghosh[1]; [1]University of California, Merced, United States; [2]University of California, Santa Cruz, United States

Organo-metallic Halide Perovskite (OMHP) thin films have been of great interest in the field of photovoltaics due to the rate at which their power conversion efficiency (PCE) has increased while maintaining low production costs. Perovskite quantum dots (PQDs) have also garnered interest for similar applications. Despite this, both PQDs and OMHP thin films have their drawbacks. Thin films have chemical stability issues, particularly in the presence of moisture and oxygen, while PQDs have not demonstrated efficiencies as high as their thin film counterparts. Some of these issues could be addressed by combining the two to form heterostructures of PQDs layered atop OMHP thin films. We have investigated charge and energy transfer mechanisms between spin-coated methylammonium lead iodide (MAPI) thin films and PQDs, where we varied both the PQD composition and the ligand molecules used for functionalizing their surfaces. We have used organic-inorganic PQDs ($MAPbBr_3$) with insulating and conducting ligands, and inorganic PQDs ($CsPbBr_3$) with insulating ligands, for a systematic study. All the selected PQDs have band gaps larger than that of MAPI, allowing for multiple routes of energy and charge transfer, not just between the PQDs and the MAPI film but also between the quantum dots themselves. Using photoluminescence (PL) spectroscopy, we have found that the emission from both $MAPbBr_3$ and $CsPbBr_3$ dots was quenched, while the MAPI film emission intensity was increased. Further, the charge carrier recombination lifetimes of the MAPI films with PQDs were significantly longer, nearly twice as long, compared to bare films, indicating that the PQDs were passivating the surface trap states in the films. However, all these changes in the thin films' optical properties depended on the types of ligands on the PQD surfaces, the excitation energy used on the heterostructures, and even the density of PQDs on the film. In particular, we discovered that a high density of close-packed PQDs reduced both emission intensity and recombination lifetimes of the MAPI films. Our results demonstrate an approach to modulating thin film behavior that could have applications not only in the field of traditional optoelectronics but also in novel areas, such as environmental sensing and detection.

The authors acknowledge funding from NASA grant no. NNH18ZHA008CMIROG6R and NSF grant no. NSFDGE-2125510.

5:00 PM EL17.06.08
Enhancement of Optical Gain in $MAPbI_3$ Perovskite Thin Films via Surface Treatment with Organo-Ammonium Halide Additives Hoonil Yang[1,2], Chieun Choi[2] and Yoon-Kyu Song[2]; [1]Samsung Electronics, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)

Solution-processed organo-lead halide perovskite has emerged as a promising next-generation light-emitting devices owing to the low process cost, wavelength tunability from visible to near-infrared light, and narrow full width half maximum (FWHM) characteristics [1]. Unlike perovskite materials used in photovoltaic devices, the materials used in light-emitting devices often require small grain sizes to spatially confine excitons at nano scale, thus ensure high luminous efficiencies by inhibiting exciton dissociation and increasing the radiative recombination rate. However, it is difficult to achieve high emission intensity with small grain perovskites at a large thickness, because the large framework may aggravate defects such as pinholes and grain boundary gaps [2]. Also, a thin film with small grain perovskites may generate high density of non-radiative recombination centers at the surface defects via deformation and decomposition [3].
In this work, we propose to use 4-fluorobenzylammonium iodide (FPMAI), a bulky organo-ammonium halide additive, for surface treatment through recrystallization of methylammonium lead iodide ($MAPbI_3$) perovskite thin film, thereby decreasing the grain sizes and suppressing defects in the perovskite film at relatively large thickness. The FPMAI molecules are well attached to $MAPbI_3$ nanocrystals and has high surface coverage due to its short alkyl chain length and high binding energy to perovskite. Also, we realized it is an appropriate additive to form perovskite nanocrystals with reduced defect sites in a thin film with relatively large thickness. We have fabricated FPMAI-treated perovskite thin films and demonstrated an enhanced optical gain of the perovskite films by showing the amplified spontaneous emission (ASE) under picosecond pulse pumping. As a result, the ASE threshold are reduced

approximately $6\ \mu J/cm^2$, and the optical gain coefficient are increased from 316.3 cm^{-1} to 507.1 cm^{-1}. Furthermore, we have measured significant increases in photoluminescence (PL) intensity and PL lifetime, thus show that non-radiative recombination processes are suppressed in the perovskite films with FPMAI surface treatment. Our result shows that the optical gain is improved through the surface treatment method with organo-ammonium halide additives, and it can be applied to highly efficient light emitting devices in the future organic optoelectronic systems.

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5:00 PM EL17.06.10
Enforcing Blue Light Emission of Mixed Halide Perovskite Light-Emitting Diodes Enabled by Multiple Inorganic Chloride Doping Jung Jae Do, Lakshmi P. Prabakar and Jae Woong Jung; Kyung Hee University, Korea (the Republic of)

Perovskite-based light emitting diodes (PeLEDs) are promising candidates for next-generation display technologies due to their potentials such as solution processing, excellent color purity, and color tunability. However, the blue-emitting PeLEDs lag far behind those of green or red-emitting perovskites in terms of optoelectronic properties and long-term operative stability, strongly restricting the commercialization of the display technology. In this study, we first introduced CsCl in a typical sky-blue PeLEDs ($PEA-CsFAPbBr_3$) to enlarge the optical band gap and to enforce pure blue color emitting properties. Yttrium chloride (YCl_3) is then added in the perovskite emitter as an additional inorganic chloride dopant to hamper severe phase segregation and ion migration in the perovskite emitters. As a result, the multiple inorganic chloride salts simultaneously enforce pure blue electroluminescence and phase stabilization, leading to improved quantum efficiency and long-term operative stability of the pure blue PeLEDs, achieving a stable electroluminescence device at 473 nm with a full-width half-maximum (FWHM) of 17 nm. The optimized blue-light PeLEDs exhibited a maximum external quantum efficiency (EQE) of 1.06% and excellent operational stability (LT50 > 250 min), which suggests the efficacy of the multiple inorganic chloride salts for improving optoelectronic properties of pure-blue perovskite LEDs.

5:00 PM EL17.06.11
Steric Effects in Br-Based Sky-Blue Perovskites for High Quantum Efficiency Jiweon Kim[1], Ilgeum Lee[1], Lina Quan[2], Edward H. Sargent[3], Seung Soon Jang[4] and Dong Ha Kim[1]; [1]Ewha Womans University, Korea (the Republic of); [2]Virginia Tech, United States; [3]University of Toronto, Canada; [4]Georgia Institute of Technology, United States

Recently, perovskite light-emitting diodes (PeLEDs) have promoted considerable research interest as a next-generation LED that can replace the existing OLED and QLED due to the attractive properties of metal halide perovskite (MLH) materials such as outstanding carrier mobility, bandgap tunablity, great chemical flexibility, and remarkable color purity. However, MLH has yet met the critical requirement for viable LED devices such as inferior moisture stability, stable blue emitter, and cost-effective large area fabrication. To remedy the disadvantage, quasi-2D perovskites, e.g. $(PEA)_2(MA)_{n-1}Pb_nBr_{3n+1}$ have been proposed that evidenced improved humid-stability and tunable optoelectronic properties. In this respect, here, we show a generalized strategy to develop Br-based blue quasi-2D perovskites with enhanced stability and spectral tunability. By controlling the ratio of cation spacers, we could establish a protocol to fine-tune the spectral range of the blue emissive perovskites which may open a pathway toward commercialized PeLEDs.

5:00 PM EL17.06.14
Manipulated Interface for Enhanced Energy Cascade in Quasi-2D Blue Perovskite Light-Emitting Diodes Yun Seop Shin and Jin Young Kim; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Quasi-two-dimensional (2D) perovskites have recently emerged as emitters in blue perovskite light-emitting diodes (PeLEDs). The cascading energy-transfer process between different 2D phases plays an essential role in the high performance of this class of PeLEDs. Herein, we propose an interfacial engineering strategy by incorporating a zwitterionic additive, L-phenylalanine, into the hole-injection layer (HIL), enabling suppression of trap-assisted deactivation channels by virtue of the coordination interactions between the additive and Pb2+ defects in the perovskite phase. In addition, the introduction of L-phenylalanine reduces the release of metallic indium species from indium tin oxide substrates initiated by acidic HILs, resulting in the suppression of luminescence quenching in the perovskite layer. The synergetic benefits create an ideal energy landscape, blocking energy losses and boosting PeLED performance with a peak external quantum efficiency of 10.98% at 480 nm and extended device lifetimes. Our approach provides a versatile strategy to achieve high-performance blue PeLEDs.

5:00 PM EL17.06.15
Strong Photoluminescence of GaP Through ZnS/GaP Reverse Type I Quantum Dot Hongjoo Shin; KAIST, Korea (the Republic of)

GaP has an innate crystal structure of zin blende and an indirect bandgap. Although its light conversion efficiency is not high due to intrinsic limitations resulting from the energy band structure, it is a material used for solid-state light-emitting diodes (LEDs) due to economic advantages. For these reasons, several computational studies have been conducted to search conditions under which GaP can have a direct bandgap. Simulation results expected a direct bandgap of GaP can be obtained when it has i) a wurtzite structure or ii) a zinc blende structure with a radius of 1 nm or less. Direct bandgap wurtzite GaP was proven through artificially grown GaP nanowire on a (111) oriented zinc blende GaP substrate in 2013. However, unlike the typical direct bandgap material, it forms a pseudo-direct bandgap between the dark conduction band and the heavy hole band, limiting its optical properties. In addition, there has been no experimental study that confirmed direct bandgap formation of zinc blende GaP via quantum confinement because synthesis if
Here, we experimentally demonstrated the direct bandgap of zinc blende GaP based on the high photoluminescence (PL) intensity and quantum yield. This was realized through the reverse type I quantum dot, which has an opposite order of band gap size between the core and the shell of general QD. In ZnS/GaP reverse type I quantum dots, electrons and holes are confined to the GaP shell rather than the ZnS core, and PL is exhibited by the GaP shell. In addition, ZnS has the advantage of stable stacking of GaP shell because of the similar lattice parameter (ZnS: 5.40A, GaP: 5.45A). We confirmed that ZnS/GaP actually has a zinc blende structure via XRD analysis, and the radius difference of 0.48 nm between ZnS and ZnS/GaP was confirmed through STEM image. These results suggest that GaP is stacked on the ZnS core surface with a one-unit cell thickness (monolayer), achieving a direct bandgap. As a result, it showed strong PL intensity even after two times purification processes and was able to achieve a high absolute PL quantum yield of 29.6%. In addition, it was confirmed that PL quantum yield hardly decreased even after 55 days of stability test. This study demonstrates a new pathway to switch many indirect-gap semiconductors to light-emitting materials with a high efficiency and good stability.

5:00 PM EL17.06.16
Controlling $MAPbI_3$ Crystallization from Gamma-butyrolactone for Slot Die Coated Thin Films Using Air Knife Maimur Hossain, Jesse Starger,

Jesse Efymow, Ryan Barrett, Jacob Bolduc, Nicolas Alvarez, Richard Cairncross, Aaron Fafarman and Jason Baxter; Drexel University, United States

Solvents play a crucial role in developing high quality hybrid organic–inorganic perovskite films using roll-to-roll slot die coating methods which is an efficient process for the fabrication of large area optoelectronic devices. γ-butyrolactone (GBL) is a well explored solvent for direct growth of lead halide-based perovskite single crystals. GBL coordinates weakly with Pb^{2+} center in precursor solution compared to other solvents (N, N-dimethylformamide, dimethyl sulfoxide, etc.) due to its lower Gutmann's donor number, D_N. Thus, GBL favors the formation of Pb-I-Pb bonds necessary for the octahedral framework and subsequent rapid single crystal growth. Methylammonium lead iodide ($MAPbI_3$) in GBL follows retrograde solubility, wherein there exists a threshold temperature (~60 °C) beyond which solubility decreases as temperature increases. This behavior provides a mechanism to drive supersaturation (and subsequently nucleation and bulk crystal growth) by increasing temperature, without the need for evaporation. However, the strong tendency towards single crystal growth at elevated temperatures poses a challenge for the deposition of pin-hole free perovskite thin films from GBL-based inks because elevation of processing temperature can push the precursor solution towards supersaturation rapidly. To achieve interconnected, compact and uniform morphology, the drying rate must be carefully tuned to control the nucleation and growth rates.
In this work, we describe a facile slot die coating method using a hot air knife and preheated substrate to control the perovskite crystallization and produce better quality thin films from GBL. To mitigate the dominating impact of retrograde solubility and have better control of morphology, a low concentration $MAPbI_3$ precursor solution was utilized to delay supersaturation. The crystallization of $MAPbI_3$ in GBL as function of processing temperature and drying rate was studied by microscopy. The phase and morphology of resulting films were characterized using XRD, SEM and AFM. $MAPbI_3$ crystallization at low temperatures was found to be thermodynamically controlled, which favors solvent-perovskite adduct formation. The perovskite films deposited at temperatures below 60 °C and without any air knife had poor morphology dominated by sparse, 10-100s μm sized needle-shaped crystals with large voids between them. This crystal phase can be attributed to solvent-perovskite adducts like $(MA)_2(GBL)_2Pb_3I_8$ that do not easily decompose into the perovskite crystalline structure. Slow evaporation of a thick layer of GBL perovskite solution can trigger this kind of GBL-perovskite adduct formation. High temperature processing mitigated the adduct formation, but crystal growth kinetics of the perovskite phase produced relatively poor film coverage. In contrast, the combination of hot air knife and heated substrate produced a smooth film with better coverage due to faster drying rate and better control over crystallization kinetics. In this work, we thoroughly studied crystallization of $MAPbI_3$ during large area coating and its correlation with solvent and different drying conditions. This provides insight about the processing condition which is crucial to control morphology during fabrication of large area optoelectronic devices.

5:00 PM EL17.06.17
Detection of Circularly Polarized Light Based on Perovskites with High Chirality Hyunjeong Lee, Minju Kim, Jiweon Kim and Dong Ha Kim; Ewha Womans University, Korea (the Republic of)

Recently, chiral nanomaterials have attracted significant attention for potential applications in diverse fields such as ferroelectrics, chiro-spintronics and chiroptoelectronics. Among them, hybrid organic-inorganic chiral perovskites are considered critical candidates as alternative active layers owing to their superior optoelectronic properties such as circulary polarized light (CPL) detection and effective light absorption.[2] In addition, in the ABX_3 structure of perovskite, it is possible to easily introduce chiral properties by adjusting the A site cations. Until now, chiral perovskites using (R, S)-α-methylbenzylamine, (R, S)-phenylethylamine, (R, S)-1-(1-naphthyl)ethylamine etc. have been studied as chiral organic cations.[1, 2] However, the development of perovskite-based CPL photodetectors with appreciable function is still limited. So, it is necessary to increase the performance of the CPL photodetector by developing chiral perovskites with a high g-factor.
In this work, we suggest a new class of chiral perovskites by integrating aromatic organic cations. Record-high level g-factor value is obtained compared with the existing materials reported so far. We confirmed the outstanding optical properties of 1D and 2D chiral perovskites, respectively, through dimensional control of chiral perovskites. Further, the excellent crystallinity of chiral perovskite using new chiral organic cations increases the charge transfer, resulting in enhanced efficiency of the CPL photodetector. These new chiral perovskites are expected to open the pathway for multifunctional chiroptic applications.

SESSION EL17.07: Photophysics of Colloidal Quantum Dots and Perovskites
Session Chairs: Noel Giebink and Lina Quan
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3006

8:30 AM *EL17.07.01
Nonequilibrium Lattice Dynamics in Photoexcited 0D and 2D Perovskites Richard D. Schaller[1,2]; [1]Argonne National Laboratory, United States; [2]Northwestern University, United States

Limited understanding exists as to the response of highly ionic metal halide lattices upon photoexcitation. Structural deformations such as polaron formation influence local energetics and photophysical properties, which can heavily influence utility of these materials in optoelectronics. This talk will discuss structural response of 0D and 2D lead halide perovskites from direct investigations using ultrafast transient X-ray diffraction as a function of optical excitation fluence. 0D structures show slow initial evolution of structure that recovers with a timescale that depends dramatically on cation identity. For 2D structures both powder X-ray diffraction and time-resolved photoluminescence linewidths narrow over 1 ns following optical excitation for the fluence range studied, concurrent with slight redshifting of the optical bandgaps. Observations are attributed to transient relaxation as well as ordering of distorted lead iodide octahedra stimulated chiefly by electron–hole pair creation. In the case of (BA)2PbI4, appearance of the (110) reflection in following excitation would suggest a transient crystal phase transition. However, through high energy single crystal XRD we find reflections that violate glide plane conditions in the reported Pbca structure, conveying that the literature assignment of the space group is incorrect and is instead P212121. In cases of both 0D and 2D perovskites, lattice relaxation times exceed electronic carrier lifetimes which can be understood in terms of their poor thermal dissipation, but also suggests shallow potentials wells.

9:00 AM *EL17.07.02
Coherent Exciton Transport in Perovskite Quantum Dot Superlattices Libai Huang; Purdue University, United States

The performance of quantum dot (QD) devices in optoelectronic and quantum information applications relies on not only the properties of the individual QDs but also the collective properties arising from interactions between QDs within a solid. The interactions between QDs determine whether long-range coherence and transport can be achieved. Due to their large oscillator strengths, perovskite QD superlattices (SLs) have the potential for exciton superradiance. However, the ultrafast dephasing processes can limit their coherence lengths. We provide a detailed study on the key factors that control exciton delocalization and transport in perovskite QD SLs. Through temperature-dependent and time-resolved ultrafast microscopy measurements, we demonstrate coherent exciton propagation in highly ordered SLs. We unravel the effect of disorder by comparing SLs with varying degrees of inhomogeneity. Our results point to the exciting opportunities in engineering exciton coherence in perovskite solids.

9:30 AM EL17.07.03

Hong-Ou-Mandel Interference in Colloidal $CsPbBr_3$ Perovskite Nanocrystals Alex E. Kaplan[1], Chantalle Krajewska[1], Andrew H. Proppe[2,1], Weiwei Sun[1], Tara Sverko[1], David B. Berkinsky[1], Hendrik Utzat[3,1] and Moungi G. Bawendi[1]; [1]MIT, United States; [2]University of Ottawa, Canada; [3]University of California, Berkeley, United States

The continued innovation of on-demand sources of non-classical light is critical to fully realizing the technological potential of quantum photonics. In particular, single, indistinguishable photons from quantum emitters are the fundamental building blocks of many quantum optical applications, such as quantum networks, linear optical quantum computing, and quantum teleportation, Hong-Ou-Mandel (HOM) interference is the cornerstone photon-photon interaction that governs these quantum light technologies. In perfect HOM interference, two indistinguishable photons incident on a beam splitter leave coalesced, due to the overlap of their identical wavefunctions. Pure-dephasing processes, interactions which collapse and obfuscate the phase information of the photon-generating exciton wavefunction in a quantum emitter, impact the indistinguishability of sequentially emitted single photons. As such, HOM interference serves not only as an integral tool to quantum computing, but also an important heuristic for the pure-dephasing rate in a quantum emitter.
In our work, we show sizeable HOM interference in colloidal cesium lead bromide perovskite nanocrystals (PNCs), a first for colloidal, solution-processed material. Unlike other quantum emitters that require Purcell enhancements and device architectures to increase the radiative rate and suppress dephasing, these PNCs have yet to undergo the optimizations seen for other emitters. By comparing correlation functions for indistinguishable and distinguishable photons, the visibility of HOM interference can be calculated. We demonstrate that PNCs exhibit HOM visibilities which are factors higher than expected from indirect measurements. Our work showcases the potential of PNCs to become the first colloidal transform-limited quantum light source.

9:45 AM EL17.07.04

Exciton–Phonon Interactions in Lead Halide Perovskite Nanocrystals Revealed by Single-Dot Photoluminescence Spectroscopy Takumi Yamada[1], Kenichi Cho[1], Hirokazu Tahara[1,1], Terumasa Tadano[2], Hidekatsu Suzuura[3], Ryota Sato[1], Masaki Saruyama[1], Toshiharu Teranishi[1] and Yoshihiko Kanemitsu[1]; [1]Kyoto University, Japan; [2]National Institute for Materials Science, Japan; [3]Hokkaido University, Japan

Lead halide perovskite semiconductors are recently attracting much attention as a new class of optoelectronic device materials, because of their outstanding optical and electronic properties at room temperature. It is considered that strong electron–phonon interactions play a key role in unique optical and transport responses of halide perovskites [1]. They determine the effective carrier mass, the carrier mobility, the photoluminescence (PL) linewidth, the Urbach tail of optical absorption, and so on. The efficient anti-Stokes PL and the slow hot-carrier cooling are also closely related to strong electron–phonon interactions [2–5]. Since individual nanocrystals (NCs) show extremely high PL quantum yields and narrow PL linewidths, longitudinal-optical (LO) phonon replicas reflecting electron–phonon interactions can be observed in the PL spectra at cryogenic temperatures. Therefore, single dot spectroscopy is a powerful tool to investigate the exciton–phonon interactions of perovskite NCs.
Here, we prepared $CsPbBr_3$, $FAPbBr_3$, and $MAPbBr_3$ perovskite NC samples and measured their PL spectra of single NCs [6–8]. At low temperatures, $CsPbBr_3$ NCs show very sharp PL lines including fine-structure splitting in the PL peaks of excitons, biexcitons, and the LO-phonon replicas of excitons. We discuss the exciton–phonon and trion–phonon interactions in perovskites from the PL fine structures in $CsPbBr_3$ NCs. We found that the LO-phonon energies are independent of the NC size. However, the Huang–Rhys (HR) factors of excitons, i.e., the strength of the exciton–phonon coupling, depend on the LO-phonon energy. Both HR factors for excitons and trions increase as the NC size decreases. The HR factors of trions are larger than those of excitons in larger NCs. We conclude that the size-dependent HR factors for excitons and trions are closely related to the spatial distributions of the electron and hole wavefunctions in the NC.
Part of this work was supported by JST-CREST (JPMJCR21B4) and JSPS KAKENHI (JP19H05465, JP20K03798, JP21K03424, and JP22H01990).

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10:00 AM BREAK

10:30 AM *EL17.07.05

Sensational Sensitization—Triplet Generation at the Perovskite/Organic Interface Colette M. Sullivan and Lea Nienhaus; Florida State University, United States

Photon upconversion describes a process which effectively shortens the wavelength light emitted upon irradiation, yielding photons with a higher energy than the incident photons. To ensure compliance with energy conservation laws, this process occurs by combining the energy of two low energy photons. In the triplet-triplet annihilation upconversion process of interest here, the photon energy is combined by forming a high energy singlet state from two lower energy triplet states. However, since direct optical excitation of triplet states is 'spin-forbidden', sensitizers are used to indirectly populate the triplet state.

Successful triplet sensitizers span a broad range of material classes including metal-organic complexes, inorganic nanomaterials such as quantum dots or nanoplatelets, and bulk perovskite thin films. Understanding the fundamental energy transfer mechanism across the hybrid organic/inorganic interface is crucial for the advancement of optoelectronic devices based on this process. The exact energy transfer mechanism at the interface of inorganic and organic materials remains obscure, particularly where there is a large amount of structural inhomogeneity or high defect density within the material.

To date, rubrene has been the most investigated annihilator. However, it is not the ideal annihilator for use with lead halide perovskites. Here, I discuss the recent developments of perovskite-sensitized upconversion, including new annihilators such as 1-chloro-9,10-bis(phenylethynyl)anthracene (1-CBPEA), which enables solid-state near-infrared-to-green upconversion.

11:00 AM *EL17.07.06

Interlayer Triplet Sensitized Luminescence in 2D Hybrid Perovskites-- Photophysics and Applications YunHui L. Lin and Justin Johnson; National

Renewable Energy Laboratory, United States

Recently, hybrid perovskites have gained attention as sensitizers for molecular triplet generation. Layered, two-dimensional (2D) perovskites are especially well-suited for this purpose because the triplet donor (inorganic framework) and triplet acceptor (organic layer) are self-assembled into adjacent sheets, so that with the appropriate energetics, triplets can be driven across the interface. By leveraging interlayer energy transfer, this emerging class of 2D perovskites has potential to impact several energy-related fields and processes, including solar photochemistry, photonics, and optoelectronics. In this talk I will discuss how several 2D perovskite design parameters affect photophysical outcomes. In particular, we will (1) examine how exciton energy offsets and frontier orbital alignments between the metal-halide and molecular layers affect the dynamics of ultrafast energy transfer and (2) discuss how organic layer morphology and composition can be engineered to generate multi-colored triplet-based molecular emission. Ultimately, 2D hybrid perovskites, with their vast compositional and structural tunability, offer an exciting platform for manipulating energy flow for light-emitting applications.

11:30 AM EL17.07.07
Many-Body Correlations and Bound Exciton Complexes in $CsPbX_3$ (X=Br, Br/Cl) Quantum Dots Chenglian Zhu[1,2], Tan Nguyen[3,3], Simon C. Böhme[1,2], Anastasiia Moskalenko[1,2], Dmitry Dirin[1,2], Maryna Bodnarchuk[2], Claudine Katan[3], Jacky Even[3], Gabriele Raino[1,2] and Maksym V. Kovalenko[1,2]; [1]ETH Zürich, Switzerland; [2]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [3]Univ Rennes, France

All-inorganic lead-halide perovskite ($CsPbX_3$, X = Cl, Br, I) quantum dots (QDs) have emerged as a competitive platform for classical light emitting devices (in the weak light-matter interaction regime, *e.g.,* LEDs and laser)[1], as well as for devices exploiting strong light-matter interaction and operated at room-temperature.[2] Many-body interactions and quantum correlations among photogenerated exciton complexes play an essential role, e.g., by determining the laser threshold, the overall brightness of LEDs, and the single-photon purity[3, 4] in quantum light sources. To date, a thorough account of many-body interactions in these newly developed soft perovskite QD compounds is still missing. Here, by combining single-QD optical spectroscopy performed at cryogenic temperatures in combination with configuration interaction (CI) calculations, we address the trion and biexciton binding energies and unveil their peculiar size dependence. We find that trion binding energies increase from 7 meV to 17 meV for QD sizes decreasing from 30 nm to 9 nm, while the biexciton binding energies increase from 15 meV to 30 meV, respectively. CI calculations quantitatively corroborate the experimental results and suggest that the effective dielectric constant for biexcitons slightly deviates (5%) from the one of the single excitons, as a result of lattice distortions in the multiexciton regime. Our findings provide a deep insight into the multiexciton properties in all-inorganic lead-halide perovskite ($CsPbX_3$) QDs, essential for classical and quantum optoelectronic devices.

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11:45 AM EL17.07.08
Extending the Defect Tolerance of Halide Perovskite Nanocrystals to Hot Carrier Cooling Dynamics Junzhi Ye[1,2], Navendu Mondal[3], Ben Carwithen[3], Yunwei Zhang[4], Linjie Dai[1], Xiangbin Fan[1], Pratyush Ghosh[1], Clara Otero Martinez[5], Zhongzheng Yu[1], Ziming Chen[3], Neil Greenham[1], Samuel D. Stranks[1], Lakshminarayana Polavarapu[5], Akshay Rao[1], Artem Bakulin[3] and Robert Hoye[2]; [1]University of Cambridge, United Kingdom; [2]University of Oxford, United Kingdom; [3]Imperial College London, United Kingdom; [4]Sun Yat-sen University, China; [5]University of Vigos, Spain

One of the key enabling properties of low-bandgap lead-halide perovskite nanocrystals ($CsPbX_3$ NCs) for optoelectronic applications is their tolerance to point defects. Thus far, the discussion around defect tolerance has mostly focussed on recombination of charge-carriers from the band-edge. But understanding influence of these defects on hot carrier (HC) cooling will also be critical for achieving more efficient NC-based devices, but has not been thoroughly explored thus far. Here, we address this knowledge gap by elucidating the influence of intentionally-introduced traps (primarily halide vacancies) on HC relaxation above the band-edge in $CsPbX_3$ NCs with different halide compositions ($CsPbBr_3$, $CsPbBr_xI_{3-x}$, and $CsPbI_3$). The HC cooling kinetics in these different NC systems are probed by energy-dependent photoluminescence quantum yield measurements, along with pump-probe (two-pulse) and pump-push-probe (three-pulse) transient absorption measurements. We show that the presence of defect states increases the chances of HC trapping, which speeds up the cooling process. However, the change in HC cooling lifetime due to the trap densities becomes smaller as the composition moves from Br-based NCs to I-based NCs. Based on density function theory (DFT) calculation and hot carrier kinetic modelling, the cooling speed is governed by both defect densities and defect position relative to the conduction band edge. Shallower defects would allow faster trapping and de-trapping process for the carriers, which it helps to maintain the free carrier densities and allow free carriers to cool slowly with the effect of Auger reheating. This work firstly demonstrated experimental observations of the defect-tolerance nature of perovskite NCs to hot carriers, which provides insights into designing high-efficiency photovoltaic devices by managing defect densities for different bandgap perovskites.

SESSION EL17.08: Structure-Property Relationship
Session Chairs: Xiwen Gong and Farnaz Niroui
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3006

1:45 PM EL17.08.05
Structure-Property Relationships for 2D Halide Perovskites with Large Cage Cations Xiaotong Li[1], Yongping Fu[1], Laurent Pedesseau[2], Shelby Cuthriell[1], Constantinos Stoumpos[3], Jacky Even[2], Claudine Katan[2], Peijun Guo[4], Richard D. Schaller[1] and Mercouri G. Kanatzidis[1]; [1]Northwestern University, United States; [2]CNRS, France; [3]University of Crete, Greece; [4]Yale University, United States

In 2D perovskites, the choice of the A-site perovskitizer cations is not entirely limited by the so-called Goldschmidt tolerance factor. The stabilizing effect of the spacer cations makes it possible to tolerate larger A-site cations as perovskitizers. By solving the single-crystal structures of $(BA)_2(A)Pb_2I_7$ where BA = butylammonium, and A = methylammonium (MA), formamidinium (FA), dimethylammonium (DMA) or guanidinium (GA), we have proven that the relatively large DMA and GA can serve as the A-site cation of 2D perovskites despite the fact that they are too large to formally satisfy the Goldschmidt rule. As the size of the A-site cations increases, the Pb−I bonds are elongated, which reduces the orbital overlap of Pb s- and I p-orbitals, thus decreasing the electronic bandwidths and increasing the bandgaps, as confirmed by DFT calculations. This increases the local distortions of the PbI_6

coordination environment and leads to a decrease of PL intensity and shortening of PL lifetime. The expanded cages also result in soft and anharmonic lattices, as supported by Raman spectra. Exciton-exciton annihilation processes occur in these systems with the rates being slower in the structures with larger A cations. Similar trends are also observed in lead bromide perovskites as well as tin and germanium iodide systems. Understanding the structure-property relationships of these compounds will help illustrate how the large A-site cations may influence physical properties of both 2D and 3D perovskites and facilitate their future optoelectronic applications.

2:00 PM EL17.08.03
Heterostructure Formation Origin and Size-Dependent on Phase Segregation in Mixed Halide Perovskite Nanoparticles Donghoon Shin, Minliang Lai and Chad Mirkin; Northwestern University, United States

Mixed halide perovskites consisting of multiple ions at the same lattice site (ABX_3) are an emerging class of semiconductors, with potential as high-performance optoelectronic materials. The promise of this class of materials derives from the fact that incorporation of multiple ions is a facile means to tune material properties such as band structure, emission and absorption efficiency, exciton binding energy, and carrier lifetime. Indeed, it has been well established that mixed-cation and mixed-halide composition perovskites lead to enhanced device performance and stability. However, simply using multiple ions during synthesis does not always lead to structures with desirable properties, due to the various degrees of ionic mixing and types of nanoscale arrangements possible in the complex perovskite. In addition, the source of mixing or segregation should be experimentally studied on the scale of an individual particle, enabling ones to deconvolve the effects of ion size, grain boundary, and ion migration on the final crystal morphology. Herein, an emerging method termed evaporation-crystallization polymer pen lithography (EC-PPL) is used to synthesize and systematically study the degree of ionic mixing of $Cs_{0.5}FA_{0.5}PbX_3$ (FA = formamidinium; X = halide anion, ABX_3) crystals, as a function of size, temperature, and composition. These experiments have led to the discovery of a heterostructure morphology where the A-site cations, Cs and FA, are segregated into the core and edge layers, respectively. Simulation and experimental results indicate that the heterostructures form as a consequence of a combination of both differences in solubility of the two ions in solution and the enthalpic preference for Cs-FA ion segregation. This preference for segregation can be overcome to form a solid-solution by decreasing crystal size (< 60 nm) or increasing temperature. Finally, we utilized these tools to identify and synthesize solid-solution nanocrystals of $Cs_{0.5}FA_{0.5}Pb(Br/I)_3$ that significantly suppress photo-induced anion migration compared to their bulk counterparts, offering a route to deliberately designed photostable optoelectronic materials.

2:15 PM BREAK

3:15 PM *EL17.08.04
Deterministic On-Site Growth of Halide Perovskite Nanocrystals for On-Chip Optoelectronics Farnaz Niroui; Massachusetts Institute of Technology, United States

Despite notable developments in halide perovskite thin-film devices, their integration into on-chip nano-optoelectronics has been limited by a lack of control over nanoscale patterning. Prone to degradation, these materials are often not compatible with the conventional top-down fabrication processes. Bottom-up assembly, on the other hand, can avoid such damage yet current strategies often lack the versatility to accomodate deterministic spatial control at the individual nanocrystal level for integration with other functional device components. Here, we introduce two techniques to enable on-site synthesis of nanocrystals down to a quantum dot-level in a scalable manner and compatible with device integration. In one, halide perovskite nanocrystals with sub-10 nm spatial accuracy and tunable sizes down to 20 nm are synthetized on-site guided using topographical templates with chemical texturing that localize growth precursors to the nanoscale. Using this platform, we have demonstrated arrays of on-chip nanoscale light emitting diodes (nano-LEDs) utilizing single nanocrystals with applications in optical communications, lasers, augmented and virtual reality displays, and quantum technologies. We will then discuss an approach that we have developed using a scanning probe technique for on-site fabrication of deterministically positioned halide perovskites quantum dots on-chip. We have used this technique to demonstrate deterministic arrays of perovskite single-photon sources with performance that can be engineered by direct integration with photonic cavities, enabling applications in quantum technologies.

3:45 PM EL17.08.06
Halogen Loss Pathways Rationalize Light-Induced Halide Segregation and Photoluminescence Quenching at Perovskite/Organic Hole Transport Layer Interfaces Zhaojian Xu[1], Daniel Astridge[2], Ross Kerner[3], Xinjue Zhong[1], Junnan Hu[1], Jisu Hong[1], Kai Zhu[3], Joseph J. Berry[3,4,5], Antoine Kahn[1], Alan Sellinger[2] and Barry P. Rand[1,6]; [1]Princeton University, United States; [2]Colorado School of Mines, United States; [3]National Renewable Energy Laboratory, United States; [4]Renewable and Sustainable Energy Institute, University of Colorado Boulder, United States; [5]University of Colorado Boulder, United States; [6]Andlinger Center for Energy and the Environment, Princeton University, United States

Metal halide perovskites have been widely implemented in various optoelectronic devices, but their poor stability under light illumination remains a big challenge. While the intrinsic photostability of isolated perovskite samples has been widely discussed, it is important to explore how charge transport layers, which are necessary for a functional device, impact photostability. In this study, we investigate the effect of organic hole transport layers (HTLs) on the spectral stability, reflecting light-induced halide segregation, and temporal stability, reflecting light-induced PL quenching, of the perovskite photoluminescence (PL) spectrum. By employing a series of HTLs with different highest occupied molecular orbital (HOMO) levels, we observe and rationalize a nonmonotonic relation between the rate of light-induced halide segregation for mixed-halide perovskite and HOMO energy of HTLs. Then, combining PL and cross-sectional scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM–EDX), we assert a connection between halogen diffusion into HTLs and enhanced non-radiative recombination at perovskite/organic HTL interfaces. Finally, we conclude that both instabilities in PL spectrum are related to and affected by halogen loss from the perovskite layer into the HTL, with the HTL HOMO energy ultimately determining the PL behavior at perovskite/organic HTL interfaces under light illumination. These findings highlight the detrimental effect of halogen oxidation and diffusion within perovskite devices on stability, and also provides guidelines for the design of HTLs with suitable HOMO levels to mitigate halogen diffusion.

4:00 PM EL17.08.07
Machine Learning Assisted Synthesis of Low-Dimensional Hybrid Lead Halide White Phosphors for Solid-State Lighting Hailong Yuan[1], Luyuan Qi[2], Michael Paris[1], Florian Massuyeau[1] and Romain Gautier[1]; [1]CNRS-IMN, France; [2]Certara, France

In the past few years, phosphor converted white LEDs have been widely adopted for lighting owing to their remarkable energy efficiency. However, the low color rendering of such white illumination is the main limitation of the commercialized LEDs and, for this reason, white LEDs have limited use in different areas such as medicine. A bright white emission replicating the solar spectrum (i.e., with ultra-high color rendering and tunable color temperature) is necessary to reach such high quality lighting but discovering a single-phase white phosphor with such characteristics remains challenging as it requires to navigate in complex multidimensional spaces (composition of the host matrix/ dopants, experimental conditions…). Thus, such high quality single phase white phosphor has never been discovered.
To navigate in a complex multidimensional space with the aim of designing sun like white phosphors, we decided to substitute the human decision

component of the materials discovery process by machine learning (ML) models. [1] The Mn doped solid-solution $(TDMP)Pb(Br_xCl_{1-x})_4$:yMn ($0 \leq x \leq 1$) (TDMP = trans-2,5-dimethylpiperazine) was investigated. With the guidance of such ML tools, a series of single-phase sun-like white phosphors with ultra-high color rendering indexes (above 92) and tunable correlated color temperature (from 3000K to 7000 K) were precisely designed. This is the first report of such ultra-high color rendering and broad range of tunable color temperatures for a phosphor.
[1] H. Yuan, L. Qi, M. Paris, F. Chen, Q. Shen, E. Faulques, F. Massuyeau, R. Gautier, *Advanced Science* **2021**, *8*, 2101407.

4:15 PM EL17.08.08
Spacer Cation Control of Auger Recombination in Ruddlesden-Popper Perovskite Light-Emitting Diodes Tomoki Furuhashi, Anil Kanwat, Sankaran Ramesh, Nripan Mathews and Tze Chien Sum; Nanyang Technological University, Singapore

Quasi-2D perovskites are important materials for perovskite light-emitting diodes (PeLEDs) as the multi-quantum well (MQW) structure of the quasi-2D perovskites enhances performance of PeLEDs by efficient carrier funnelling. However, PeLEDs suffer from efficiency roll-off which is the large efficiency drop under high current density. One of the factors which causes efficiency roll-off is Auger recombination. Auger recombination is affected by the excitonic binding energy, exciton-phonon coupling, and the density of trap states. Different organic spacer cations could change these parameters by causing different distortion of the octahedral structure. Thus, studying the effect of different spacer cations on the Auger recombination behaviour in 2D perovskite is crucial to design PeLEDs with reduced roll-off. In this talk, I will discuss the use of ultrafast spectroscopy to investigate the effect of spacer in 2D perovskite on Auger recombination. Using photoluminescence and transient absorption spectroscopy, the modulation of the Auger process by the spacer will be elucidated. We will also discuss the effect of crystal structure change induced by different spacer cations on Auger recombination process, which provide insights into optimising the performance of PeLEDs based on 2D perovskites.

SESSION EL17.09: Novel Optical Property of Light Emitting Materials
Session Chairs: Himchan Cho and Tae-Hee Han
Friday Morning, April 14, 2023
Moscone West, Level 3, Room 3006

8:30 AM *EL17.09.01
Metal Organochalcogenolates—An Emerging Family of Low-Dimensional Light Emitters William Tisdale; Massachusetts Institute of Technology, United States

Metal organochalcogenolates (MOCs) are an emerging class of low-dimensional hybrid organic-inorganic semiconductors. Silver phenylselenolate (AgSePh), a prototypical 2D MOC, is a natural quantum well structure exhibiting narrow blue emission, large exciton binding energy, and in-plane anisotropy. Like transition metal dichalcogenides and 2D lead halide perovskites, MOCs can be synthesized in the form of three-dimensional crystals consisting of 2D layers held together by van der Waals forces. However, MOCs are distinguished from perovskites and other vdW crystals by the presence of organic ligands covalently bound to each 2D inorganic layer, which imparts chemical robustness and a unique handle for tuning the electronic properties.

In this talk, I will discuss efforts from my lab to synthesize new AgSePh derivatives with varying dimensionality, and characterize the excitonic nature of light emission and electron-phonon interactions in this new hybrid organic-inorganic materials family.

9:00 AM *EL17.09.02
Organic Semiconductor-Incorporated Perovskite (OSiP) Light-Emitting Materials and Devices Letian Dou; Purdue University, United States

Organic-inorganic hybrid halide perovskites are exciting new semiconductors that show great promising in low cost and high-performance optoelectronics devices including solar cells, LEDs, photodetectors, *etc*. However, the poor stability is limiting their practical use. In this talk, I will present a molecular approach to the synthesis of a new family of organic-inorganic hybrid material - Organic Semiconductor-incorporated Perovskite (OSiP). Energy transfer and charge transfer between adjacent organic and inorganic layers are extremely fast and efficient, owing to the atomically-flat interface and ultra-small interlayer distance. In addition, I will show that the energy alignment between organic and inorganic components and the assocaited optical properties can be modulated via “chemical tuning” or “pressure-gating”, opening up many new opportunities for next-generation light-emitting applications. Using these novel hybrid materials, I will demonstrate the fabrication of high quality polycrystalline thin films and highly stable and efficient LED devices with suppressed ion migration and improved external quantum efficiency, color purity, and operational lifetime.

9:30 AM EL17.09.03
Synthesis and Properties of Novel PL-Active 2D Lead-Free Double Perovskites Based on Alloys of $(PA)_4AgBiBr_8$ Andrew B. Wong; National University of Singapore, Singapore

In this work, novel two-dimensional lead-free double perovskites ($(R)_4M_aM_bM_cX_8$, a+b+c=2) were synthesized to achieve novel compositional and dimensional tunability. Herein, $(PA)_4AgBiBr_8$ was alloyed with combinations of Na/In as well as Ag/In with the goal of forming PL active materials. Moreover, the samples were tuned to be PL-emissive under room temperature via a manganese alloying strategy. Bandgap and PL emission turnability were explored through halogen substitution (chlorine and iodine). An enhanced PL emission was observed for mixed halogen phases. Three emission pathways are investigated including band edge emission, emission stemmed from self-trapped excitons, and the unique energy transfer process of alloyed Mn^{2+} ions, which will be discussed.

9:45 AM BREAK

10:15 AM *EL17.09.04
Low Dimensional Metal Halide Perovskites and Hybrids for Light Emitting Diodes Biwu Ma; Florida State University, United States

Metal halide perovskites and perovskite-related organic metal halide hybrids have recently emerged as new generation light emitting materials with exceptional structure and property tunability. By controlling the morphological dimensionality of metal halide perovskites with ABX_3 structure, low dimensional perovskite nanocrystals, e.g. 2D nanoplatelets, 1D nanowires, and 0D quantum dots, have been developed to exhibit enhanced optical properties and stability as compared to 3D counterparts. Besides 3D ABX_3 perovskites, organic metal halide hybrids with low dimensional structures at the molecular level can be prepared by using appropriate organics and metal halides, in which metal halide building blocks form 2D, 1D, and 0D structures that are completely isolated and surrounded by organic cations. These organic metal halide hybrids exhibit unique properties that are different from those of 3D ABX_3 perovskites. For instance, tunable broadband emissions with near-unity photoluminescence quantum efficiencies have been achieved in a series of 0D organic metal halide hybrids. In this talk, I will present our recent efforts on the development and study of highly luminescent and stable low dimensional metal halide perovskites and organic metal halide hybrids. Their applications in electrically driven light emitting diodes (LEDs) will be discussed.

10:45 AM EL17.09.05
The Origin of Chiroptical Activity in Chiral Perovskite Sunihl Ma[1], Ji-Young Kim[1], Chan Uk Lee[2], Jooho Moon[2] and Nicholas A. Kotov[1]; [1]University of Michigan–Ann Arbor, United States; [2]Yonsei University, Korea (the Republic of)

Chiral perovskites have been extensively studied as a promising candidate for spintronic- and polarization-based optoelectronic devices due to their unusual spin-related properties such as strong spin-orbit coupling, long spin-life time exceeding 1ns and large Rashba splitting. However, the origin of chiroptical activity in chiral perovskites is still unknown, as the chirality transfer mechanism has been rarely studied. Since the chiral perovskite with the Sohncke chiral space group of $P2_12_12_1$ was reported in 2003, their chiroptical phenomena have been interpreted based on their crystallinity. Although (i) crystallization into a chiral crystal structure induced by chiral organic molecules, (ii) chiral distortion on the surface of chiral perovskite nanoparticles, and (iii) chiral dislocations can provide the explanation of their optical and electronic properties, the electronic interactions between the chiral organic molecules and achiral inorganic framework, should also be considered. Here, we discuss the possibility of the chirality transfer via electronic interaction between the chiral organic molecules and achiral inorganic framework related to the strength and direction of hydrogen bonding. We systematically consider the effect of asymmetric hydrogen bonding and related change in the chiroptical activity of chiral perovskite by inducing the conformational change of stacking order between the two chiral organic molecules. First, through the spatial confined growth of chiral perovskite in anodized aluminum oxide template, we can successfully impose the micro-strain into the lattice of chiral perovskite, resulting in rearrangement of chiral organic molecules. As a results, remarkable chiroptical behavior with different absorption of $2.0\ 10^{-3}$ and distinct photoluminescence of $6.4\ 10^{-2}$ for left- and right-handed circularly polarized light was observed in nanoconfined chiral perovskites even at room temperature. Theoretical calculations verify that the chirality transfer phenomena mediated by the asymmetric hydrogen bonding between the chiral organic molecules and achiral inorganic frameworks is critical factor for promoting the chiroptical activity of chiral perovskites. Furthermore, the incorporation of guest molecules into the lattice of chiral perovskite evoke the rearrangement of chiral organic molecules, which also can lead to change in chiroptical activity as well as electrical properties. Through solid-state nuclear magnetic resonance spectroscopic measurements and theoretical calculations, we verify the change in the degree of chiral lattice distortion associated with different electronic interaction between the inorganic framework and guest molecules. Finally, as a preliminary proof-of-concept, a vertical-type circularly-polarized light photodetector based on chiral perovskites was developed, exhibiting an outstanding performance with a distinguishability of 0.27 and responsivity of $0.43\ A\ W^{-1}$. Our findings suggest that electronic interactions between the building blocks should be considered when interpreting the chirality transfer phenomena and designing hybrid materials for future spintronic and polarization-based devices.

11:00 AM EL17.09.06
Large Optical Anisotropy Factors of a Chiral Bismuth Iodide Hybrid Organic-Inorganic Semiconductor Alan J. Phillips[1,2], Liang Yan[3], Yi Xie[4], Matthew Hautzinger[2], Heshansamuditha Hewawalpitage[5], Peter Sercel[6], David B. Mitzi[4], Z. Valy Vardeny[5], Wei You[3] and Jeffrey Blackburn[2]; [1]Colorado School of Mines, United States; [2]National Renewable Energy Laboratory, United States; [3]University of North Carolina at Chapel Hill, United States; [4]Duke University, United States; [5]The University of Utah, United States; [6]Center for Hybrid Organic Inorganic Semiconductors for Energy, United States

Chiral materials are important tools for interconverting the spin angular momentum of circularly polarized light with electronic spin to help realize a wide variety of emerging spin-based technologies. Here we demonstrate that thin films of a Bismuth-based chiral 0D hybrid organic-inorganic semiconductor (HOIS) exhibit large anisotropy values for circularly polarized light emission (CPLE) that approach 50% circular polarization. The observed anisotropy is strongly correlated with the crystallographic orientation of the thin film and is also strongly temperature-dependent, with a marked anti-correlation with exciton transition linewidth. Detailed analysis of the CPLE anisotropy indicates large contributions from structure-dependent scattering that are analogous to the so-called "LDLB" effect observed for circular dichroism, caused by interactions between linear dichroism and linear birefringence. Although this effect has been observed for organic thin-film composites, this first demonstration in a HOIS system provides a unique route for enhancing carrier spin polarization and polarization-dependent emission in self-assembled hybrid semiconductors. These results provide a fundamental framework for understanding and harnessing the properties of low dimensional and low symmetry chiral HOIS materials for circularly polarized light applications.

11:15 AM EL17.09.07
Narrow Intrinsic Homogeneous Linewidths and Electron-Phonon Coupling of InP Colloidal Quantum Dots David B. Berkinsky, Andrew H. Proppe and Moungi G. Bawendi; Massachusetts Institute of Technology, United States

InP quantum dots (QDs) are the material of choice for QD display applications. They have been used as active layers in QD light-emitting diodes (QDLEDs) with high efficiency and color purity. Optimizing the color purity of QDs requires understanding mechanisms of spectral broadening. While ensemble-level broadening can be minimized by synthetic tuning to yield monodisperse QD sizes, single QD linewidths are broadened by elastic/inelastic exciton-phonon scattering and fine-structure splitting. Here, using photon correlation Fourier spectroscopy, we extract average single QD linewidths of 50 meV at 293K for red emitting InP/ZnSe/ZnS QDs, among the narrowest for colloidal QDs. By measuring InP/ZnSe/ZnS single QD emission lineshapes at temperatures between 4K – 293K, and modelling the spectra using a modified independent boson model, we find that acoustic phonon coupling and fine-structure splitting, which contribute similarly to the homogeneous linewidth, are most prominent at low temperature, whereas pure dephasing is the primary broadening mechanism at elevated temperatures, and optical phonon coupling contributes minimally across all temperatures. By measuring CdSe/CdS/ZnS QD emission lineshapes across the same temperature range, we find that optical phonon coupling is a larger contributor to the lineshape at elevated temperatures likely as a result of the more polar nature of CdSe/CdS/ZnS. For the first time, we are able to reconcile narrow low-temperature linewidths and broad room temperature linewidths within a self-consistent model that enables parameterization of linewidth broadening, for different material classes. Our findings reveal that red-emitting InP/ZnSe/ZnS QDs have intrinsically narrower linewidths than typically synthesized CdSe QDs, suggesting that these materials could be used to realize QDLEDs with unprecedented color purity.

11:30 AM EL17.09.08
Directional Light Amplification in Perovskite LEDs by Hybrid Photonic-Plasmonic Modes Zher Ooi[1], Alberto Jimenez[2,3], Yuqi Sun[1], Jordi Ferrer Orri[1], Hayden Salway[1], Krzysztof Galkowski[1], Changsoon Cho[1], Caterina Ducati[1], Samuel D. Stranks[1] and Miguel Anaya[1]; [1]University of Cambridge, United Kingdom; [2]Max Planck Institute for Solid State Research, Germany; [3]Universidad de Cordoba, Spain

Halide perovskites show excellent optoelectronic properties including bandgap tunability, high radiative recombination rates and narrow emission lines that make them promising candidates for the next generation LEDs. However, their thin film character is yet to be exploited to enable full control over the emission properties, opening avenues to surpass the luminous efficacies of conventional LEDs and facilitating their widespread adoption.

In this talk, we present a novel green perovskite LED architecture where enhanced emission and directionality on demand is achieved by means of a hybrid photonic-plasmonic structure. We show how a code based on the transfer matrix model boosted by a genetic algorithm identifies the best combination of materials and thin film thicknesses to maximise outcoupled light with very narrow and controllable angular dispersion; all in a realistic fashion compatible with the fabrication of efficient LEDs. This strategy leads to hybrid photonic-plasmonic modes highly confined throughout the whole cross-section of the perovskite emitter while ensuring a good band alignment of the building blocks for efficient charge carrier injection and radiative recombination.
The experimental realization of the optimum designs allows us to demonstrate devices with amplified green emission selectively enhanced at different angles. Our low temperature process can tune the perovskite thickness on a nanometric scale to enhanced electroluminescence on demand from forward direction (0°) to up to 40°. This approach expands the role of the perovskite film from a mere emitter to an active photonic layer participating in the strong interference phenomena arising from the designed photonic-plasmonic nanostructures. This strategy is truly unique as opposed to standard methods where emitters are just embedded into the optical cavities. Our methodology is versatile and easily integrable into cost-effective perovskite LEDs with emission lines covering the entire visible spectrum. Thereby opening avenues for their application in displays and light sources where control over angular dispersion of light is crucial.

SESSION EL17.10: Virtual Session: Perovskite LEDs and Lasers
Session Chairs: Lina Quan and Barry Rand
Tuesday Morning, April 25, 2023
EL17-virtual

8:00 AM *EL17.10.01
Synthesis and Applications of Low-Toxicity Near-Infrared-Emitting Colloidal Quantum Dots Zhi Kuang Tan; National University of Singapore, Singapore

Many emerging technologies rely on near-infrared emitters for covert illumination and sensing. Examples include the facial recognition devices found on our smart-phones, sensing devices on fitness tracking watches, gaming consoles, robotic cleaners and self-driving cars. Colloidal quantum dots are excellent emitters that could be conveniently solution-processed, and could potentially find useful applications in these devices. Unfortunately, there are very few known colloidal quantum dots that operate in the near-infrared spectral range. Some examples include PbS and and CsPbI3, which contain restricted heavy metals. In this talk, I will discuss new strategies to prepare low-toxicity heavy-metal-free core-shell colloidal quantum dots with high luminescence efficiencies and with long emission wavelengths of above 900 nm. I will also present some of their applications in optoelectronic devices, such as in light-emitting diodes and in luminescent solar concentrators.

8:30 AM *EL17.10.02
Suppression of Ion Migration for Stable Perovskite LEDs Zhengguo Xiao; University of Science and Technology of China, China

The external quantum efficiency (EQE) of perovskite LEDs (PeLEDs) has dramatically improved to above 20% in the past few years. Operation stability becomes the most challenging issue for the application of perovskite LEDs. Ion migration was acknowledged to be one of the main causes of degradation of perovskite LEDs.

In this talk, we will present our efforts to improve the stability of perovskite LEDs, including 1) suppression of ion migration with incorporation of bulky organoammonium ligands, 2) enhanced operation stability in all-inorganic perovskite LEDs due to the suppressed ion migration, and 3) absence of ion migration in tin halide perovskite LEDs under device working conditions. and 4) Suppressed ion migration in perovskite single-crystal LEDs with enhanced operation stability.

9:00 AM *EL17.10.03
Bottom Surface Induced Phases Distribution of Quasi-Two-Dimensional Perovskite for Efficient Blue Light-Emitting Diodes Jingbi You; Chinese Academy of Sciences, China

Performance of blue perovskite light-emitting diodes (PeLEDs) is still lagging far behind green and red emissions. Inferior carrier injections, non-radiative recombination and random phase distribution mainly account for limited advances in quasi-two-dimensional blue PeLEDs. Here, we modulated of hole injection layer by addition alkali metal salt CsCl, a better band alignment and improved charge injection have been achieved. More interestingly, the modified substrate induced the following growth of perovskite layer with better phase distribution, which lead to the less non-radiative recombination and enhanced charge transport. Accordingly, a maximum external quantum efficiency of 16.07% had been demonstrated in the sky-blue PeLEDs, with a stable emission peak located at 486 nm and improved operational stability. This strategy contributes an effective way for the fabrication of high-performance and stable blue PeLEDs toward practical applications.

9:30 AM EL17.10.04
Enhanced Blue Emission in Rb_2HfCl_6 Double Perovskite via Bi^{3+} Doping and Cs^+ Alloying Haoyue Wan, Fengyan Jia, Filip Dinic, Benjamin Rehl, Muhammad Imran, Yanjiang Liu, Watcharaphol Paritmongkol, Pan Xia, Yuan Liu, Sasa Wang, Yakun Wang, Oleksandr Voznyy, Sjoerd Hoogland and Edward H. Sargent; University of Toronto, Canada

Lead-free double perovskites offer non-toxic properties and strong emission via alloying and doping. Herein we report the synthesis of pure Rb_2HfCl_6 microcrystals as well as Cs-alloyed and Bi-doped $RbCsHfCl_6$ microcrystals. While pure Rb_2HfCl_6 is almost non-emissive, alloying with Cs and Bi doping led to strong deep blue emission at 466 nm with the photoluminescence quantum yield increase from ~0% to 66%. Density functional theory studies attest to improved phase stability upon Cs alloying and link photoluminescence to Bi^{3+} dopant-induced localized states.

9:35 AM *EL17.10.05
2D Perovskite Passivation Strategy for High Efficient Solar Cells—What's Behind? Giulia Grancini; University of Pavia, Italy

Three-dimensional (3D)/low-dimensional (LD) perovskite solar cells (PSCs) offer an effective strategy to overcome the trade-off between perovskite solar cells device performance and stability. Improving the device longevity, while concomitantly simultaneously enhancing increasing the solar cell open circuit voltage and fill factor of the solar cell is the current challenge. Despite being one of the most popular and effective way processing techniques, whether the presence of this surface LDP layer would be - or not-represents the winning crucial path for the future of this technology remains elusive. In particular, atomic layer combined surface and bulk passivation using surface modifiers such as organic dopants, casts the doubts on the effective need for of having an homogeneous LDP cover capping layer. In this talk, I will discuss the interfacial passivation with different cations such as M-PEAI, M-PEABr, and M-PEACl, showing the role of the passivation and how different halides affect the device performance of the devices. In addition, I will compare recent results obtained in the 3D/LDP configuration with the surface cation passivation strategy, which can still pushes produce the performances to values comparable to the LDP/3D bilayers. I will providing a comprehensive perspective on the benefits from of the two different strategies, but also presenting how LDP interfaces can play a role in alternative new configurations, such as tandem solar cells [1,2].

Acknowledgements I acknowledge the “HY-NANO” project that has received funding from the European Research Council (ERC) Starting Grant 2018 under the European Union’s Horizon 2020 research and innovation programme (Grant agreement No. 802862).

Reference
[1] Degani et al, Sci Advances 7, 49, 2021
[2] Degani et al, submitted

SYMPOSIUM

April 10 - April 27, 2023

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SESSION EL18.01: Conjugated Polymers
Session Chairs: Ying Diao and Jie Xu
Monday Morning, April 10, 2023
Moscone West, Level 3, Room 3018

8:00 AM EL18.01.01
Polyborosiloxane-Conjugated Polymer Blends as a Self-Healing Material for Wearable Sensors Peter Finn and Bob C. Schroeder; University College London, United Kingdom

The need for durable and flexible electronics is emerging as a high research priority as electronic materials are being integrated into wearable devices for bioelectronic monitoring and sensing applications. Since silicon is rigid and brittle and not suitable for wearable technology, this has led to the use of organic materials as the active layer in flexible devices. However, organic materials still exhibit wear and tear after prolonged use and irreversible damage will lead to decreased device performance and eventual failure. Therefore, new properties need to be introduced to prevent this issue which will hopefully lead to a more reusable society.

Self-healing has received a lot of attention recently and is a strong candidate for improved durability and reusability. A self-healing material can reform and repair damage without the need of outside help and is split up into extrinsic and intrinsic systems. Extrinsic healing is governed by an external source embedded into the material that promotes reformation such as micelles releasing catalysts for new bond formation. Whereas intrinsic healing is governed by functionalities inherent to the structure of the material. A long list of intrinsic moieties have been used for self-healing including hydrogen bonding, ionic interactions, covalent bonding, π-π interactions and supramolecular structures which has lead to promising results. Many of these intrinsic functionalities have been implemented into polymers making them ideal candidates to combine with polymeric organic semiconductors as new self-healing electronic materials.

Herein, we have combined the semiconducting properties of conjugated polymers with polyborosiloxane, a polysiloxane polymer crosslinked with boric acid. Polyborosiloxane intrinsically contains dative B-O bonds enabling a reversible and dynamic system needed for self-healing. Via either blending or crosslinking the two polymers and exploring the electrical characterisation under mechanical stress, our findings show that this new class of viscoelastic materials have potential for durable and wearable electronics.

8:15 AM EL18.01.02
Redox-Active Polymeric Ionic Liquids for Semiconducting Polymer Dopants Saejin Oh, Phong H. Nguyen, Thi Tran, Kan Tagami, Audra J. DeStefano, Dafei Yuan, Andrei Nikolaev, Songi Han, Rachel A. Segalman, Javier Read de Alaniz and Michael L. Chabinyc; University of California, Santa Barbara, United States

Semiconducting polymers are attractive materials for flexible organic electronic applications due to their low cost and ease of processability. For such materials, controlling the doping level, conductivity, and device stability is important for improving the performance of organic electronic devices. Electrical doping is usually achieved through the introduction of small-molecules that undergo charge transfer leading to either *p*- or *n*-type doping. While there are various molecular *p*-type dopants that are widely used with semiconducting polymer doping, their range is relatively limited. The small-size of molecular dopants make it challenging to control the precise ion penetration depth into solid films and limits detailed understanding in how the ion penetration affects the charge transport. Here, an efficient *p*-type dopant with a radical-cation bearing polymeric ionic liquid (PIL) is introduced to dope poly(3-hexylthiophene) (P3HT). In our previous study, we have successfully designed a low T_g and charge conducting phenothiazine (PTZ) based PIL with partial oxidation of the PTZ units, with TFSI as the charge balancing counter anion. Upon formation of bilayers of the PIL and P3HT, efficient charge transfer occurs between the two polymer layers. The facile redox reaction at the phenothiazine-TFSI PIL and the semiconducting polymer interface enables efficient electron transfer while preventing the redox active unit from penetrating into the bulk. Furthermore, the electrical conductivity upon polaron generation in P3HT films is comparable to most known dopants. This new redox-active PIL not only induces facile charge generation to attain high electrical conductivity, but also opens up a new possibility to broaden the choice of *p*-type dopant for semiconducting polymers.

8:30 AM *EL18.01.03
Solution-Processable N-Doped Transparent Organic Conductor Jianguo Mei; Purdue University, United States

In this talk, we will introduce our latest development on the **solution-processable n-doped transparent organic conductor.**

9:00 AM *EL18.01.04
Autonomous Platform (Polybot) for Electronic Polymers Discovery Jie Xu; Argonne National Laboratory, United States

In the past 40 years, conjugated polymers have been widely studied and used in many novel applications, such as printable electronics, wearable electronics and flexible energy devices, because of their unique characteristics of (opto)electronic property, mechanical softness and low-cost manufacturing. The high throughput production of conjugated polymer thin films at low temperatures is a critical processing step in the manufacturing of devices. However, the processing of these nanometers-thick layers generally occurs under strong deformations/stressors and rapid flows, conditions under which equilibrium thermodynamics does not apply, resulting in significant structural variabilities in ways that are hard to predict. As a result, it remains a central challenge to control the assembly of these conjugated polymers towards desired multi-scale morphological orderings, which critically impact their solid-state properties (e.g., electronic property, optical property, mechanical property, stability, etc.). I will introduce a new experimental paradigm we recently developed that combines the strengths of rapid and robust experiment acquisition from robotic technologies (i.e., high-throughput processing and characterization) and fast analysis of complex datasets using machine learning (ML) for autonomously controlling conjugated polymer assembly towards targeted structures for desired solid-state properties. Utilizing this autonomous platform (PolyBot, https://www.anl.gov/cnm/polybot), we were able to identify the processing path much more efficiently and extract the high-dimensional formulation-processing-property relationships for revealing the general design principles. This new experimental framework is amenable to continuous improvement, such that sophistication can be added over years to continually redefine the cutting-edge of autonomously conjugated polymer discovery.

9:30 AM EL18.01.05
From Chlorinated Solvents to Branched Polyethylene and Paper—New Materials and Methods for Sustainable and Greener Printed Electronics Simon Rondeau-Gagne; University of Windsor, Canada

Among the new semiconductors developed in the last decade, π-conjugated semiconducting polymers possess particularly outstanding properties, including good charge transport properties, low elastic moduli and high biocompatibility/low toxicity. As the impact of semiconducting polymers is increasing in various fields, limited attention has been given to their environmental footprint. From their manufacturing and processing using toxic high-boiling point solvents to their application in electronics that can accumulate in the environment, the environmental footprint of organic semiconducting materials is non-negligible; it is imperative to develop alternate manufacturing processes and molecular designs to improve current materials and make more sustainable technologies. Developing novel applications for these materials in environmental sciences is also a promising avenue to reduce their environmental footprint while simultaneously exploiting the unique chemistry of these materials to create new opportunities.

To tackle the emerging environmental and manufacturing challenges related to the utilization of semiconducting materials in printed electronics, our team recently developed new strategies to design and process semicrystalline semiconducting polymers in non-toxic solvents rather than high boiling points, toxic chlorinated solvents commonly used to generate printed electronics. The first part of this presentation will focus on the use of a low-molecular-weight non-toxic branched polyethylene (BPE) as a solvent to process diketopyrrolopyrrole-based semiconducting polymers. We exploited a solvent-induced phase separation (SIPS) technique to produce thin films of semiconducting polymers for the fabrication of organic field-effect transistors (OFETs). OFETs based on the semiconducting films processed from BPE showed similar device characteristics to those prepared from chloroform without thermal annealing, confirming the efficiency and suitability of BPE to replace traditional chlorinated solvents for green organic electronics. In the second part of this presentation, we will discuss the recent progress realized in our group to prepare thin film electronics on paper substrates from environmentally benign processes and materials. While there are numerous substrates used for the development of flexible organic electronics, paper has become a leading candidate as an environmentally sustainable substrate incorporating flexibility, thermal stability, and cost effectiveness. With various solution deposition techniques, fabrication and optimization of a paper-based organic thin film transistor is explored with the goal to integrate greener substrates into the production of large-scale organic flexible electronics.

Throughout this presentation, a detailed characterization of the solid-state morphology of the materials in thin films will be discussed, as well as the new structure-property relationships unveiled during our investigation. The results obtained from a multimodal characterization performed on both materials and devices will be highlighted, and a particular focus will be put on the molecular design of the materials and their synthesis.

9:45 AM EL18.01.06
Mixing-Induced Orientational Ordering in Liquid-Crystalline Organic Semiconductors of PE-BTBT-C_n Kiyoshi Nikaido[1], Satoru Inoue[1], Reiji Kumai[2], Toshiki Higashino[3], Satoshi Matsuoka[4], Shunto Arai[1] and Tatsuo Hasegawa[1]; [1]The University of Tokyo, Japan; [2]High Energy Accelerator Research Organization (KEK), Japan; [3]National Institute of Advanced Industrial Science and Technology (AIST), Japan; [4]Nagasaki University, Japan

Recent reports show that several high-mobility organic semiconductors (OSCs), composed of rod-like π-electron cores linked with alkyl chains, exhibit thermotropic liquid-crystalline (LC) phases, which attracts considerable attentions. A typical example is 2-alkyl-7-phenyl-[1]benzothieno[3,2-*b*][1]benzothiophene (Ph-BTBT-C_n, where *n* represents the number of carbon atoms in alkyl chain) [1,2], which exhibits a field-effect mobility higher than 10 cm^2/Vs [1,3]. The compounds exhibit smectic liquid crystalline (LC) phases at elevated temperature [1,2]. However, the actual liquid crystal phases have not been understood in detail so far, in terms of emerging mechanism as well as the molecular arrangement structure. It should be significant to reveal the roles of substituents and the way to control the layered structure utilizing the LC phase for the development of the OSCs.

Herein we focus a novel series of OSCs of PE-BTBT-C_n, in which the phenyl group in Ph-BTBT-C_n is replaced with a phenylethynyl (PE) group of slightly longer length and rotational freedom [4]. The compounds show unique molecular arrangements closely related to LC phases: In cases where the alkyl group of PE-BTBT-C_n is longer than the PE group ($n \geq 8$), we obtained a typical bilayer-type herringbone (*b*-LHB) phase in which the orientations of the molecular long axes in each layer are aligned at room temperature, and observed a transition to the smectic liquid crystal (SmE) phase at a high temperature. However, when the alkyl and PE groups have approximately the same length ($n = 6$), the arrangement takes on a disordered LHB (*d*-LHB) structure, as revealed by a crystallographic analysis using electron diffraction [4]. In this case, the herringbone-type ordering between BTBT skeletons in the molecular layer is maintained, despite the random orientation of the molecular long axis. As the transition to the SmE phase disappears at high temperatures, we deduce that the *d*-LHB phase is the frozen phase of the SmE phase. Owing to the emergence of LC-like *d*-LHB phase at a particular alkyl chain length of $n = 6$, the compound provides a unique platform to investigate the competition between ordered and disordered phase depending on the alkyl chain length, and the way to control the layered ordering of rod-like OSCs.

With use of the material system, we successfully found that a drastic structural ordering from *d*-LHB to *b*-LHB phase can be induced by mixing a small amount of longer-alkylated molecule to PE-BTBT-C_6 through solution processes [5]. The mixing-induced ordering phenomenon was clearly observed by the change in the film morphology of the mixtures of PE-BTBT-C_6 and PE-BTBT-C_{12} which was probed by the combination of atomic force microscope, thin-film X-ray diffraction (XRD) and X-ray reflectivity measurements. The enhancement in the hole mobility in the single-crystalline organic thin film transistors (OTFTs) was also observed along with the mixing-induced ordering, which indicates that the method can be useful to achieve high-mobility OTFTs. The temperature-composition phase diagrams were systematically investigated by temperature-controlled powder XRD and differential scanning calorimetry (DSC) measurements. The phase diagrams and the entropy of transition from crystal to LC phase reveals that the emergence of *d*-LHB and *b*-LHB phase is determined by the competition of smectic LC phase and *b*-LHB phase. Based on the results, we discuss the origin of the mixing-induced phenomenon and the essential roles played by the temporary LC phase in the crystallization of layered crystal phases through solution processes.

[1] H. Iino *et al.*, *Nat. Commun.* **6**, 6828 (2015).
[2] S. Inoue *et al.*, *Chem. Mater.* **27**, 3809 (2015).
[3] T. Hamai *et al.*, *Phys. Rev. Appl.* **8**, 054011 (2017).
[4] S. Inoue *et al.*, *Chem. Mater.* **34**, 72 (2022).
[5] K. Nikaido *et al.*, *Adv. Mater. Interfaces* 2201789 (2022).

10:00 AM BREAK

10:30 AM *EL18.01.07
Chiral Organic Semiconducting Materials for Next-Generation Flexible Optoelectronics Joon Hak Oh; Seoul National University, Korea (the Republic of)

Chiral organic semiconducting materials are expected to open new opportunities for next-generation flexible optoelectronics. I will introduce fabrication of chiral supramolecular assemblies using organic semiconductors and their structure-chiroptical property relationships. I will present synthesis of chiral supramolecular biocoordination polymers and their applications in various flexible sensors. I will also introduce a skeleton merging approach that can distort the planar semiconducting backbone, which enables high-performance broadband circularly polarized light detections up to the near-infrared spectral region. In addition, a simple yet powerful method to fabricate chiroptical flexible layers via supramolecular helical ordering of conjugated polymer chains will be introduced. These findings provide guidelines for enhancing chiroptical properties using supramolecular chirality and rational molecular design of organic semiconductors toward high-performance chiral optoelectronics. In addition, these results demonstrate an effective strategy to realize on-chip detection of the spin degree of freedom of photons necessary for encoded quantum information processing and high-resolution polarization imaging.

11:00 AM EL18.01.08
Optimization of Carbohydrate-Bearing Semiconducting Polymers: A Case Study toward Greener High-Performance Electronics Madison Mooney and Simon Rondeau-Gagne; University of Windsor, Canada

Semiconducting polymers are vital to the development of next-generation electronics due to their excellent physical and optoelectronic properties. These materials possess several advantages over current silicon-based electronics, including good mechanical features, synthetic tunability, and the potential for emerging properties such as self-healing and biocompatibility. Another major advantage of semiconducting polymers is their solution processability, which allows manufacturers to access a wide variety of new fabrication techniques such as spin-coating and inkjet printing to produce thin-film electronics. While solution processing offers many new avenues for electronics production, it also leads to a major ecological concern. Due to the extended π-conjugation of these materials, their solubility is often limited to toxic, halogenated solvents that can be extremely harmful to humans and the environment. As such, the significant environmental toll of processing these materials at an industrial scale needs to be proactively considered.

In recent years, several strategies have been proposed to avoid the use of such toxic solvents, either by careful selection of new solvent systems or engineering of polymer structures to alter their solubility. Using a molecular engineering approach, we developed alcohol-processable semiconducting polymers using carbohydrate side chains. These pendant groups were chosen because they are bio-sourced, non-toxic and contain many alcohol groups. The use of carbohydrates to improve solubility has been extensively used in the medical industry, but has not previously been applied to electronic materials. The extensive hydrogen bonding of these new side chains significantly improved solubility of the semiconducting polymer in more polar solvents, including n-butanol. The use of carbohydrate moieties was also found to have little impact on electronic performance in organic field-effect transistors (OFETs), making this a viable approach toward greener electronics fabrication without sacrificing performance. Interestingly, these new side chains were found to have significant impacts on thin film morphology and solid-state stacking when incorporated into the polymer in different ratios. Since morphology and packing can directly affect charge mobility, the use of these carbohydrate side chains has been systematically investigated in semiconducting polymers as not only an avenue toward eco-friendly device manufacturing, but also a novel way to improve charge transport for high-performance OFETs. This work presents an in-depth case study of the effects of polymer structure and processing conditions on electronic performance. This foundational study demonstrates that novel side chain engineering is key to the future of environmentally conscious next-generation electronics.

11:15 AM EL18.01.09
Highly Conductive and Stable N-Type Conducting Polymer Zhifan Ke[1], Ashkan Abtahi[1], Jinhyo Hwang[1], Ke Chen[1], Jagrity Chaudhary[1], Inho Song[1], Kuluni Perera[1], Kyle Baustert[2], Kenneth R. Graham[2] and Jianguo Mei[1]; [1]Purdue University, United States; [2]University of Kentucky, United States

The search for solution-processable, environmentally and thermally stable conducting polymers is warranted, due to their applications in displays, solar cells, touch screens, and emerging printed electronics. Here, we report an n-doped organic conductive ink from oxidative polymerization. The resulting conductive polymer thin films exhibit low sheet resistance with high optical transmittance. This conductive polymer can function as transparent conductors and electrodes in electrochemical devices.

11:30 AM EL18.01.10
High Optoelectronic Performance in PEDOT Thin Films Fabricated by Oxidative Chemical Vapor Deposition Meysam Heydari Gharahcheshmeh; San Diego State University, United States

Conjugated conducting/semiconducting polymers have attracted enormous attention because of their unique characteristics, such as metal-like conductivity, optical transparency, ionic conductivity, and mechanical flexibility. Engineering the texture and nanostructure of conjugated conducting/semiconducting polymers to enhance the interchain charge transfer integral is a promising approach to overcome the charge localization and electrical conductivity enhancement. Here, ultraconformal poly(3,4-ethylenedioxythiophene) (PEDOT) thin films were grown using antimony pentachloride ($SbCl_5$) oxidant via water-assisted (W-A) oxidative chemical vapor deposition (oCVD). Engineering the π-π stacking distance through tuning the oxidant saturation ratio (OSR) yields a high-record of electrical conductivity (ca. 7520 S cm^{-1}) in as-deposited PEDOT thin films grown by W-A oCVD method. In addition, the optoelectronic figure of merit () in the range of 94 was achieved in PEDOT thin films, which is 1.9× and 6.7× higher than its counterparts grown by vanadium oxytrichloride ($VOCl_3$) and iron chloride ($FeCl_3$) oxidizing agents, respectively. Furthermore, the recent integration of oCVD PEDOT in solar cell and electrochemical energy storage devices will be presented.

SESSION EL18.02: Wearable Systems
Session Chairs: Simiao Niu and Sihong Wang
Monday Afternoon, April 10, 2023
Moscone West, Level 3, Room 3018

1:30 PM EL18.02.01
A Hemispherical Image Sensor Array Fabricated with Organic Photo-memory Transistors Yeongin Kim[1,2], Chenxin Zhu[1,1], Wen-ya Lee[1], Anna Smith[3], Haowen Ma[4], Xiang Li[4], Donghee Son[1,5], Naoji Matsuhisa[1], Jaemin Kim[1], Won-Gyu Bae[1], Sung Ho Cho[6], Myung-Gil Kim[1], Tadanori Kurosawa[1], Toru Katsumata[7], John W. To[1], Jin Young Oh[1,8], Seonghyun Paik[1], Soo Jin Kim[1], Lihua Jin[1,9], Feng Yan[4], Jeffrey Tok[1] and Zhenan Bao[1]; [1]Stanford University, United States; [2]University of Cincinnati, United States; [3]University at Buffalo, The State University of New York, United States; [4]Nanjing University, China; [5]Sungkyunkwan University, Korea (the Republic of); [6]Samsung Display, Korea (the Republic of); [7]Asahi Kasei, Japan; [8]Kyung Hee University, Korea (the Republic of); [9]University of California, Los Angeles, United States

Hemispherical image sensors simplify lens designs, reduce optical aberrations, and improve image resolution for compact wide-field-of-view cameras. To achieve hemispherical image sensors, organic materials are promising candidates due to the following advantages: tunability of optoelectronic/spectral response and low-temperature low-cost processes. Here, we developed a photolithographic process to prepare a hemispherical image sensor array using organic thin film photo-memory transistors with a density of 308 pixels per square centimeter. Our design includes only one photo-memory transistor as a single active pixel, in contrast to the conventional pixel architecture, consisting of select/readout/reset transistors and a photodiode. Our organic photo-memory transistor, comprising light-sensitive organic semiconductor and charge-trapping dielectric, is able to achieve linear photo-response (light intensity range, from 1 to 50 W m^{-2}), along with responsivity as high as 1.6 A W^{-1} (wavelength = 465 nm) for a dark current of 0.24 A m^{-2} (drain voltage = -1.5 V). These observed values represent the best responsivity for similar dark currents among all the reported hemispherical image sensor arrays to date. We further developed a transfer method that does not damage organic materials for hemispherical organic photo-memory transistor arrays. Our developed techniques are scalable and are amenable for other high-resolution 3-dimensional organic semiconductor devices.

1:45 PM EL18.02.02
Wearable Stretchable Microneedle-Based Patch for Online Detection of Multiple Biomarkers in Interstitial Fluids Rawan Omar and Hossam Haick; Technion-Israel Institute of Technology, Israel

With the increasing number of aging populations, the outbreak of new infections and diseases, and the stressed lifestyle, the need for sophisticated advanced technologies for online health monitoring is increasing. In this regard, measuring and evaluating health related biomarkers and physiological indexes have a considerable advantage and is considered an informative prognostic tool for health assessment. However, these biomarkers are usually measured and analysed using bulky laborious equipment, painful and time-consuming methods which require expert personnel to perform, may cause irritations and infections and are usually collected and analysed offline and not continuously. Using wearable biosensors for online biomarkers monitoring can be a promising approach to overcome this condition. In this regard, biosensors based on field-effect transistors (FETs) have promising advantages, including high sensitivity, quick response, and easy fabrication. Most of the currently developed FET designs are used only for sensing sweat and in-vitro blood/interstitial fluids (ISF). Using ISF for online detection of biomarkers and long-term health monitoring with FETs has not yet been fully resolved. In this work, we developed an innovative stretchable, flexible, skin-conformal and quick-response microneedle-based extended gate FET (MN-EGFET) biosensor patch for online and real-time detection of multiple biomarkers including glucose, sodium, cortisol, and pH in the ISF for minimally invasive health monitoring along with high sensitivity, low limit of detection, excellent biocompatibility, and on-body mechanical stability. On-body measurements were also carried out on a healthy individual to evaluate the long-term health monitoring performance of our wearable microneedle device against a gold standard commercial device. Both devices were found to show a similar performance and tendency, indicating the great promise for our device in clinical and on-body applications. This wearable microneedle device was also integrated with a flexible wireless data transmission chip including Internet-of-Things (IoT) cloud, to transmit the data continuously to a smartphone, demonstrating its effectiveness as a diagnostic and monitoring tool in primary and specialized healthcare, as well as its potential in real-life home healthcare and clinical applications.

2:00 PM *EL18.02.03
Air-Stable Ultra-Flexible Organic Photonic System for Health Care Application Tomoyuki Yokota[1], Kenjiro Fukuda[2] and Takao Someya[1]; [1]The University of Tokyo, Japan; [2]RIKEN, Japan

Optical bio-imaging is a non-invasive method to measure biological information from outside of the body, such as fluorescent probes, photoacoustic imaging, and near-infrared spectroscopy have been widely used as medical devices. In recent years, along with the development of semiconductor technology, the miniaturization of these imaging devices has been progressing. In particular, organic optical devices are being actively applied to healthcare by integrating them into wearable devices due to the featured characteristics such as high efficiency, flexibility, lightweight. For example, a flexible device that integrates an OLEDs and an OPD can be attached to a finger and measure the pulse wave by measuring the light reflected in the body. It is also possible to measure the blood oxygen ratio by a two-color light source such as red and green, or red and near-infrared light. Other biometric data such as veins and fingerprints image can also be taken by using high-resolution imaging sensors. It is important to improve the adhesion between the device and the body in order to perform such in vivo imaging with high accuracy. In this study, we developed an ultra-flexible photonic system in which the organic light-emitting diode and organic photodiode are integrated on the same substrate by improving the air stability of ultra-flexible organic light-emitting diodes and photodiodes. By applying an inverted structure, the ultra-flexible organic light-emitting diode has been operated over 10 days even without a high-barrier passivation layer. The ultra-flexible OLED shows high air stability in which the current density is maintained at more than 50% of the initial state. The organic photodiodes also show high air stability, with less than 1% change in photocurrent and less than 10 nA/cm^2 dark current after 10 days. The sensor system that integrates these air-stable optical devices is extremely thin with a total thickness of 3 µm. Therefore, it can be directly attached to the skin, and the pulse wave can be measured simply. Furthermore, we succeeded in measuring the pulse wave propagation time by combining the optical system with an electrocardiogram. When the blood pressure value was calculated from the measured pulse wave propagation time, a high correlation coefficient of 0.89 was achieved with the value measured by a conventionally used cuff-type blood pressure monitor system.

2:30 PM EL18.02.04
Wireless Body Area Sensor Network Based on Stretchable RFID Design Simiao Niu; Rutgers, The State University of New Jersey, United States

Body area sensor network (BodyNET) is a promising platform for next-generation healthcare and realizing its full potential requires seamless hybridization between on-body sensors and both rigid circuits for signal readout, conditioning and wireless transmission components. Rigid sensors based BodyNET has already been demonstrated due to its fabrication compatibility with existing integrated circuit technologies while the integration of soft on-skin sensors into the BodyNET still remains a grand challenge. So far, the integration of rigid silicon circuits and stretchable sensors on a single substrate has only been realized through the introduction of rigid islands and stretchable interconnects. However, the weak interfaces between soft and rigid parts severely compromise the robustness of such systems. Therefore, physical separation of stretchable sensors from rigid readout circuits that completely eliminate all fragile interfaces may be an effective strategy towards an intimate and robust BodyNET system.
Here, we demonstrate a bodyNET system comprised of battery-free and chip-free stretchable sensors attached on multiple skin locations to gather human physiological and movement signals, which are wirelessly operated by silicon readout circuits attached to textiles. The physically-separated stretchable sensors and silicon readout circuit are communicated via passive radio frequency identification (RFID) technologies. The stretchable sensor tags are fabricated via printing intrinsically stretchable materials on elastic substrates, and are completely free from rigid silicon chips and batteries to avoid potential stress concentrated regions and improve system robustness. The main technical challenge encountered here is the strain-induced changes of both sensor antenna inductance and resistance that can affect readout effectiveness. We address this issue by adapting an unconventional detuned RFID tag design and verify its appropriateness by both simulation and experiments. Our design enables the bodyNET system to maintain full functionality even when the on-skin sensors are stretched to 50% strain. To further enable multiple sensors in one RFID tag, we have fabricated and integrated a high frequency intrinsically stretchable rectifying diode and low voltage driven intrinsically stretchable ring oscillators for RF energy harvesting and frequency modulation. Finally, the bodyNET is demonstrated by connecting multiple sensor nodes and smartphone through Bluetooth. Our hands-free bodyNET could continuously, simultaneously and accurately monitor human's respiration, pulse and body movements. Thus, this platform constitutes a powerful tool in analyzing relevant human activities and physiological signals, hence enabling critically-needed possibility for real-time physiological studies. [1]

Reference:
1. S. Niu, N. Matsuhisa, ... , X. Chen*, Z. Bao*, *Nature Electronics*, 2019, 2, 361
2. S. Niu, W. Wang, N. Matsuhisa, ... , Z. Bao*, Manuscript in preparation.

2:45 PM EL18.02.05
Rechargeable Cyborg Insects with Ultrathin Organic Solar Cell Module Kenjiro Fukuda[1], Yujiro Kakei[1,2], Shumpei Katayama[1,2], Hirotaka Sato[3], Shinjiro Umezu[2] and Takao Someya[1,4]; [1]RIKEN, Japan; [2]Waseda University, Japan; [3]Nanyang Technological University, Singapore; [4]The University of Tokyo, Japan

Cyborg insects have been proposed for applications such as urban search and rescue. Body-mounted energy-harvesting devices are critical for expanding the range of activity and functionality of cyborg insects. However, achieving a power output of 10 mW or higher using energy harvesters mounted on living movable insects for wireless locomotion control remains challenging. To integrate devices into small animals with limited surface areas and carry loads29, device design and integration strategy of large-area solar cells is required to obtain sufficient power output and simultaneously maintain the basic behavioral abilities of insects. Because the output power of the solar cell is proportional to the area, both the load of the device and the contact between the device and the moving joints considerably impair motion abilities.
Here, we report a power-rechargeable cyborg insect that uses a mounted ultrasoft organic solar cell module that does not impair the insect's basic motion abilities and demonstrates recharging wireless locomotion control with all components integrated on insects. We developed a combined strategy of ultrathin film electronics and an adhesive–nonadhesive interleaving structure on the insect abdomen to secure their basic motion abilities, confirming their effectiveness quantitatively with traversing obstacles and self-righting ability from an upside-down orientation on the ground. These tests revealed that a 5 µm thick or less polymer (having Young's modulus of several GPa) adhered with an interleaving structure could secure unchanged motion abilities. The ultrathin organic solar cell module (3 series connection) adhered onto a 3D-printed curved insect surface model achieves a power output of 17.2 mW, which corresponds to power per weight of 8.69 W g–1. Finally, recharging and wireless locomotion control was realized using living cyborg insects that contained electronic components. After the simulated sunlight illumination was applied to the organic solar cell module on G. portentosa for 30 min, turn-right locomotion control was wirelessly conducted. The stimulation signals were wirelessly transmitted for 2.1 min with the charged battery. During this period, locomotion control was attempted multiple times, which confirmed that the wireless control was successfully performed repeatedly. The approach presented in this study contributes to expanding the range of activity and realizes diverse functions for the cyborg insects.

3:00 PM BREAK

SESSION EL18.03: Flexible and Stretchable Devices I
Session Chairs: Yeongin Kim and Francisco Molina-Lopez
Monday Afternoon, April 10, 2023
Moscone West, Level 3, Room 3018

3:30 PM *EL18.03.01

Intrinsically-Stretchable Conductors for Conformal Tissue-Device Interfacing Dae-Hyeong Kim[1,2]; [1]Institute for Basic Science, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)

Recent advances in flexible and stretchable electronics have attracted great attention due to its potential applications in personalized bio-integrated healthcare devices. The mechanical mismatch between conventional rigid electronic devices and soft human tissues oftentimes causes various issues, such as a low signal-to-noise ratio of biosensors, inflammations on the tissue interfacing with the bioelectronics, skin irritations in the case of long-term wearing of the device, and ineffective electrical stimulations in feedback therapies. Ultra-flexible and stretchable bioelectronic devices have a low system modulus and intrinsic softness, and thereby have a potential to solve these issues. Nanomaterials and their composites with the elastomeric matrix are a particularly promising material candidate for realizing this soft bioelectronics concept. In this talk, the unique strategies in the synthesis of nanmaterials, processing as stretchable functional nanocomposites, seamless integration into soft bioelectronics, and their wearable and/or implantable device applications are presented. These efforts have combined recent breakthroughs in nanomaterials and soft electronics, and are expected to address unmet clinical challenges.

4:00 PM *EL18.03.03
Flexible Iontronics Using Neuro-inspired Ion Dynamics Do Hwan Kim; Hanyang University, Korea (the Republic of)

Creating artificial iontronics that shows the tactile recognition and memory-based motion tasks by tactile neural network of human somatosensory system has been a big challenge in wearable and stretchable neuromorphic optoelectronics as well as neuro-inspired robotic systems. In particular, biomimetics has emerged as a burgeoning area in the field of deformable tactile sensor and memory skins that has led innovations in material designing and device structure manipulation with the aim of imitating tactile encoding functionality of human, intelligently.
Herein, inspired by the sophisticated physiological ion dynamics of living cells as well as nerves, we describe a uniquely designed deformable iontronics. Novel bottom-up strategy employed here resulted into supramolecular polymer networks through non-covalent interactions between poroelastic artificial ions and viscoelastic polymer chains or through mechano-sensitive ion dynamics triggered by hydrogen-bonding and ion-dipole interaction, which endows effective tactile augmentation under mechanical stimuli, showing high signal-to-noise level without any interference. This design for neuro-inspired iontronic channel allows for high-performance synaptic plasticity as well as ultrasensitive mechano-transduction over a wide spectrum of pressure, which can serve next flexible, neuromorphic haptic interface platform for human-machine interactive real metaverse.

4:30 PM EL18.03.04
Nature Inspired Sensors for Liquid Environments Wen Cheng, Xinyu Wang and Benjamin C. Tee; National University of Singapore, Singapore

Liquid environments present significant challenges to accurate pressure sensing. Often, flexible materials in solid state pressure sensors grapple with optimization for sensitivity, hysteresis and linearity. In my talk, I will share some strategies to solve this tri-factor optimization problem for pressure sensing in liquid environments. Our proposed approach was inspired by organic hydrophobic surfaces in natural organisms such as the lotus plant (*Nelumbo nucifera*) and pitcher plants (*Nepenthes L.*). By utilizing a multi-species approach, we enabled the highest linearity pressure sensors to date while simultaneously achieving high sensitivity and low hysteresis.

4:45 PM EL18.03.05
Retina-Inspired Organic Optoelectronics for Intelligent Visual Systems Ke Chen, Hang Hu, Inho Song, Ashkan Abtahi and Jianguo Mei; Purdue University, United States

Retina is an important component in the human eye that help human beings get around 80% of knowledge from surroundings. As a type of bio-inspired optoelectronics, artificial retinas have been developed to mimic the functionalities of the human visual system. They are designed to function as bionic eyes for visually impaired persons or offer vision for advanced humanoid robots. To date, most of artificial retinas rely on silicon electronics, which are often rigid and brittle. This makes non-invasive implantation and seamless interfacing to soft biological tissues challenging. On the other hand, organic semiconducting materials have demonstrated biocompatibility, mechanical comfortability, and responsivity to the analytes in biological media, making them a promising candidate for next-generation artificial retina. Here, we report an organic optoelectronic device as an artificial retina. In the device, light can manipulate ion insertion into the bulk photoactive layer, enabling the modulation of multilevel nonvolatile conductance states at low operating voltages (~1 V) and the imitation of ion flux-regulated synaptic activity inherent in living systems. The nonvolatile properties are regulated by both light intensity and wavelength across the entire visible spectrum, demonstrating the capabilities of perceiving and memorizing various visual information of the device. Taking advantage of integrated function of light perception, processing and memorization of the device, we designed and simulated a single-layer synapse array as artificial retina that enables face recognition and a hardware convolution neural network for large-scale object recognition.

SESSION EL18.04: Flexible and Stretchable Electronics
Session Chairs: Ho-Hsiu Chou and Aristide Gumyusenge
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3018

10:30 AM *EL18.04.01
Nanocomposite Materials for Flexible Electronics Xiaodong Chen; Nanyang Technological University, Singapore

Flexible sensing devices not only enrich daily lives by providing enhanced smart functions, but also provide health information by monitoring body conditions. For example, patchable sensors have the potential to better interface with human skin, thus improving the sensitivity of detection of health indicators. However, the crucial aspects toward the advancement of such sensors rely on the development of novel nanocomposites with mechanically durable materials, which allow maintaining the function under the deformed states. In this talk, I will present our latest progress on developing nanocomposite materials to building electronic skin, including manufacturing of conformal bioelectronic interfaces, conformal sensor development and their integration of individual devices into systems for sense digitalization.

11:00 AM EL18.04.02
Stretchable Light-Emitting Polymers and Devices based on Thermally Activated Delayed Fluorescence (TADF) Sihong Wang; University of Chicago, United States

The vast amount of biological mysteries and biomedical challenges faced by humans provide a prominent drive for seamlessly merging electronics with biological living systems (e.g. human bodies) to achieve long-term stable functions. Towards this trend, one of the key requirements for electronics is to possess biomimetic form factors in various aspects for achieving long-term biocompatibility. To enable such paradigm-shifting requirements, polymer-based electronics are uniquely promising for combining advanced electronic functionalities with biomimetic properties. Among all the functional materials, stretchable light-emitting materials are the key components for realizing skin-like displays and optical bio-stimulation. In this talk, I will mainly introduce our research in imparting stretchability onto "third-generation" electroluminescent polymers that can harness all the excitons through thermally activated delayed fluorescence (TADF), thereby with a theoretical near-unity quantum yield and high OLED efficiency. Our developments of fully stretchable OLED devices show the promise of achieving all the desired EL and mechanical characteristics, including high efficiency, brightness, switching speed, stretchability, and low driving voltage.

11:15 AM EL18.04.03
Neuromorphic Sensorimotor Loop Embodied by Monolithically Integrated Low-Voltage, Soft E-Skin Weichen Wang; Stanford University, United States

Artificial skin that simultaneously mimics the sensory feedback and mechanical properties of natural skin holds significant promise for next-generation robotic and medical devices. However, achieving such a biomimetic system that can seamlessly integrate with the human body remains a challenge. Through rational design and engineering of material properties, device structures, and system architectures, we realize a monolithic soft prosthetic e-skin without rigid electronic components. It is capable of multimodal sensing, neuromorphic pulse train signal generation, and closed-loop actuation. With a tri-layer high-κ elastomeric dielectric, we achieved low sub-threshold swing comparable to poly-Si transistors, low operation voltage, low static power consumption, and medium-scale circuit integration complexity for stretchable organic devices.Our e-skin mimicked the biological sensorimotor loop where a solid-state synaptic transistor elicited stronger muscle actuation when increased pressure stimuli was applied.

11:30 AM *EL18.04.04
Multifunctional Use of Electrolytic Fluid for Distributed Energy, Hydraulic Actuation, and Data Transport Robert Shepherd and Chongchan Kim; Cornell University, United States

Animals are semi-discretized. Systems of organs that perform multiple functions and are spatially discrete from each other, yet interconnected chemically and electrically. The complexity of animals such as vertebrate mammals allow for adaptation within a single generation that has allowed many examples of species that have thrived without genetic modification even during periods of significant environmental change. In the search for generally adaptive robots, useful for far field exploration missions, we believe that a similar model of complex, multifunctional, and interconnected organ systems of animals should be embraced, rather than avoided. Of course, it is not yet that simple to be complex, but we will present approaches we have used to distribute sensing, actuation, energy, and computation in soft robots. The framework we use for guiding our design evolution is Autonomous Materials, where we push the manufacturing of robots towards forming processes, and multifunctional use of material chemistry. The resulting machinery presented will be organic both in chemical makeup and subsystem analogy to organisms.

SESSION EL18.05/SB09.03: Joint Session
Session Chairs: Yuanwen Jiang and Francisco Molina-Lopez
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3018

1:30 PM *EL18.05/SB09.03.01
Skin-Inspired Sensors and Electronics Zhenan Bao; Stanford University, United States

In this talk, I will present recent progress in our development of skin-inspired sensors and electronic circuits.

2:00 PM *EL18.05/SB09.03.02
Novel Devices and Fabrication Techniques for Bioelectronics George G. Malliaras; University of Cambridge, United Kingdom

Bioelectronic medicine provides a new means of addressing disease via the electrical stimulation of tissues: Deep brain stimulation, for example, has shown exceptional promise in the treatment of neurological and neuropsychiatric disorders, while stimulation of peripheral nerves is being explored to treat autoimmune disorders. To bring these technologies to patients at scale, however, significant challenges remain to be addressed. Key among these is our ability to establish stable and efficient interfaces between electronics and the human body. I will show examples of how this can be achieved by leveraging novel device architectures and fabrication techniques that led to high performance under demanding conditions.

2:30 PM BREAK

3:00 PM *EL18.05/SB09.03.03
Recent Progress of Nanomesh Electrodes for Continuous Monitoring of Skin Electrical Resistance Takao Someya[1,2], Akihito Miyamoto[3], Hiroshi Kawasaki[3], Sunghoon Lee[1], Tomoyuki Yokota[1] and Masayuki Amagai[3]; [1]The University of Tokyo, Japan; [2]Riken, Japan; [3]Keio University, Japan

We report on recent progress nanomesh electrodes that can be attached directly on the skin. In particular, we have continuously monitored the skin electrical resistance by nanomesh electrodes for a long period of time while maintaining the natural skin condition that does not inhibit water evaporation. The skin electrical resistance by nanomesh electrodes is inversely proportional to the transepidermal water loss, which is widely used as a method for directly evaluating the barrier function of the stratum corneum of the skin. Although transepidermal water loss could not be measured continuously for a long period of time, we have succeeded in visualizing dynamics of skin physiological functions by monitoring of the skin electrical resistance by nanomesh electrodes for 30 hours.

3:30 PM *EL18.05/SB09.03.04
Non-Fibrotic Bioelectronics and Devices on Diverse Organs Xuanhe Zhao; Massachusetts Institute of Technology, United States

Implanted biomaterials and devices face compromised functionality and efficacy in the long-term by foreign body reaction and subsequent formation of the fibrous capsule at the implant-tissue interface. Here, we demonstrate that an adhesive implant-tissue interface can avoid fibrous capsule formation by minimizing the establishment of the inflammatory microenvironment and subsequent infiltration of inflammatory cells at the implant-tissue interface. Histological analysis shows that the adhesive implant can preserve the implant-tissue interface without fibrous capsule formation on diverse organs including the abdominal wall, colon, stomach, lung, and heart over 12 weeks in rat models in vivo. In vitro protein adsorption, multiplex Luminex assays, quantitative PCR, immunofluorescence analysis, and RNA sequencing are additionally performed to validate the hypothesis. We further demonstrate long-term bi-directional electrical communication enabled by implantable electrodes with an adhesive interface over 4 weeks in a rat model in vivo. This finding may offer a promising strategy for long-term implant-tissue interfacing without fibrous capsule formation.

4:00 PM DISCUSSION TIME

4:30 PM *EL18.10.03
Printable Stretchable Electroactive Composites for Soft Electronics Pooi See Lee; Nanyang Technological University, Singapore

Stretchable and printable conductors play a crucial role in the design of soft electronics, textile electronics and the evolution of wearable technology. We have earlier demonstrated an extremely stretchable and printable conductor with high conductivity and durable stretching cycling with the incorporation of liquid metal. Recently, we further showed that through an in-situ polymerization approach, high volume fraction of liquid metal particles can be incorporated into the composites to obtain flexible printable thermal interface materials with anisotropic thermal conductivity.[1] On the other hand, designing electroactive composites based on urethane matrix with metal flakes has led to the formation of printable stretchable conductors on textiles that can be activated by sweat. A sweat-activated battery was demonstrated with the stretchable textile conductor.[2] In order to realize stretchable ionic conductors that are self-healable and thermally stable, organohydrogel based on chemically linked ionic side chain to the polymeric gel matrix was designed and synthesized. Inkjet printing of the organohydrogel on an elastomer can lead to high interfacial toughness. Applications of the electroactive gel composite in sensing, actuation and controllable manipulation for soft electronics will be illustrated.[3]

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3. D. Gao, G. Thangavel, J. Lee, J. Lv, Y. Li, J-H Ciou, J. Xiong, P. S. Lee, (submitted).

SESSION EL18.06: Poster Session I
Session Chairs: Ho-Hsiu Chou, Francisco Molina-Lopez and Sihong Wang
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL18.06.01
Newly Achievable Diameters of Electrospun Nanoparticle-Containing Poly(3-hexylthiophene) and Poly(ethylene oxide) Nanofibres Driven by Viscosity Reductions for Organic Photovoltaic Applications. Ryan Schofield[1], Dillon McGurty[1], Colin Johnston[1,2], Barbara Maciejewska[1], Hazel Assender[1] and Nicole Grobert[1]; [1]University of Oxford, United Kingdom; [2]Oxford Materials Characterisation Service (OMCS), United Kingdom

Limiting the environmental impact of the world's ever-increasing energy demand is among the most pressing issues of our time, and photovoltaics provide an opportunity to help fulfil this. However, the thin active layers of Organic Photovoltaics (OPVs) deliver incomplete light harvesting, and so there has been considerable research in increasing absorption. Amongst successful approaches is electrospinning nanofibres of photoactive polymers, which produces highly crystalline, aligned polymer versus their film counterparts, and has been shown to improve optical absorption in OPVs.[1,2,3]

However, exciton diffusion lengths of these materials are short, and therefore most excitons formed within large nanofibres are quenched before reaching the fibre surface for separation. Only considering exciton diffusion, the ideal nanofibre diameter would be around 20 nm. However, due to the inherent difficulty in spinning conjugated polymers, only recently have poly(3-hexylthiophene) (P3HT) nanofibres been spun with diameters < 100 nm, through the addition of poly(ethylene oxide) (PEO) and a polar co-solvent.[4]

Here, we report a method to further reduce the achievable diameters of P3HT (and PEO) nanofibres through the addition of silver/gold nanoparticles. These nanoparticles induce a dynamic non-Einsteinian reduction in viscosity, allowing thinner fibres to be spun as the solution ages. Our studies reveal the viscosity may reduce by more than 90% depending on the loading and type of nanoparticles, and the aging time. PEO nanofibre diameters can be halved, with champion nanowebs of 70 nm, 30% thinner than the state of the art.[4] In the absence of nanoparticles, solutions with this reduced viscosity would be below the critical polymer overlap concentration and produce beaded fibres. However, our fibres retain a uniform morphology suggesting the nanoparticles impede beading. After 120 hours of aging, diameters of nanoparticle-doped P3HT/PEO nanofibres can be reduced by 60%, to < 100 nm. Following the removal of PEO, we yield the first instance of electrospun plasmonic photoactive nanofibres suitable for OPV applications, and at < 80 nm, the smallest reported electrospun P3HT nanofibres.

The combination of crystalline polymer nanofibres and plasmonic nanoparticles provide a dual enhancement in light absorption, and being thinner, are expected to provide more effective charge separation. This method of 'printing' is compatible with flexible substrates and has the potential to be adapted for roll-to-roll processing.

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5:00 PM EL18.06.02
Hydrogen Bonding-Controlled Transfer-Printing of PEDOT:PSS Films for Flexible and Stretchable Electronics Carla Volkert[1], Renan Colucci[1], Pol Besenius[2], Paul W. Blom[1] and Ulrike Kraft[1]; [1]Max Planck Institute for Polymer Research, Germany; [2]Johannes Gutenberg University, Germany

The conductive polymer poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) is of great interest for a variety of applications in flexible and stretchable electronics. However, to advance novel applications on appropriate substrates, innovative, and reliable methods for processing conductive polymers are still needed. Here, we present a fast, dependable, and easy PEDOT:PSS transfer printing method on flexible, transparent, and biodegradable polyvinyl alcohol (PVA) targets. In contrast to previous work, this method neither depends on acid nor doping treatments nor surface soaking treatments. Furthermore, our approach is compatible with common strategies to induce stretchability and increase the conductivity of PEDOT:PSS. Key to this method is the chemical engineering of hydrogen bonds. To adjust the mechanical properties, glycerol is incorporated in varying amounts into the PVA targets. Moreover, the water-soluble targets allow for environmental-friendly decomposition.

5:00 PM EL18.06.03
Gold Nanowire Network Electrodes for Flexible Organic Thin-Film Transistors Toward Practical Use Satoshi Takane[1,2], Yuki Noda[1], Naomi Toyoshima[1], Takafumi Uemura[1,2], Yuki Bando[1,2] and Tsuyoshi Sekitani[1,2]; [1]Osaka University, Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan

Flexible organic thin-film transistors (OTFTs) have gained substantial interest owing to their wide range of applicability in wearable healthcare devices[1], electric skins[2], and bendable displays[3]. However, the metal thin-film electrodes used in OTFTs have several drawbacks, such as the fragility under bending strain owing to the high Young's modulus of metal[4], or the poor material and process efficiency of their formation method by the vacuum deposition. In this context, metal nanowires are a promising alternative for OTFT electrodes because of their high flexibility[5] and low-cost solution processability[6]. Among the various kinds of metal nanowires, gold nanowires (AuNWs) are most suitable for practical applications such as healthcare devices, owing to their potential air stability[7] and biocompatibility[8]. In this study, a flexible OTFT using AuNW network electrodes as source/drain/gate (AuNW-OTFT) was fabricated and characterized. For the fabrication of AuNW-OTFT, AuNW network electrodes were successfully formed on a flexible thin-film substrate using the thermal pressing transfer method. The fabricated top-gate bottom-contact AuNW-OTFT demonstrated typical p-type characteristics (mobility: 6.0×10^{-2} cm^2/Vs, on/off ratio: 10^5, threshold voltage: 1.7 V) and lower contact resistance (0.99±1.2 MΩcm) than that of an OTFT with vacuum-deposited Au electrodes in the same device configuration (12±2.3 MΩcm). Moreover, the AuNW-OTFT exhibited high mechanical durability, which was proven by the absence of significant characteristic changes before and after bending (bending radius:0.8 mm)[9].

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5:00 PM EL18.06.04
Indacenodithiophene-Based Polymer with Polydimethylsiloxane Side Chains for Fluid Semiconductor Yuto Ochiai, Kyohei Nakano and Keisuke Tajima; RIKEN CEMS, Japan

Wearable devices such as smartwatches have become a part of our everyday life. In order to provide greater wearing comfort and motion-following performance, mechanical flexibility and elasticity are the next demands of electronic materials. Therefore, the development of new stretchable semiconductor polymer (SCP) materials that combine high electronic functionality and mechanical flexibility is attracting more attention. In general, SCPs have an extended π-conjugated structure and are highly crystalline and brittle. At the same time, the structural ordering among the molecules such as crystallinity and aggregation structure largely affects their semiconductor properties. When the ductility of the materials is desired, lowering the structural order at the multi-scale is a common option but this leads to the trade-off relationship between the semiconducting properties and the stretchability, which would be the fundamental limitation of improving the mechanical properties by using highly crystalline SCPs. On the other hand, there have been reports of SCPs such as the indacenodithiophene-benzothiadiazole (IDTBT) backbone that exhibit high semiconductor properties similar to those of conventional highly crystalline and high charge mobility SCPs, even though they adopt an almost amorphous structure in the solid state. The long alkyl side chains of IDTBT introduced in a sterically overhanging the main-chain plane could disrupt intermolecular aggregation and the π-stacking. On the other hand, the main chain has high planarity with intramolecular structural order, which was proposed to contribute to the narrow distribution of density of states in thin films. Owing to the above characteristics, IDTBT exhibits high semiconducting properties despite its amorphous nature.
In this study, we have selected the IDTBT as the backbone structure to develop an intrinsically stretchable semiconductor materials that utilize intramolecular structural ordering. We designed and synthesized the polydimethylsiloxane (PDMS) side chain introduced IDTBT (PoSi100), improving mechanical ductility and significantly inhibiting intermolecular interactions. As the result, we successfully synthesized an intrinsically stretchable SCP with high conjugation planarity using the IDTBT backbone. Furthermore, we found that the backbone planarity is maintained even in a molecular design that significantly inhibits intermolecular interactions. The PDMS side chain improves mechanical flexibility and solves the reversibility problem that has been an issue in IDTBT. Thanks to those improved mechanical properties, Posi100 exhibited very stable semiconductor properties against mechanical deformation. This work demonstrates that utilizing the backbone structural ordering is an effective molecular design for creating novel semiconducting polymers with intrinsic stretchability.

5:00 PM EL18.06.05
Battery-Free, Wireless, Ionic Liquid Sensor Arrays for Continuous Monitoring of Pressure and Temperature at Skin Interfaces of Patients in Bed and Wheelchair Hyeonseok Han[1], Yong Suk Oh[1,2], Seokjoo Cho[1] and Inkyu Park[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Changwon National University, Korea (the Republic of)

Pressure injuries are a wound caused by prolonged pressure on skin tissue, deteriorated by an increase in local skin temperature. For the prevention of pressure injuries, clinical practice guidelines, recommended by the National Pressure Injury Advisory Panel (NPIAP), involve repositioning at regular intervals. However, frequent repositioning leads to decreasing the quality of sleep in patients, increasing a high risk for back pain or musculoskeletal injuries for patients or caregivers.

Recent advances in technologies of wireless platform offer physiological signals for prevention, diagnosis, and treatment of diseases at early stage. Among the wireless platforms with multimodal sensors, Near Field Communication (NFC) platforms have great potential for continuous monitoring of pressure and temperature at skin interfaces without a risk of secondary injuries caused by bulky batteries. However, it is challenging to continuously measure pressures with high accuracy and reliability on locations of interest due to a mismatch between the effective area of body weight and the interfacial area of the single sensor. A few reports suggest several pressure sensor arrays for measurement of pressure distribution at locations of interest. In this context, sensor arrays integrated with the NFC platforms and systems can support capabilities for continuous monitoring of pressure distribution at skin interfaces over full body coverage for long term monitoring.

For clinical applications, the pressure sensor should have a thin, soft form factor for conformal, irritation-free contact to skin, excellent sensitivity, negligible hysteresis, high linearity and cyclic stability over required pressure range. Furthermore, by collecting the pressure sensors in proximity to one another or using the pressure sensor arrays, capabilities for accurate, reliable, and continuous measurement of pressure distribution can provide a quantitative basis for the guideline of appropriate repositioning to resolve the issues associated with the mismatch in effective area. In addition, spatial temperature distribution measured on the skin surface can serve as one of additional indicators related to the skin breakdown arising from an increase in tissue metabolism and oxygen consumption.

This paper introduces a method for continuous multi-site monitoring of pressure and temperature distribution from strategically deployed sensor array at critical skin interfaces via a battery-free, wireless ionic liquid pressure sensor. The pressure sensor based on an internal flow of ionic liquid filled inside a roof collapsed microchannel shows excellent sensitivity as well as negligible hysteresis, high linearity, and cyclic stability over relevant pressure range. The characteristics of the sensor integrated with the NFC platform, verified by experimental measurement and numerical simulation, present technical foundations. In addition, the strategic deployment of the wireless, multiple devices in proximity to one another mounted at different locations of curved skin provides continuous, quantitative information for simultaneously capturing pressure and temperature distribution under change in posture. Clinical trials on two hemiplegic patients demonstrate the feasibility of the sensor arrays for decreasing local pressures and temperatures of patient under minimal repositioning confined on bed or wheelchair integrated with the battery-free, wireless system by providing medical staffs with accurate, statistical information of pressure and temperature at locations of interest in real time. The collected data support the medical team to achieve cost effective pressure relief (e.g., minimal repositioning) in respect of labor force, time, and disease management without frequent repositioning or rolling the whole body of the subject, which leads to a high risk for back pain or musculoskeletal injuries.

5:00 PM EL18.06.07
Large-area Ultrasonic Spray Deposition and Rapid Plasma Curing of Transparent Conducting Oxides for Printable Electronics Thomas W. Colburn, David W. Collinson and Reinhold H. Dauskardt; Stanford University, United States

Indium tin oxide (ITO), fluorine-doped tin oxide (FTO), and other transparent conducting oxides (TCOs) are pivotally important as electrode layers in optoelectronic devices. ITO thin-films have remained vital as n-type electrodes for perovskite solar cells, organic LEDs, and transparent flexible electronics. Commonly implemented solution based deposition methods of TCOs such as sol-gel processing utilize lengthy and thermally-intensive anneals at temperatures >400 °C which prevent high-throughput manufacturing and limit possible substrates for flexible applications. Sol-gel produced TCOs can also struggle from lower conductivity and lower film density which can inhibit performance as an electrode. As a result, sputtered TCOs are commonly used to generate films on both rigid and flexible substrates at the sacrifice of cost and throughput.

With growing interest in scalable manufacturing of large area electronics at lower fabrication costs, next-generation thin-film deposition techniques are required to mitigate the thermally and capital-intensive demands of traditional sol-gel and vacuum-based processes. Here, we present a fully vacuum-free, rapid deposition of large area TCOs utilizing ultrasonic spray printing at 10 m/min followed by a 5-10 minute forming gas plasma anneal to yield ITO thin-films with high figures of merit and low roughness. The spray deposition utilizes a solution containing metal nitrates and acetylacetonate salts with a chelating fuel source. The fuel source and nitrate ion reduce the required applied temperatures for solution fabrication by providing a local in-film energy source that is capable of yielding oxidation at temperatures as low as 200 °C. The cure is followed by an open-air forming gas plasma treatment to introduce oxygen vacancies and additional electron charge carriers. The resulting films on glass, with areas over 18 cm^2, have Haack figures of merit >9x10^{-3} 1/Ω with average transparencies >90% in the visible spectrum and sheet resistances of <40 Ω/■. Transferring the deposition approach to flexible substrates such as polyimide is the focus of on-going efforts. The resulting manufacturing platform allows for the rapid, open-air fabrication of TCOs on large areas as electrode layers and substrates for printable, flexible electronics.

5:00 PM EL18.06.08
Excitonic Transitions from the Γ to Γ and Γ to X Valleys in Surface Passivated $In_{1-x}Ga_xP$/ZnS Colloidal Quantum Dots Aritrajit Gupta[1], Justin Ondry[1], Margaret H. Hudson[1], Min Chen[1], Richard D. Schaller[2,3] and Dmitri V. Talapin[1,2]; [1]University of Chicago, United States; [2]Argonne National Laboratory, United States; [3]Northwestern University, United States

Crystal momentum k is not a good quantum number to describe band structures in quantum confined nanocrystalline systems, thereby blurring the distinction between direct and indirect semiconductors as conventionally defined in the bulk. A transition to indirect behavior in bulk $In_{1-x}Ga_xP$ alloyed phases with higher gallium content is well documented. However, the effect of quantum confinement on the direct to indirect transition in this system has yet to be established, because high-quality colloidal nanocrystal samples have remained inaccessible. Herein we report a molten salt In-to-Ga cation exchange to prepare $In_{1-x}Ga_xP$ nanocrystals and subsequent ZnS shelling protocol to achieve high radiative efficiency. The synthesis is rigorously oxygen-free, allowing us to obtain bright $In_{1-x}Ga_xP$/ZnS core-shell particles of decent emission color purity with photoluminescence quantum yields exceeding 80% and PL emission linewidths as narrow as 50 nm FWHM. Steady-state and time-resolved photoluminescence studies indicate that radiative decay lifetime in these highly emissive samples increases monotonically while the quantum yield decreases with higher gallium content. Transient absorption studies on these core-shell nanocrystals allow us to establish direct or indirect-like behavior in these samples in terms of the presence or absence of excitonic bleach features. These insights allow us to establish cation exchange in molten inorganic salts as a viable route towards synthesizing nontoxic high quality $In_{1-x}Ga_xP$/ZnS QD emitters with desirable optoelectronic properties.

5:00 PM EL18.06.10
In-Plane Electric Field Driven, Stretchable Alternating Current Electroluminescent Devices Seongkyu Song and Soon Moon Jeong; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

Although significant progress has been made in the development of new techniques for emerging electroluminescent devices, leading to various technologies such as soft robots, actuators, flexible/stretchable/wearable electronics, and self-healable devices, most of the reported devices have coplanar structures, which require planar electrodes and a thin emitting layer (EML). This is particularly challenging in the case of stretchable electroluminescent devices, which require electrodes exhibiting both high transmittance and low resistance even in the stretchable state since thin EMLs have a low tolerance to external mechanical deformations. Here, we report an in-plane electric-field-driven, stretchable composite system capable of simultaneously producing intense electroluminescence and mechanoluminescence under an electromechanical stimulus.[1] The patterned silver-nanowires-array embedded into the PDMS-supported ZnS:Cu layer (ZnS:Cu/PDMS) used as an electrode in our device offers a unique advantage, that is, because the in-plane electric field generates electroluminescence in the EML, light need not be transmitted by the electrode.[2] This obviates the need of electrodes with high transmittance and stretchability. Furthermore, the in-plane electric field is unaffected by the ZnS:Cu/PDMS thickness; thus, a thick EML can be used, which contributes

to both electroluminescence and mechanoluminescence. Using the thick EML, a significantly high electroluminescence luminance (a factor of 2.08-3.79 compared to that of a coplanar-structured device) and high brightness of 1,324 cd/m^2 at 9.12 V/μm were achieved, which indicate that the electric field expands throughout the thick EML. Furthermore, the device with the thick EML exhibits strong mechanoluminescence and good durability under the simultaneous application of electromechanical stimulus. Our results represent a breakthrough in electroluminescence and mechanoluminescence research and that our findings provide important insights for the development of novel multimodal functional light sources, leading to unprecedented applications.
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5:00 PM EL18.06.11
Gate-Deterministic Remote Doping Enables Highly Retentive Graphene-MXene Hybrid Memory Devices on Plastic Yonghyun A. Kwon, Seonkwon Kim, Soo Young Cho, Jung Woo Moon, InCheol Kwak, Dong Gue Roe, Seonmi Eom and Jeong Ho Cho; Yonsei University, Korea (the Republic of)

In this work, a highly retentive and synaptic-functional transistor memory device architecture based on the gate-deterministic remote doping of graphene via surface-oxidized $Ti_3C_2T_X$ MXene nano-floating-gates (NFG) is presented. By using solution-phase size-sorting followed by controlled surface oxidation process, a regulated distribution of MXene nanoflakes comprising metallic $Ti_3C_2T_X$ as the core surrounded by TiO_2-a high dielectric constant insulator-as the shell is achieved. The size-sorted core/shell-like MXene nanoflakes show a self-sustainable charge trapping/detrapping behavior, which is highly feasible for realizing non-embed NFGs for transistor memory devices. Interestingly, unlike the conventional NFG-embedded architecture, the introduction of core/shell-like MXene under an electrolyte-gated graphene field-effect transistor (GFET) architecture induces a cooperative evolution of the hysteresis loop associated with ionic motion in the electrolyte gates and charge trapping/detrapping in the nanoflakes, resulting in a deterministic remote doping of the graphene layer. The resulting device exhibited a highly retentive memory behavior, which can be optimized by the nanoflake size distribution. In addition, synaptic functions having mechanical flexibility can be successfully emulated using MXene-based GFETs fabricated on a flexible polyethylene naphthalate substrate.

5:00 PM EL18.06.12
Ultrasensitive and Shape-Reconfigurable Smart Strain Sensor with Tunable Sensitivity and Selectivity Seungjae Lee, Youngoh Lee, Cheolhong Park and Hyunhyub Ko; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Bio-inspired sensors, mimicking the unique structures and superior sensory functions of natural creatures, have attracted intense research interests for applications in wearable devices, robotics, and human-machine interfaces (HMIs). Recently, inspired by the spider mechanosensory system, crack-based strain sensors have attracted intense interests due to high sensitivity and easy fabrication. However, previous strain sensors based on the randomly distributed cracks have limited sensitivity, strain range, and reproducibility. For a wide range of application, the ability to tune the sensitivity is important. Previously reported strain sensors with tunable sensitivities showed not only high sensitivity under low tensile strain, but also high stretchability over wide range. However, tunable sensitivities were not achieved in a single sensor and multiple sensors with different sensitivities were required. Tuning sensitivities in a single sensor in a simple way is required for diverse applications. For the ultrahigh sensitivity with tunable sensitivities in a single sensor, we propose a new design of crack-based strain sensor. Firstly, to increase the sensitivity under subtle stimuli, we utilized rectangular patterned cracks by introducing the nanoscale line pattern on the sensor, which allowed the precise control of crack, resulting in an ultra-high gauge factor (GF) of 2.23×10^9 at 2% strains. Secondly, for the tunable sensitivities in a single sensor, we employed a thermo-responsive shape memory polymer (SMP) as a stretchable substrate. As the SMP can be programmed into a temporary shape and recover back to the original shape in response to thermal stimuli, the crack asperity can be precisely adjusted, affecting the initial resistance and the resulting final sensitivity. Under 1% strain, the sensitivity increased after shape reconfiguration (GF = 3.54×10^7) and recovered to the original value (GF = 1.11×10^6). Our ultrasensitive smart strain sensor with tunable sensitivity can be applied to acoustic sound detection with the increased signal-to-noise ratio and rapid response time of 0.025 ms at high acoustic frequencies. Furthermore, it can be applied in wearable healthcare applications, including devices monitoring various human body signals.

5:00 PM EL18.06.13
Low Voltage Organic Transistors with Carrier Mobilities over 10 cm^{2}V^{-2}s^{-1} Using Six-Branched Organic Azide with Ultrahigh Crosslinking Efficiency Myeongjae Lee[1], Byung-il Choi[2], Jeong Ho Cho[3] and BongSoo Kim[4]; [1]Korea University, Korea (the Republic of); [2]Korea Testing & Research Institute, Korea (the Republic of); [3]Yonsei University, Korea (the Republic of); [4]Ulsan National Institute of Science and Technology (UNIST), Korea (the Republic of)

The great demand for flexible and wearable electronics over the past few years has led to the development of solution-processable organic thin film transistors (OTFTs) possessing the outstanding advantages of large area, low cost, low processing temperature, and mechanical flexibility. To fabricate OTFTs in an industrial level, following requirements should be met: high carrier mobility, low-voltage-operation, compatibility with reliable high-resolution patterning process, and high mechanical and electrical stability. Here, we report the synthesis of six-branched crosslinker (6Bx) having an ultrahigh photo-crosslinking efficiency and its application to photo-patterning gate dielectric (GD) polymers and channel semiconducting (CS) polymers in polymer-based OTFTs. The use of 6Bx permits the generation of a high-resolution-patterned ultra-thin polymer gate dielectric with a low leakage current (7×10^{-9} A cm^{-2} at 1 MV cm^{-1}). Moreover, crosslinking the GD polymer interfaced with *p*- or *n*-type CS polymer induces alignment of CS polymer chains at the interface. This yields excellent hole and electron mobilities of 12.42 and 10.11 cm^2 V^{-1}s^{-1}, respectively, from p- and *n*-type OTFTs operated at < 3 V, which are remarkably improved carrier mobilities at substantially low operation voltages compared to those by conventional test beds. Further, the fabrication of logic gates and ring oscillators demonstrates the reliability of polymer OTFTs crosslinked with 6Bx. This work presents a universal strategy for high mobility, reliable, and low-voltage-operating OTFTs.

5:00 PM EL18.06.14
The Applications of van der Waals Assembly method in Solution-Processed Organic Monolayer Single-Crystals Transistor Zhenfei He[1] and Paddy K. L. Chan[1,2]; [1]The University of Hong Kong, Hong Kong; [2]Advanced Biomedical Instrumentation Centre, Hong Kong

Solution-processed large-area 2D organic single crystals with high mobility, low contact resistance, and good uniformity, are decent players for high-performance organic field-effect transistors (OFETs). However, the deposition of large-area high-quality crystals is still challenging on various substrates because of the strict requirements on substrate conditions such as roughness, surface energy, and chemical compatibility. Besides, the thermal damage at the metal deposition would cause defects in the 2D organic crystals and hurt the device's performance. To overcome these compatibility issues during the fabrication process, we introduce a damage-free, mediate layer-assisted OFET van der Waals assembly method for as-grown, high-quality 2D crystals. First, we would introduce some applications of our van der Waals assembly method for the bottom gate top contact device structure. The assembled monolayer 2,9-Didecyldinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (C_{10}-DNTT) OFET device with SiO_2/ octadecyl trichlorosilane (OTS) dielectric exhibits high mobility of 10.4 cm^{2}V^{-1}s^{-1} which is comparable to as-grown crystals. We further assembled monolayer C_{10}-DNTT to a hydrophobic dielectric where is hard to direct solution shearing. The bias stress stability of OFET gets significantly improved from a 55% current change to a 12% change for 10000 s bias stress on this high-κ hydrophobic dielectric with low trap state density and a small subthreshold swing (SS) of 63 mV/decade is achieved. Our

assembly method is suitable for the advanced circuit, and a depletion-mode flexible inverter with a high gain of 650 under the low power voltage of 4 V is demonstrated. We integrated this low operating voltage organic amplifier with gel electrodes as a potable Electrocardiography (ECG) sensor, which could be powered by coin cells. With a high signal-to-noise ratio of 34 dB, this sensor could detect a clear ECG pattern for diagnosis. It is believed that our ECG sensor manifests the prospect of continuous monitoring for human health management.
Second, we would explore the 2D organic semiconductor in the OFET device structure of bottom gate bottom contact. Bottom-contact device structure with a ramp source/drain contact edge, which favors side-wall injection, is a promising structure to break the bottleneck of contact resistance in OFET. However, this pre-patterned bottom-contact substrate would affect the crystallinity of the 2D organic crystals during the solution shearing. Our van der Waals assembly method is a decent technique to overcome this issue. Here, we would compare the contact resistance at the bottom-contact structure between the direct solution shearing and the assembly method and study the contact interface by electron microscope. We would treat the source/drain electrodes with various self-assembled monolayers (SAMs) to modify the work function and study the fermi-level pinning effect in 2D organic single crystals. We believe our work would offer some evidence to strengthen the faith in contact resistance improvement.

5:00 PM EL18.06.15
Synthesis and Characterization of Arylic Pressure Sensitive Adhesive with Novel Silane Derivatives based on Ethylene Glycol Chain for Foldable/Flexible Application Min Hye Seo, Ju Hui Kang, SangKug Lee and Ho Jun Song; Korea Institute of Industrial Technology, Korea (the Republic of)

Pressure sensitive adhesives (PSAs) are representative viscoelastic materials. Due to unique adhesion characteristics, PSAs have been widely used to the various application fields such as for electric/electronic process films, heat-resistant protection, display protection liquid crystal films and medical film. The acrylic PSA has excellent transparency and heat resistance, and is composed of soft segment, hard segment and functional segment. The soft segment affects the flexibility. The hard segment determines the cohesive properties of the adhesive. The functional segment determines its physical properties. It is easy to control the properties of PSA through processes such as the composition of the functional monomers. In this study, we designed and synthesized a novel acrylic PSA by introducing a silane group to an ethylene glycol-based acrylate and photopolymerization method. For silane acrylate, the chain length was controlled by using an ethylene glycol group. Introduction of silane group at the end of the structure would exhibit improved modulus property of acrylic PSA. The molecular weight of the synthesized PSA without silane acrylate is 870,000 g/mol (based on Mw), which increases to 1,140,000–1,440,000 g/mol upon adding the silane acrylates. the synthesized PSA showed the storage modulus of the high-temperature region because of hydrogen bonds of silane moiety. In the case of 100% strain of 3 wt% DESGA film, it showed excellent shear recovery properties of 96.7% because of the hydrogen bonding of the silane groups.

5:00 PM EL18.06.16
Computational Fluid Dynamics of Slot Die Coating of Alumina Nanoparticle Suspension for Ceramic 3D Printing Jeonghong Ha and Jong Wan Ko; Korea Institute of Industrial Technology, Korea (the Republic of)

Additive manufacturing of ceramics can be classified as slurry-based, powder-based, and bulk solid-based methods depending on the feedstock type. Among them, the slurry-based AM methods can obtain high-density ceramic parts by controlling the content of ceramic powder and the viscosity of the solvent. The coating quality of the slurry significantly greatly affects the final quality of slurry-based 3D printing parts [1]. A slot die coating is a coating method in which slit-shaped nozzle moves on a substrate with ejecting the slurry to form a film, and is mainly used for application of high-viscosity ceramic slurries. Slurry properties such as viscosity, contact angle, and surface tension, coater operating conditions such as feed rate and coating interval, and die shape such as die lip angle, die lip length, and nozzle spacing are the main variables that determine the coating quality [2]. In this study, the coating properties in the ceramic slurry coating process using the slot die coating method were evaluated using computational fluid dynamics. Coating characteristics was analyzed depending on the operating conditions of the coater, and process window was derived to obtain the uniform thickness of the ceramic slurry layer.

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5:00 PM EL18.06.18
Printable Carbon Nanotube-Cellulose Ink Devices for Rapid Liquid Identification Rodrigo G. Lacerda; Univ Federal de Minas Gerais, Brazil

The development of a new generation of smart sensors that allow monitoring of industrial processes in real-time, and of wearable and flexible devices are paradigms of the current 4.0 industry. One can envision applications such as multi-component complex liquid and gas sensors, wearables for healthcare, paper-based sensors, and electronic solutions for Smart city applications. Another area of increasing demand is the rapid test, identification and monitoring of various liquid samples in various fields such as fuel adulteration, water quality, solvents and beverages. Usually, liquid testing requires conventional analytical techniques, such as absorption/emission spectroscopy (AAS/AES), X-ray fluorescence spectroscopy, and inductively coupled plasma mass spectrometry (ICP-MS), which are complex, expensive and require experts to carry them out (and often require several pretreatment steps with high-cost materials). Electronic tongue is a category of liquid sensor that could solve the problems cited. These devices comprise an array of non-specific sensors that, with an appropriate method of multiple data processing, learn and extract the desired information, constituting one of the promising candidates for developing smart sensor technologies. Additionally, the Internet of Things (IoT) also requires devices to be integrated into a variety of systems and different surfaces of our daily life, which demands the production of low-cost, reliable, and scaled-up production of sensors. However, the lack of reproducible large-scale production of liquid sensors, besides the constant need for sensor recalibration, has hindered broader commercialization of such devices.
Ink printing technology is one of the most promising approaches to fulfill all the demands and issues described above, which naturally leads to the challenge of developing new smart-ink-based materials for several applications. carbon nanotube ink films have been reported as field-effect transistors, transparent conductors, gas sensors, supercapacitors, pH sensing, among others. Different approaches to ink printing methods have been explored, such as aerosol jet, inkjet, syringe, roll-to-roll printing and stamp methods. It is also important to point out that scalable production methods for the growth and functionalization of carbon nanotubes would significantly reduce costs and make workable a printing technology based on this material.
In this work, a conductive ink based on micro fibrillated cellulose (MFC) and multi-walled carbon nanotubes (MWCNT) was used to produce transducers for rapid liquid identification. The transducers are simple resistive devices that can be easily fabricated by scalable printing techniques. We monitored the electrical response due to the interaction between a given liquid with the carbon nanotube-cellulose film over time. Using principal component analysis of the electrical response, we were able to extract robust data used to differentiate several liquid categories. We show that the proposed liquid sensor can classify different liquid systems, includingorganic solvents (e.g., acetone, chloroform, and alcohol) and is also able to differentiate low concentrations of glycerin in water (10-100 PPM). We have also investigated the influence of two vital liquid properties: dielectric constant and vapor pressure on the physical transduction mechanisms of MFC-MWCNT sensors, which were corroborated by independent heat flow measurements (thermogravimetric analysis). The proposed MFC-MWCNT sensor platform may help paving the way to rapid, inexpensive, and robust liquid analysis and identification. Our

flexible MFC-MWCNT ink can provide a step forward towards scale-up and commercialization of the technology that involves liquid identification and monitor of mechanical stress.
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5:00 PM EL18.06.19
Open-Air Spray Deposition of Ultrathin Organic Bathocuproine Layers for Printed Electronics Justin P. Chen, Juliet Risner-Jamtgaard, Thomas W. Colburn, Margarita Golding and Reinhold H. Dauskardt; Stanford University, United States

Bathocuproine (BCP) is a small organic molecule that is typically used as an ultrathin hole blocking interlayer (< 10 nm thickness) in organic solar cells and perovskite solar cells. A popular method for BCP film deposition relies on a lengthy and expensive vacuum thermal evaporation process that introduces scalability challenges and high capital equipment costs at large-scale manufacturing levels. Solution spincoating is another method for BCP film deposition on small substrates, but it is incompatible with large-scale and in-line roll-to-roll manufacturing. Open-air ultrasonic solution spray deposition is an attractive alternative method utilizing only simple and low-cost equipment that is compatible with flexible substrates and roll-to-roll processing in large-area industrial fabrication.
We report on the successful open-air, room temperature ultrasonic spray deposition of an ultrathin (<7 nm) and highly transparent BCP film with low roughness. Unlike evaporated films that have an *in-situ* Quartz Crystal Monitor to measure film thickness, solution-processed BCP films lack a convenient film thickness metrology. We combine a suite of characterization techniques that span a range of equipment complexity, measurement time, and measurement sensitivity including: Ellipsometry, X-Ray Reflectivity, Angle-Resolved X-ray Photon Spectroscopy, Auger Spectroscopy, and Transmission Electron Microscopy. We discuss the advantages and disadvantages of each characterization technique but find strong agreement across this multi-faceted approach. Finally, we demonstrate our spray deposition technique by fabricating BCP films on perovskite solar cells at high-throughput linear processing speeds of up to 9 m/min and achieve solar power conversion efficiencies >18%.

5:00 PM EL18.06.21
Context Aware Mechanics and Electromagnetics for Chronically Wearable Devices Philipp Gutruf; University of Arizona, United States

The concept of digital medicine, which relies on streams of continuous information from the body to gain insight into health status, manage disease and predict onset health problems, is currently relying on biosensors with limited capabilities.[1][2] Key technological hurdles that slow the proliferation of this approach are means by which clinical grade biosingals are continuously obtained without frequent user interaction.[3] To overcome these hurdles, solutions in power supply and interface strategies that maintain high fidelity readouts and function chronically are critical. Current approaches for high fidelity recordings typically rely on adhesive interfaces that are subject to epidermal turnover, limiting sensor lifetime. Additionally, they rely on electrochemical power supplies which are subject to frequent recharge, add bulk and weight, require user interaction and introduce motion artefacts. Here we introduce a new class of devices that overcomes the limitations of current approaches by utilizing context aware mechanical and electromagnetic design facilitated through digital to create unique personalized devices optimized to the wearer. Specifically, we introduce new methods to use behavioral analysis of a user group to shape design to enable indefinite device lifetimes.[4] These elastomeric, 3D printed and laser structured constructs, called biosymbiotic devices, enable adhesive-free interfaces and the inclusion of high performance, far field energy harvesting to facilitate continuous wireless and battery-free operation of multimodal and multi device, high-fidelity biosensing in an at-home setting without user interaction. We present devices that can operate over weeks at the time, enable new sensing paradigms such as circumferential muscle strain, high fidelity absolute position sensing, mK resolution thermography and 3D printed optofluidics to capture an encompassing and evolving record of health.
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5:00 PM EL18.06.22
Crack Suppression of Cu Interconnect by Twin Engineering for Improving Reliability of Flexible Devices Seongi Lee[1], Jun-Hyeok Hyun[2], Sang-Ha Shin[2], Eun-Jung Kim[2], Youngchang Joo[1] and So-Yeon Lee[2]; [1]Seoul National University, Korea (the Republic of); [2]Kumoh institute of Technology, Korea (the Republic of)

Recently, as the form factor of electronic devices has been diversified, the demand for commercialized flexible devices is rapidly increasing. Compared to rigid devices, flexible devices are much more susceptible to performance degradation and device failure because flexible devices cannot avoid fatigue deformation such as bending or stretching. In addition, flexible devices are evolving to have a large strain. For example, in the case of bending deformation, it is evolving toward reducing the bending radius. Therefore, the reliability of flexible devices is drawing great attention from the electronics industry and the design and fabrication of reliable flexible electrodes is one of the most important challenges these days.

In this study, we designed a fatigue crack-free Cu interconnect by introducing twin boundaries through alloying. We adapted alloying method for twin engineering because alloying can lower the stacking fault energy of the material, resulting in both growth twin and deformation twin in the material. The Cu-Al alloy interconnect was fabricated by Chip-On-Target sputtering method with a thickness of 150 nm on the polyimide substrate. A sliding bending test of 100,000 cycles (5 Hz) was carried out for fatigue deformation, and we applied various bending strains to the interconnects. Comparing to pristine Cu interconnect, Cu-Al 1.5 at. % interconnect showed 70 % decrease at the resistance change under bending strain with 1.5%. Moreover, the crack was not observed in the Cu-Al interconnect after the 100,000 bending cycles. We analyzed the microstructure of the Cu-Al interconnect before and after deformation, and observed grain refinement by twin-dislocation interaction during bending fatigue deformation. Based on the microstructure analysis, we can infer that the low stacking fault energy of Cu-Al induced abundant twin boundaries which generate microstructural change instead of surface cracking for the release of deformation energy, the Cu-Al interconnect shows low electrical change during bending fatigue. We suggest that the low amount of alloying of Al at Cu for lowering stacking fault energy can be an attractive solution for the reliability of the flexible device.

5:00 PM EL18.06.23
Highly Conductive and Strain-insensitive Nanocomposite Enabled by Adaptive Organization of Silver Nanomaterials Chansul Park and Dae-Hyeong Kim; Seoul National University, Korea (the Republic of)

Skin electronics require a stretchable conductor whose resistance is invariable under repetitive skin deformations. However, obtaining such a strain-insensitive electrode with high conductivity is challenging because those two properties have been considered mutually exclusive. Here we report on the highly conductive and strain-insensitive nanocomposite enabled by adaptive organization of nanomaterials. The nanocomposite is composed of multi-dimensional surface-modified silver nanomaterials and block copolymer elastomers. The surface modification of nanomaterials with 1-alkanethiols enables them to have mobility in viscoelastic matrix. The movable nanomaterials can be organized in the ordered form along various strain conditions. The organization of silver nanomaterials can stably maintain percolation networks, minimizing resistance change of nanocomposite. When multi-dimensional nanomaterials are mixed in an appropriate combination, the nanocomposite exhibits the negligible resistance variation (< 1% under 1000 cycles of 50% strain) under various strain conditions while attaining high conductivity of ~30,000 S/cm.

5:00 PM EL18.06.24

Origin of Improved Performance in Insulating Polymer Blend Organic Thin-Film Transistors Based on *mono*-Alkylated BTNTs Ryo Miyata[1], Satoru Inoue[1], Ken Nakajima[2] and Tatsuo Hasegawa[1]; [1]Tokyo University, Japan; [2]Tokyo Institute of Technology, Japan

In recent years, there has been significant progress in the development of a class of organic semiconductors (OSCs) composed of rod-like π-electron cores linked with alkyl chains, which show high layered crystallinity and are useful to produce high-performance organic thin-film transistors (TFTs)[1,2]. The materials are solution-processable and are expected to allow device processing under ambient temperature and pressure. A particular example is monoalkylated benzothieno[3,2-*b*]naphtho[2,3-*b*]thiophenes (*mono*-C_n-BTNTs) that present excellent solubility and thermal durability, showing high intrinsic field-effect mobility exceeding 10 $cm^2V^{-1}s^{-1}$ in the form of single-crystal TFTs [3]. However, the application of these OSCs is still limited in terms of the practical fabrications because the single-crystal thin films require a long time to produce. By contrast, polycrystalline thin films can be fabricated by simple methods, such as spin coating, although the device mobility of polycrystalline TFTs has degraded to 1/10 that of single-crystal TFTs.
We here focus on the trade-off problem: Is it possible to achieve compatibility between enhancing TFT performance and fabricating practical TFTs? We found that using binary blends of an insulating polymer and the OSC demonstrated that polycrystalline TFTs exhibit high mobility exceeding 4 $cm^2V^{-1}s^{-1}$, very sharp switching characteristics with the subthreshold swing of about 180 mV/dec, and small device-to-device variations in low-voltage operations [4]. Additionally, these polymer blended TFTs can be fabricated simply by combining spin coating and thermal annealing. The achieved performances of the polycrystalline TFTs are comparable to the highest level that has been reported so far[5,6]. To elucidate the origin of the improved TFT performances, we measured thin film morphology by bimodal atomic force microscopy (AFM) and investigated the effect of contact resistances on TFT performances by Kelvin probe force microscopy (KPFM). We successfully revealed the origin of improved performances in the polymer blended TFTs, where the phase-separated structure, formed spontaneously between the OSC and polymer, takes critical roles in obtaining enhanced TFT performances.
We utilized 2-C8-BTNT as the OSC and poly(methyl methacrylate) (PMMA) or polystyrene (PS) as insulating polymers. We fabricated bottom-gate bottom-contact TFTs by vacuum deposition of Au electrodes on SiO_2/Si substrates, followed by spin-coating and thermal annealing with the polymer-blended solutions. As a result, it was found that the TFT performances were found to be most enhanced when we blended PMMA into the OSC solution. We analyzed the phase separation structure of OSC/PMMA blended thin film and the origin of enhanced performances by bimodal AFM and KPFM. It reveals that the PMMA blend system exhibited well-defined vertical phase separation (top OSC layer/bottom PMMA layer). Constructing this phase separation structure enables forming a well-ordered and homogeneous semiconducting layer over a large area, which can maximize the electrical performances in polymer blended TFTs. We believe these findings are significant as they should accelerate the realization of printed electronics using high-performance printed organic TFTs.

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5:00 PM EL18.06.26

Comparison of Ultraviolet-Initiated Crosslinkable Additives for Improved Stability in Organic Solar Cells by Modulating Main Chains Yelim Choi, Dae Hwan Lee and Taiho Park; Pohang University of Science and Technology, Korea (the Republic of)

UV-initiated crosslinkable additives in organic solar cells have the potential to fix metastable bulk heterojunction, hence resolving issues of burn-in loss and long-term instability. We present useful application for crosslinkable additives as solvent additives, radical scavengers, and stretchability enhancers and crosslinkers according to its main chain structure between -Br in end groups. We separated crosslinkable additive into two types of alkyl and siloxane main chain, predicting distinct roles. Initially, 1,8-dibromooctane (DBr-octane) provides enhanced thermal and light stability without sacrificing efficiency in fullerene system. The DBr-octane devices revealed burn-in free performance, maintaining 90% of their original efficiency after 600 miniutes at 85 degree celsius, and light stability, keeping 90% of their initial efficiency after 360 minutes under 1 SUN. To ensure stretchability, we treated crosslinkable additive with the siloxane main chain molecule, bis(3-bromopropyl)-terminated poly(dimethyl siloxane) (DBr-siloxane), in the active layer. After 1000 bending cycles at a bending radius of 1.8 mm, the DBr-siloxane-treated film stretched up to 70%, meanwhile the flexible device of the fullerene system maintained an initial efficiency of over 60%.

5:00 PM EL18.06.28

Highly Stretchable and Positive-Piezoconductive Silicone Composite Using Nickel Powder and Ionic Liquids Yuji Isano, Ryosuke Matsuda and Hiroki Ota; Yokohama National University, Japan

In this study, a new conductive rubber with positive piezoconductivity, whose conductivity increases 10 million times with tensile strain, and which can be elongated by up to 600%, is proposed. The proposed material consists of silicone (Ecoflex00-30) as a matrix, nickel powder as a filler, and ionic liquid as an additive. In previous studies, maximum extensibility of only 100% was achieved because the matrix elasticity was limited by the large amount of conductive material required for the positive piezoconductivity. In this study, Positive piezoelectric conductivity due to the inclusion of a large amount of filler and high stretchability were both achieved by the gelation of silicone by the addition of ionic liquid, which caused an increase in the matrix stretchability.

Conductive rubber is a composite of stretchable rubber and conductive filler, like carbon nanotube, graphene, and metal particles. This material has elasticity due to the rubber and conductivity due to the filler. Therefore, the material is used for wearable devices and soft robotics.

In general, conductive rubbers decrease in conductivity with elongation. This is caused by the breakdown of electrical contact between conductive particles inside the conductive rubber as it elongates. This property is called negative piezoconductivity. Conductive rubbers with negative piezoelectric conductivity can be used as strain sensors by measuring their resistance, and are utilized for feedback control in wearable devices and soft robots.

On the contrary, conductive rubbers with positive piezoconductivity, whose conductivity increases with elongation, have also been studied. Some of them show a rapid increase in conductivity under tensile strain. These positive piezoconductive rubbers are used as strain sensors as well as those with negative piezoconductivity, or as switches in stretchable circuits that take advantage of the rapid change in conductivity.

However, it is necessary to mix a large amount of conductive filler to induce a sufficient resistance change as a circuit element for a positive piezoconductive rubber. On the other hand, an increase in the amount of conductive filler mixed with the rubber material causes a decrease in the elasticity of the overall composite. Therefore, both sufficient conductivity enhancement by strain and high elasticity are required for positive piezoconductive materials for applications with high deformability, such as stretchable devices and soft robots.

The conductive rubber developed in this studyas a maximum elongation of 600%, comparable to that of raw silicon rubber, in spite of holding three times as much Ni powder as rubber by mass. This occurs due to the ionic liquid being held in the silicone rubber in a liquid state.

The conductivity of stretched composite was increased 10 million times higher than the non-stretched condition. The increase in conductivity can be explained by the decrease in composite cross-sectional area due to tensile strain, which caused the aggregation of Ni powder. In addition, the elongation ratio at which the resistance drop begins can be controlled according to the mass of Ni powder contained inside.

The composite was demonstrated for application to soft robots and wearable devices. The composite was incorporated into an electrical circuit to read the deformation of the soft robot and elbow bending in a single series circuit. Unlike existing conductive rubbers with negative piezoelectric conductivity, which require an external evaluation circuit to switch by strain, the conductive rubbers developed in this study realized a switch by elongation without an external circuit.

5:00 PM EL18.06.29
Stability of Ternary Interfaces in Printed Organic Thin-Film Transistors Showing Extremely Sharp Switching Operation Keito Murata[1], Gyo Kitahara[1], Satoru Inoue[1], Toshiki Higashino[2], Satoshi Matsuoka[1], Shunto Arai[1], Reiji Kumai[3] and Tatsuo Hasegawa[1]; [1]The University of Tokyo, Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan; [3]Condensed Matter Research Center and Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Japan

Inverted-coplanar or bottom-gate-bottom-contact (BGBC) type has several unique advantages in fabrication and application of organic thin-film transistors (OTFTs), because it allows apply a variety of fabrication processes for dielectric and/or electrode components without bringing unfavorable influences on the channel organic semiconductor (OSC) layers. However, it is also generally known that it becomes more difficult to operate BGBC-type OTFTs, as compared to bottom-gate-top-contact (BGTC) type OTFTs. Recently, it was demonstrated that both high mobility and ideal on/off switching are successfully realized in BGBC-type printed OTFTs by adopting highly lyophobic gate dielectric layers that use amorphous perfluoropolymer of Cytop. However, peculiar channel material dependence is still observed in the device performance. Here, we report that one of crucial requirements for realizing excellent device performance is the stability of semiconductor/metal/insulator ternary interfaces in the BGBC-type OTFTs.
We manufactured semiconductor single-crystal thin films of various layer numbers and materials (phenyl/alkyl-substituted benzothieno[3,2-b]benzothiophene (Ph-BTBT-C$_n$) and phenyl/alkyl-substituted benzothieno[3,2-b]naphtho[2,3-b]thiophene (Ph-BTNT-C$_n$)) on highly lyophobic Cytop gate dielectric surfaces by extended meniscus-guided coating technique. We found that some TFTs exhibit notable time-dependent degradation, whose degradation speed depends significantly on the material, layer number, and also the encapsulation. For example, the single layer TFTs with Ph-BTBT-C$_n$ exhibited mobility as about 5 cm^2/Vs immediately after device fabrication, but decreased to 0.06 cm^2/Vs after 50 hours. In contrast, multilayer (3 layers) TFTs exhibited excellent time stability up to about 400 hours, and maintained initial mobility of 8 cm^2/Vs. Kelvin probe force microscopy (KPFM) measurements revealed that observed degradation is associated with the occurrence of contact resistance at around the source electrodes, whereas the degradation is dramatically reduced by stacking multilayer (two or more layers) OSC films. Microscopic characterizations by atomic force microscopy (AFM), and in-plane x-ray diffraction (XRD) indicated the sign of film deterioration at ternary interface, in case that contact resistance is observed. The results of this study suggest the importance of the quality of the semiconductor thin films at ternary interface and is expected to serve as a clue for improving the performance of BGBC-type OTFTs.
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5:00 PM EL18.06.30
Low-Voltage Stretchable Electroluminescent Devices for Sound-in-Display Electronics Hyejin Lee, Dong-hee Kang, Young-Ryul Kim and Hyunhyub Ko; UNIST, Korea (the Republic of)

Synesthesia is a phenomenon of concurrent perception, where a particular sensory stimulation activates the other senses together. Recently, synesthetic electronic devices have attracted great attention for the precise and immediate perception of external stimuli. In particular, the visual perception of mechanical stimuli has potential applications in interactive display, electronic skins, and human-machine interfaces (HMIs). Although there have been many studies visualizing mechanical stimuli, only a few groups have demonstrated interactive displays combining loudspeakers with display devices for the visualization of sound. When visual information is accompanied by acoustic one or vice versa, humans recognize the external stimuli more efficiently by both visual and auditory senses simultaneously. For the visualization of sound waves, alternating-current electroluminescent (ACEL) devices have been used as sound-in-display electronics emitting light with corresponding sound waves. While the light emission is achieved by the field-induced electroluminescence (EL) which is emitted by the radiative recombination of electrons and holes in ZnS:Cu under the same applied AC voltage, the sound wave is generated by the dielectric elastomer actuation (DEA) under the applied voltage. Although ACEL devices having the synesthetic bimodal generation of light and sound have been previously reported, the high operating voltage and rigid properties still limit their practical applications. In this study, we propose stretchable sound-in-display electronics that can be attached to the human body and operated with a low operating voltage. Stretchable ACEL device comprises an EL phosphor of copper-doped zinc sulfide (ZnS:Cu) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) as a high-*k* dielectric between stretchable electrodes. With the high-*k* dielectrics, the voltage focused on EL phosphor becomes higher than that on low-*k* dielectrics, enhancing the emission of bright light even under the same applied voltage. As a result, our stretchable ACEL loudspeaker with the high-*k* PVDF-HFP layer emits greatly enhanced brightness of light and sound pressure at a low operating voltage (87.68 cd/m^2, 79.70 dB at operating voltage 120 V, 10 kHz) even under various mechanical deformations. such as finger flexion and wrist bending. Our suggested ACEL loudspeaker with the intuitive and precise perception by visualizing the auditory systems can find diverse wearable and HMI applications.

5:00 PM EL18.06.31
MXene Thermoacoustic Loudspeaker for Directivity-Tunable Sound Generation Geonyoung Jeong, Jinyoung Kim and Hyunhyub Ko; UNIST, Korea (the Republic of)

Thermoacoustic (TA) loudspeakers have attracted great attention because of vibration-free, lightweight, and simple design compared to conventional speakers that require large space for the vibration and complex circuit design. However, previous TA loudspeakers have limited performances owing to the low heat emission into the air and large heat dissipation into the substrate. Herein, we demonstrated MXene TA loudspeakers (MTAL) based on a titanium carbide ($Ti_3C_2T_x$) MXene conductor with low heat capacity per unit area and an ultrathin parylene substrate with low thermal effusivity. Our ultrathin

MTAL with the thickness below thermal penetration depth exhibited improved SPL output in the low frequency regime and bi-directional TA sound generation in audible range (up to 20 kHz) with the highest SPL outputs of 73.7 dB at 15 kHz with 0.5 W input power. The low bending stiffness of ultrathin MTAL with the electrostatic interaction between negative MXene layer and positive poly-L-lysine treated substrate shows stable TA outputs under various structural deformations (concave, convex and folding) and maintained stable electrical conductivity under 1,000 bending cycles with 0.5 mm radius of curvature. In addition, conformal attachment of MTAL on diverse 3D shape (cylindrical, spherical, and parabolic shape) allows directivity-tunable TA sound generation. Particularly, a configurable design of kirigami structures enables stretchable MTAL, which exhibits stable TA sound outputs under 50% strain, bending and twisting deformation. In conclusion, we demonstrated bi-directional, omni-directional, stretchable, and highly focused directional sound generation based on film, spherical, kirigami-pattern and parabolic shapes of loudspeakers, respectively. Our MTAL with deformation-independent sound generation can be utilized as the next generation speakers with the user-desired functions.

5:00 PM EL18.06.32
Cu-Ni Core-Shell Micromesh-based Electrodes for Highly Robust, Transparent, and Flexible Heaters Han-Jung Kim, Yonghwan Lee and Yoonkap Kim; Gumi Electronics & Information Technology Research Institute (GERI), Korea (the Republic of)

In this work, we demonstrated the performance of metal mesh structures-based transparent electrodes (TEs), which is effectively improved for the thermal and chemical stability with electroplating nickel (Ni) on a copper (Cu) mesh/polyethylene terephthalate (PET) film, as highly robust, transparent, wearable heaters. For this, the Cu-Ni core-shell micromesh structure-based TE was prepared on a PET substrate by a combination of photolithography and Ni electroplating processes. The figure of merit of the Cu micromesh-based TE could be improved more than four times from ~230 (Optical transmittance at 550 nm : 85.7%, Sheet resistance : 10.4 Ω/sq) to ~950 (Optical transmittance at 550 nm : 80.7%, Sheet resistance : 1.8 Ω/sq) by Ni electroplating. And, the Ni electroplating could effectively enhance the adhesion (to PET substrate), thermal and chemical stability of the metal mesh structures. In addition, the Cu-Ni core-shell micromesh-based TE showed excellent response characteristics (fast response time, low power consumption, etc.) for a wearable heater. Based on the above the results, we expect that the TE based on the metal-Ni core-shell micromesh structures can be applied not only to wearable heaters, but also to electrodes for photovoltaic cells and displays.

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5:00 PM EL18.06.33
Self-Healable Films with Ion Accumulation Multilayer Structures for High-Performance Piezoionic Self-Powered Tactile Sensor Haryeong Cho, Young-Ryul Kim and Hyunhyub Ko; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Piezoionic effect is the formation of electric potential and generation of current by the uneven local distribution of ions in ionic polymer composites in response to external mechanical stimuli. It has been utilized in electromechanical sensors for the simultaneous perception of static and dynamic forces, unlike other self-powered sensing mechanisms such as piezoelectricity and triboelectricity, which can detect dynamic forces only. However, piezoionic sensors have several limitations such as low-output signal and slow response time. Herein, we propose a multilayered piezoionic sensor with the I) ion-dipole interactive self-healable property for the enhanced device stability against mechanical deformation and II) ion accumulation layer to increase the piezoionic performance. Ion-dipole interaction between cation of ionic liquid (EMIM-TFSI) and anion of PVDF co-polymer (PVDF-HFP) enables to form the self-healable interface which can produce a stable multilayer structure under mechanical deformation. The optimized sensor (20wt% of ion contents) exhibits ~100% self-healing efficiency under 80 °C heat for 2 hours. Because the relatively light cations (EMIM) move rapidly in the strain direction which induces the ion polarization, our piezoionic sensor shows the recognition of deformation direction. The accumulated ions, which are located at the interface between the bilayer, activate ion exchange and generate the driving force for the ion moving to the interface, leading to the increase of output current signal and decrease of the response time. The sensor shows high stability under repeated bending stimuli over 1,400 cycles, and accurately distinguishes the surface roughness of rough sandpapers, paper, and glass. For applications, we demonstrate the multilayered pizoionic sensor array for the simultaneous perception of static and dynamic forces and discrimination of surface textures including braille shape and surface roughness.

5:00 PM EL18.06.34
Microfabrication and Surface Modification of 2D Materials for Flexible Chemical Sensor Platform Yeonhoo Kim; Korea Research Institute of Standards and Science, Korea (the Republic of)

Emerging novel technologies, such as flexible, foldable, and wearable electronics, need to meet their special requirements such as ease of controlling electronic properties, flexibility, and transparency. To date, metal and semiconducting materials have been used for conventional electronics, but the materials are brittle and nontransparent. In contrast, two-dimensional (2D) materials such as graphene and transition dichalcogenides have demonstrated great potential for flexible electronics and transparent electrodes due to their unique mechanical and electronic properties. In order to fully utilize the unique properties of 2D materials, geometric micropatterns of 2D materials on flexible substrates such as polymer substrates are essential to achieve technological purposes. However, due to harsh conditions such as cleaning, developing, and etching processes in the existing lithography procedures, defining elaborate micropatterns of 2D materials using the conventional photolithography processes on polymer substrates is difficult to achieve.
In this presentation, novel strategies to obtain micropatterned graphene on flexible substrates are discussed. After research on self-heating graphene micropatterns[1], direct polymer curing (DPC) transfer method was developed to overcome the low yield process. With the DPC method, entirely flexible, transparent, and self-activated graphene sensor arrays are stably fabricated on 4-inch wafer-scale polymer substrates. A sensor array composed of four graphene microchannels with different noble-metal decoration provides sufficient sensing information to discriminate gas species.[2-3] Finite element method simulations are employed to investigate the potential self-heating effect of this patterning technique. The calculation results demonstrate that the performance of the sensors can be highly enhanced when the active channels are suspended and nanopatterned. The DPC method is a state-of-the-art technique to define micropatterns of 2D materials on large-scale polymer substrates with a great potential for next-generation flexible electronics composed of 2D materials.

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5:00 PM EL18.06.35
Electrospun Elastic Nanofiber Air Filter for Active Pore Modulation and Adaptive Machine Learned Face Mask Seongmin Jeong, Yeongju Jung

and Seung Hwan Ko; Seoul National University, Korea (the Republic of)

In history of technology, the change from traditional and static technologies to adaptable modality accelerated dramatic advances. Active and responsive means were required to deal with appropriately in the world with continuous changes. Likewise, this study reports the first actively adaptive air filter technologies which can be the cornerstone of the next trend for respiratory protection.
Until now, the perception of air filter has bean established as a static and fixed characteristic. After manufactured, existing air filters generally cannot adjust properties such as permeability, pore characteristics and filtration efficiency. The surroundings connected to air filtration, however, are not constant but fluctuate over time, frequently giving preference to one of permeability and efficiency, which are in a trade-off relationship. When breathing in polluted air, a person would prefer filtering effectiveness over permeability; nevertheless, this would be the complete reverse when the person started to have breathing difficulty as a result of increased physical exercise. As a result, we commonly see incompatibility between dynamic conditions and static air filters, which is also the reason why existing personal face mask are limited. Regardless of the type and performance of the mask, it cannot continuously show excellent usefulness in a variety of real-world situation.
Here, we report the advanced active air filter, a novel type of air filter that can dynamically adjust its operating characteristics in response to numerous internal and external circumstances, in order to overcome this restriction of static air filters. This paper details a whole development cycle, including 1) idea creation, 2) concept embodiment, particularly into a personal mask, and 3) human volunteer studies and thorough evaluation. The active air filter shows a predictively adaptable and personalized respiratory protection method, maximizing the innovative dynamic modality, in particular by integrating machine-learning (ML) algorithm for automatic modulation. The authors regard that this study will provide an innovative methodological approach for next studies on respiratory protection and air filtration.

5:00 PM EL18.06.36
Precise and Stable Alignment Method for Stencil Lithography via Transfer Printing Sangyeop Lee and Seok Kim; Pohang University of Science and Technology (POSTECH), Korea (the Republic of)

Stencil lithography is a very attractive method in the micropatterning process but there are limitations in practical applications due to the difficulty for aligning the shadow mask, the shadowing effect due to the thickness of the shadow mask, and the blurring effect based on the gap between the shadow mask and the target substrate. To extend the potential applications of the stencil lithography process, we adopted ultra-thin silicon as the shadow mask material to reduce the shadowing effect. For alignment method, transfer printing by the microtipped stamp allows the facile and precise alignment and more conformal contact of the shadow mask on the target substrate and eliminates the gap in between to minimize any blurring effect. It is newly reported that 1 cm^2 shadow masks made of self-delaminated ultra-thin silicon substrates are precisely aligned and transfer printed without any damages by the microtipped stamp to enable multilayer stencil lithography processes.
The method of making an ultra-thin silicon shadow mask is followed. First, a photoresist (PR) is patterned on a silicon-on-insulator (SOI) wafer using a photolithography process. After dry etching the device layer using deep reactive ion etching (DRIE) process, the entire buried oxide layer (BOX) is etched by immersing it in a hydrofluoric acid (HF) solution. After that, when the patterned device layer and the handling layer are adhered by van der Waals force, it is put in an acetone bath for self-delamination. The floating ultra-thin silicon shadow mask is placed on a silane coated glass slide.
The microtipped stamp is fabricated with KOH wet etching and polydimethylsiloxane (PDMS) molding subsequently. KOH etching of the square array patterned SiN is performed to make a pyramidal pit array mold. Next, the mold is silane coated and PDMS precursor is poured on it. Finally, the fully cured PDMS is demolded.
For stencil lithography multilayer deposition process, the first pattern is sputtered on the silicon wafer through the shadow mask #1. The shadow mask #1 is then detached from the silicon wafer, either by submerging into the acetone bath or by the stamp. The shadow mask #2 is picked up from the silane-coated glass slide by the stamp. By observing through the microscope, the shadow mask #2 is aligned and placed on the first pattern. The second pattern is sputtered, and the mask is detached from the first pattern.
Two shadow masks are fabricated with different patterns, and the size of them is 10 mm x 10 mm with 15 mm thickness. The first pattern is 40 nm of chromium, and the second pattern is 40 nm of titanium. It is possible to conduct multilayer etching processes on silicon wafer with the metal deposited shadow masks. It was also possible to conduct multilayer etching process with the two masks. The alignment between two patterns from two shadow masks is inspected and it was found that the first and the second patterns have about 2~3 mm misalignment. It is presumably the human error since the aligning process was manually conducted.

5:00 PM EL18.06.37
Development of Stretchable Wearable Multichannel EMG Sensor with Outstanding Stretchability by Ultrarapid Laser Technique for Gesture Distinguishment and Human-Machine Interaction Jae-Seong Kim, Srinivas Gandla and Sunkook Kim; Sungkyunkwan University, Korea (the Republic of)

Gesture Distinguishment and human-machine interaction with flexible and stretchable electronic devices that can measure the electrophysiological signal is inevitable for the future trend. To obtain high accuracy, effective operation, and easy manufacturing of wearable sensors, it is important to evolve competent strategies for devising diverse materials on stretchable electronic devices with outstanding mechanical and electrical properties. Herein, we show a large-area multichannel array surface electromyography(sEMG) sensor that is processed by the ultrarapid laser ablation technique. In this work, 8 channel stretchable sEMG sensor array was achieved by ultrarapid UV laser(355μm) which does not require a mask and is considered a promising tool to process for the treatment of a wide range of materials. When the stretching test was performed with a 0-30% strain rate to 10,000 cycles with uniaxial strain, the sensor showed a negligible relative resistance difference. Besides, a human-friendly skin patch made of Ecoflex_polydimethylsiloxane-polyethylenimine (Ecoflex_PDMS-PEIE) showed soft (low modulus, ~50kPa), remarkable stretchability (>100%), high permeability for water loss(gm^{-2}h^{-1}), and good adhesion to the skin(~3.3kPa). Using this armband which consists of 8 channel stretchable sEMG sensor and Ecoflex_PDMS-PEIE skin patch, we were able to distinguish finger, wrist vertical, and horizontal movement. Through these results, we confirmed the utilization of EMG signals with body movement decisions to control the movement of the robotic hand. We anticipate our results to be a starting point for electronic skin and healthcare.

5:00 PM EL18.06.38
Development of Dense Ceramic Additive Manufacturing Process via Novel Polymer-Free Alumina Slurry Jong Wan Ko, Jungsoo Nam and Kyung I. Kim; Korea Institute of Industrial Technology, Korea (the Republic of)

The additive manufacturing (AM) process has been rapidly adapted in a wide range of industrial areas. For its ability to fabricate complex structures, AM is expected to satisfy the growing demands for complex parts that are difficult to achieve using conventional manufacturing processes. Furthermore, in the ceramic manufacturing field, AM process will provide a great opportunity to overcome the inherent low processability and expensive manufacturing cost of ceramic which hinder the manufacturing of complex parts. Unfortunately, contrary to polymer and metal, AM technologies for ceramics are still limited, especially for dense, monolithic structures. The most important challenge for dense ceramic AM is increasing ceramic contents in the feedstock while suppressing polymeric additives as low as possible. Since the polymeric additive was transited to gaseous species while in debinding process, polymeric contents in the green body apply internal pressure to the ceramic brown body, which can cause defects and cracks in the ceramic structure.

Herein, we introduce novel high alumina loading (over 50 vol.%) slurry with zero-polymeric additive compositionally designed for AM process. Instead of a polymeric binder and plasticizer, an aqueous “alumina-Sol” was applied as an inorganic binder and slurry suspension media. This “alumina-Sol” transit to an inorganic gel network and interconnect alumina particles by thermal curing, creating a dense green body consisting only of alumina and precursors of alumina. Since those slurries show viscoelasticity at every powder content, direct ink writing (DIW) was chosen as an AM process for our slurry. Through this process, ceramic structure with various geometry was successfully fabricated and sintered into a dense, monolithic structure with almost isometric shrinkage. Therefore, the chemical evolution of the developed slurry will be discussed first, and optimization of the DIW process by controlling the slurry composition and physical characteristics will be presented. The printing results using an optimized process and slurry would be demonstrated and the sintering results of the printed body would be presented.

5:00 PM EL18.06.39
A New Approach to Density Ceramic Additive Manufacturing: From Mechanism to Machine Implementation Jong Wan Ko, Dong-Hyun Kim, Chungsoo Kim and Jeonghong Ha; Korea Institute of Industrial Technology, Korea (the Republic of)

With the rapid development of 3D printing equipment and material technology, interest in industrial application possibilities is increasing. In the case of metals and polymers 3D printing technologies, are about to enter the rapid manufacturing stage beyond the rapid prototyping stage. However, in the case of photopolymer-based ceramic 3D printing(SLA or DLP type), which is currently widely used, due to the high content of photocurable polymer in the slurry used, defects (eg. pores, cavities, voids, etc.) in the 3D-printed green body during the debinding and sintering process, and in severe cases, the shape of the 3D printout is collapsed or destroyed.

In this research, we would like to introduce a new approach to ceramic 3D printing material-process-device development that does not use photocurable polymers. First, a ceramic slurry having a low polymer content (about 1 wt%) was prepared using alginic acid, a naturally-derived polymer, and an additive manufacturing process and device suitable for this slurry were developed. In particular, research was conducted with the aim of 3D printing of transition metal oxides (e.g. Al2O3, ZnO, CeO2 MnO2, etc.), which are widely used industrially as catalysts, high-temperature materials, and electric materials. Compared to the high polymer content (30 wt% or more) of the existing ceramic 3D printing slurry, a ceramic slurry containing only about 1 wt% of polymer (alginic acid) was prepared.

To realize the shape using the prepared slurry, a selective curing reaction was induced using metal ions (Al3+, Zn2+, Ce3+, Mn2+, etc.), and the additive manufacturing process was implemented by repeating these steps. The principle of forming a hydrogel by combining a carboxyl functional group on the surface of alginic acid with a metal ion was applied to the realization of a 3D printing shape. The metal ions used in the curing reaction were converted into identical oxides as the transition metal oxides in the slurry through the debinding-sintering process, thereby inducing bonding between the individual ceramic powders, resulting in dense ceramic parts. As a result, it has contributed to the improvement of the stability of the implementation of the ceramic additive manufacturing process by increasing the ceramic filling rate.

In addition to research on such ceramic slurry and hardening mechanisms, lamination mechanisms, and the additive manufacturing step process (slurry application-drying-curing reaction solution application) and machine development were conducted in parallel to enhance the industrial application potential of the technology. Through this, we intend to present the possibility of finally leaping to the rapid production stage of ceramic 3D printing technology.

5:00 PM EL18.06.40
Characterization of g-C3N4 as a Filler in the Photocuring 3D Printing Process Jong Wan Ko; Korea Institute of Industrial Technology, Korea (the Republic of)

3D printing or additive manufacturing (AM) technology is an uprising advanced manufacturing technology that possesses a high degree of design freedom to manufacture variously shaped products that were not possible with conventional manufacturing methods. Especially, this technology is actively researched in the polymer industry, which requires the fabrication of complex-shaped products, and there are polymer 3D printing methods such as fused deposition modeling (FDM), stereolithography (SLA), selective laser sintering (SLS), and digital light processing (DLP). DLP 3D printing, representative photocuring 3D printing the most widely used, has a very fast printing speed compared to other 3D printing processes because each layer is solidified and laminated by the light source of the plane unit, and the excellent precision and surface roughness of the printed product. However, DLP 3D printing has a limitation in that products have low mechanical strength owing to the inherent characteristics of photocurable resins such as low crosslinking density and difficulty in controlling the optimal curing irradiation time and anisotropy occurring during the 3D printing process. Therefore, in this study, we presented graphitic carbon nitride (g-C3N4) as a novel filler for general DLP acrylic resin to overcome the limitations of the strength of DLP products. g-C3N4 is a carbon nitride material with multiple hydrogen bonding motifs (-NH2, -NH functional groups) in the molecule, which could induce hydrogen bonding between matrix and g-C3N4, thereby increasing the intermolecular interaction, resulting in improved mechanical properties. Accordingly, we tried to investigate the characteristics of g-c3n4 as a filler and the feasibility of DLP composite products with process optimization. In the results, it was confirmed that the tensile strength of the DLP output of the composite material increased by 22% and the elastic modulus by 34% compared to the neat DLP polymer specimen respectively.

5:00 PM EL18.06.41
High Performance Flexible Organic Field Effect Transistor via Layer-by-Layer Fabrication Deng Zou[1,2] and Paddy K. L. Chan[1,2]; [1]University of Hong Kong, Hong Kong; [2]Advanced Biomedical Instrumentation Centre, Hong Kong

Organic field-effect transistors (OFETs) based on two-dimensional (2D) monolayer organic semiconductors (OSC) have demonstrated promising potentials for various applications, such as light emitting diode (LED) display drivers, logic circuits, and wearable electrocardiography (ECG) sensor. The fabrications of this class of highly crystallized 2D organic semiconductors (OSC) are dominated by solution shearing. As these organic active layers are only a few molecular layers thick, their compatibility with conventional evaporated top electrodes is restricted. Besides, sophisticated patterning techniques such as photolithography or e-beam lithography remain challenging for the organic active layers, which has also restricted their device density. In this talk, we will present our recent development on the integration of the damage-free electrode transfer stamp with a chemical-free patterning stamp to fabricate OFETs with channel lengths down to 3 mm over an area of 2 cm x 2 cm. These 2,9-didecyldinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (C_{10}-DNTT) monolayer OFETs show decent performance properties with a low threshold voltage (V_{TH}) for less than 0.5 V, a low subthreshold swing (*SS*) below 100 mV dec^{-1}, and intrinsic mobility of over 10 $cm^2\ V^{-1}\ s^{-1}$. The proposed patterning approach is also utilized to develop flexible OFET array on ultra-flexible parylene substrate with promising uniformity and conformability. By further reducing the channel length to 2 mm and utilizing it as a rectifier, the rectifying capability is up to 17.3 MHz at an input voltage of 4 V, which is capable of wireless communication. The proposed electrode transfer and patterning stamps have addressed the long-lasting compatibility problem of depositing electrodes onto 2D organic monolayer semiconductor patterning. It opens a new path to further reduce the fabrication cost and simplify the manufacturing process of OFET arrays for more advanced electronic or biomedical applications.

5:00 PM EL18.06.42
A Fully Self-Healing Multi-Sensor Patch with Bio-Inspired Adhesive Mihyeon Park and Jeong Sook Ha; Korea University, Korea (the Republic of)

Hydrogel-based self-healing sensors have been actively investigated for the flexible wearable devices with durability owing to the advantage of economic feasibility, environmental friendliness, and biocompatibility. However, solvent evaporation of hydrogels in ambient conditions results in the degradation of mechanical and self-healing performance to limit their practical application.
Here, we report on the fabrication of a fully self-healing multi-sensor patch consisting of a temperature sensor, pH sensor, and electrocardiogram (ECG) electrode with a bio-inspired adhesive. Our synthesized novel hydrophobic self-healing polyurethane (PU) with oxime-carbamate (OC) bonding is used as a substrate film to prohibit sweat-induced swelling. In the multi-sensor layer, carbon nanotube/polyaniline(CNT/PANI) is partially embedded in the self-healing PU and used as both temperature and pH sensors. In the adhesive layer, the self-healing PU with additional catechol group is patterned to have micropillar structures mimicking gecko pad and mushroom. Thus, the adhesive layer exhibits increased adhesion and self-healing efficiency via the combination of chemical and physical adhesion. Also, gold nanosheets are dry transferred to make a self-healing ECG electrode. The fabricated sensors exhibit excellent performance with high sensitivity in the temperature range between 25 °C and 45 °C, and pH values between 4 and 8, respectively, good for the detection of human body conditions. In addition, the ECG electrode shows distinguished PQRST peaks even after rinsing with water. The air-permeable micropiller adhesive exhibits strong adhesion onto skin and allows the accurate detection of biosignals even on sweaty skin. After a complete bi-section of the sensors and subsequent heating at 65 °C for 6 h, the temperature sensor fully recovers the sensitivity, and the pH sensor and ECG electrode also recover the pristine sensor signals. Furthermore, the whole patch system of vertically integrated multi-sensor layer and the adhesive layer is fully self-healed simultaneously by heating at 65 °C for 6 h, owing to the interlayer self-healing via OC bonding. This work suggests a high application potential of our fully self-healing multi-sensor patch in wearable health monitoring systems with longevity.

5:00 PM EL18.06.43
Self-powered Wearable Oximeter with Ultrahigh Responsitivity Based on CdS Nanoparticles /Tellurene Mixed-Dimensional Heterostructure
Ruifang Zhang[1,2] and Wenzhuo Wu[1,2,3]; [1]Purdue University, United States; [2]Flex Laboratory, United States; [3]Regenstrief Center for Healthcare Engineering, United States

Pulse oximetry sensors have been playing a key role in monitoring vital signs related to human health states. However, conventional pulse oximetry sensors have relatively large power consumption, rigid structure, and narrow spectral range of the photodetector. We demonstrated a dual-polarity photodetector for wearable oximeter in the form of a reflective patch-type pulse oximetry sensor, based on a mix-dimensional CdS nanoparticles (0D)/tellurene (2D) heterostructure. The heterostructure shows a photoresponsitivity of 6.7 A/W to 650 nm illumination and a photoresponsivity of 21.7 A/W to 950 nm illumination at 0V bias, much better than the reported p-n-junction-based self-powered photodetectors. More importantly, the wavelength-induced dual photoresponse extends to a broad spectral response and benefits the accuracy of oximeters. This photodetector with lightweight, small size, and low energy consumption can achieve self-powered light detection without an external power supply. Such an operation scheme, together with the ultrahigh photoresponsivity, enables the development and application of high-performance wearable oximeters that can monitor local tissue oxygenation and heart rate variability during real-time, continuous operations.

5:00 PM EL18.06.44
Self-powered Human-integrated Wearable Sensor Based on mixed-dimensional solid/liquid Heterostructures Jing Jiang[1] and Wenzhuo Wu[1,1,2]; [1]Purdue University, United States; [2]Regenstrief Center for Healthcare Engineering, United States

Self-powered sensors with high stretchability and biocompatibility are critical for next-generation wearable human-integrated applications. In this article, we reported a facile manufacturing scheme that integrates piezoelectric oxide nanowires on liquid metal electrodes for a soft piezoelectric wearable. The physical and chemical properties of the integrated mixed-dimensional sensors were systematically explored to achieve optimized sensor performance. The softness and the stretchability of the device made it possible to be worn conformably to different parts of human body, efficiently converting the subtle mechanical vibration from human physiological activities (e.g., voice, pulse, etc.) to measurable electric signals. Our work demonstrates a novel self-powered wearable device for monitoring human status, e.g., speech, cardiac health, etc.

5:00 PM EL18.06.46
Electrohydrodynamic Printing of Magnetic Alloys from Carbonyl Based Metal-organic Decomposition Inks Collin Miller and Owen Hildreth; Colorado School of Mines, United States

Iron – Cobalt alloys have important uses as magnetic cores in electrical and electronic devices. One drawback to these materials is their low ductility which limits part complexity. Designing a printable Iron – Cobalt functional ink could enable 3D printing and allow parts to have higher resolutions and more complicated geometries than traditional manufacturing methods. This work demonstrates the ability to electrohydrodynamically print magnetic alloy materials using a reactive ink precursor. Particle-free Iron – Cobalt reactive inks were made by dissolving organometallic metal carbonyls, such as Iron Pentacarbonyl and Cobalt Octacarbonyl, in organic solvents. These inks can be printed in an inert atmosphere using electrohydrodynamic printing then thermally decomposed into their metallic state using a heated bed at temperatures around 200 °C. The magnetic properties of this printed alloy are then compared to traditionally manufactured Permendur.

5:00 PM EL18.06.47
Fused Heterocyclic Aromatic Ladder Oligomers for Organic Semiconductor Applications Cameron Fiester[1], Phuong-Truc T. Pham[2], Amy Bradley[1], Amjad Nazzal[1] and Mamoun M. Bader[3]; [1]Wilkes University, United States; [2]Penn State Scranton, United States; [3]Alfaisal University, Saudi Arabia

We report the synthesis and characterization of a series of structurally related ladder oligomers composed of fused heterocyclic compounds for potential use as organic semiconductors in electronic devices. Specifically, the reactions of 2,3-dichloro-1,4-naphthoquinone and 2-aminophenol, and 2-aminothiophenol and their derivatives were employed to synthesize a series of fused heterocyclic ladder oligomers with various electron donor and acceptor groups in various configurations and molecular designs. These products were characterized using H-NMR, DSC, elemental analysis, and IR spectroscopy. Furthermore, UV-VIS and cyclic voltammetry were performed on these products to determine the optical and the electronic band gaps. We also report the single crystal structural analyses on a few of the products for which good quality crystals were successfully grown. Furthermore, results of our DFT calculations of the electronic structures of these molecules and the evolution of the calculated HOMO-LUMO levels as a function of structural modifications will be reported.

5:00 PM EL18.06.49
Carrier Mobility in Inkjet-Printed Semiconducting SWCNT Random Network Studied using Impedance Spectroscopy Manoranjan Manoranjan, Paramita K. Choudhury and Yashowanta N. Mohapatra; Indian Institute of Technology Kanpur, India

Large area printable electronics on flexible substrates is currently at a cusp of rapid development emerging as a technology with potential to transform many sectors of applications. The current suit of applications ranges from large displays, efficient lighting to generators, sensors, energy storage, e-textiles, in healthcare and biomedical applications to smart packaging. Nonetheless, despite encouraging recent advancement, there are several material challenges such as carrying out all the processes at low temperature, choosing an optimum flexible substrate, choosing a suitable solvent, stabilizers etc. in making ink functional and jettable, choosing an appropriate printing technique, and further efforts in developing suitable characterization methods.

Specifically, the realization of active devices such as printable arrays of diodes and thin film transistors (TFT) is common to most developmental efforts. Various solution processable-material systems including organic molecules, polymers, oxides such as InGaZnO, and nano-structures embedded in polymers are being tested widely. Recently, semiconducting single walled carbon nanotube(sc-SWCNT) wrapped with polymer is emerging as a material with significant application potential in the area of flexible transparent electronics due to its reasonably high carrier mobility, excellent chemical stability & mechanical flexibilities as well as compatibility with solution based processing. However, the processes and mechanisms controlling carrier transport in such films is not understood well as yet. This being critical to device application there is a need to study reliably carrier mobility in such films realized using realistic solution processes and feasible printable techniques. Attempts to measure mobility in printed layers in TFT structures is often fraught with problems of cross-sensitivities due to the quality of the device in terms of input-output characteristics, device architecture and associated contact resistances. To overcome these difficulties, we use fully ink-jet printed much simpler metal-semiconductor-metal (MSM) structures to determine mobility using impedance spectroscopy. We demonstrate determination of mobility by two different methods in which the capacitive and resistive components neatly separate out and there is no need to model I-V characteristics with assumptions regarding transport mechanisms.

In this study, we have demonstrated a fully inkjet-printed flexible sc-SWCNT based MSM structure. The semiconducting layer is printed using a commercially sourced ink (NanoIntegris IsoSol-S100), consisting of polymer wrapped sc-SWCNT. The source drain electrodes are printed using PVNanocell (PVN)-150T silver ink as a metal layer. The electrodes are sintered with optimized intense pulsed light sintering. The sample is printed on a PEN substrate. The printed layer is rinsed in toluene and annealed for 30 minutes at 100^0C to fuse and form a random network of sc-SWCNT. The effect of processing steps controlling the degree of polymer content embedded on the CNT network is investigated.

Current Voltage (IV) characteristics, Impedance (|Z|) with Frequency and Capacitance with Voltage (CV) & Frequency (CF) are investigated in the temperature range of 50-300K. We show that the two terminal devices can be modeled as a simple RC circuit with zero series resistance. We demonstrate that mobility can be obtained by different methods such as Cole-Cole plot, -Im(Z) vs Frequency and Phase vs frequency. The measured mobility is of the order of 10 cm^2/S-V which is similar to mobilities but is more reliable than those obtained in the TFT structures being independent of non-idealities due to device configuration. The temperature dependence of device characteristics and mobility is discussed in terms of possible transport models such as variable transport hopping, tunneling across distributed barriers and fluctuation induced tunneling at junctions in such printed random network of sc-SWCNT.

5:00 PM EL18.06.50
Development of a Low Cost Noninvasive Continuous Glucose Monitor Nicole Jeselson and Ahyeon Koh; Binghamton University, United States

Diabetes mellitus is an increasing public health issue that affects millions of people worldwide. To offer better control over diagnosis and treatment administration, continuous monitoring is utilized to detect glucose concentrations in the interstitial fluid (ISF) through electrochemical biosensors with reverse iontophoretic extraction. Traditional continuous glucose monitors (CGMs) involve subcutaneous microneedles which lead to complications such as biofouling and infections. To address these limitations, soft bioelectronics in a temporary tattoo platform offers a non-invasive, comfortable, and accurate method that can replace traditional invasive methods. These soft bioelectronic sensors contain an electrochemical electrode system fabricated through screen-printing that can conform to a patient's skin. We hypothesize that the detection accuracy and specificity of glucose concentrations is comparable to traditional CGMs while offering an affordable and non-invasive platform. The working principle of this sensor is to extract glucose through reverse iontophoresis after applying low-level electrical current to the epidermis. Then, the enzyme-based biosensor with glucose oxidase (GOx) detects ISF glucose concentrations via a hydrogen peroxide (H_2O_2) proxy. We fabricated the biosensors through a low cost screen-printing process utilizing conductive inks and three pre-burned 230 mesh count 18" x 20" screens to print the three layers of the biosensors. The first layer is silver/silver chloride (Ag/AgCl) ink for the counter and reference electrodes. The second layer is carbon-graphite Prussian blue mediator paste for the working electrode. Additionally, there is a third layer of insulating dielectric ink. Optical profilometry obtained the roughness of the biosensors to determine the variation in ink layer thicknesses. Results concluded the average roughness for the Ag/AgCl and carbon-graphite Prussian blue ink to be 8.68 µm and 7.90 µm, respectively. Results concluded the average thickness for the Ag/AgCl and carbon-graphite Prussian blue ink to be 57.95 µm and 98.24 µm, respectively. Electrochemistry experiments characterized the sensors including cyclic voltammetry, linear sweep voltammetry, and chronoamperometry. Characterization of the working electrode showed oxidation and reduction peaks consistent with previously reported Prussian blue electrodes, and the counter and reference electrodes showed comparable performance to commercially available alternatives. A developed linear response curve correlated varying levels of glucose in a target concentration range of 2 mM/L to 14 mM/L glucose to current output. This range covers normal, pre-diabetic, and diabetic levels of glucose. Once characterized, a skin simulator determined the ISF collection mechanism *in vitro* and evaluated the biosensor response to levels of glucose. UV-Vis Spectroscopy determined the peak wavelength and absorbance for each glucose concentration extracted into agarose gel by reverse iontophoresis. Additionally, interfering electroactive species present in the ISF were utilized to investigate the specificity of this system toward glucose. Overall, this proof-of-concept flexible biosensor is a promising alternative for continuous glucose monitoring in a non-invasive platform that offers an affordable fabrication process.

5:00 PM EL18.06.51
Skin-Interfaced, Soft Microfluidic Sweat Collection Platform with Dual-Valving Features Ji Hyun Yang[1], Uchechukuwu David[2], Yeonsik Noh[2] and Ahyeon Koh[1]; [1]Binghamton University, United States; [2]University of Massachusetts Amherst, United States

Skin-interfaced microfluidic devices have been advancing at a rapid pace, measuring various biofluids such as sweat and interstitial fluid using external or on-board sensing modalities. Current microfluidic platform relies on continuous sweat flow in the measurement of sweat analytes without temporal consideration and sample isolation. Microfluidic valving mechanism will provide temporal collection of sweat biofluid, eliminating any continuous flow requirements. Therefore, the analyzed information will reflect close to the actual information of our human body. Integration of expandable materials with traditional PDMS-based microfluidic soft-lithography techniques can offer soft microfluidic valving features. Additionally, electronics can be used to devise a controlled microfluidic platform for the advancement of skin-integrated microfluidic devices. Here, we develop a biocompatible, skin-interfaced microfluidic platform with temporal collection capabilities using thermal expandable microspheres. Additionally, we integrated electronics that allow discrete microfluidic valve control on demand through microheaters, capable of long-term biofluid collection. Soft lithography was used to produce polydimethylsiloxane (PDMS) based skin-interfaced microfluidic layers. Expandable microspheres were mixed with PDMS (1:2 weight ratio) and was included in the microfluidic device set up to provide the basis of the valving mechanism. Layers were joined together through oxygen plasma bonding. Electronics were transfer printed onto the Expandable layer for the controlled activation of the valves on the microfluidic platform. Thermal characterization of the microheaters was performed using infrared cameras. The burst pressure or the failure pressure required for the microfluidic valves was evaluated. Optical microscopic images were used to verify the closure of the microfluidic channels. Fluids of different pH were isolated and measured to simulate the temporal collection of biofluids at different concentrations. The fabricated microfluidic device could collect biofluids at skin-interfaced conditions. The transfer-printed microheaters were tested to show stable thermal energy delivery in a localized region where it is directly located at the entrance of the microfluidic chamber. Upon activation of microheaters, a rapid temperature increase was seen and the temperature rise along the conducting lines to the area of interest was minimal (less than 30°C). Characterization of both the passive valves and thermal valves shows that thermal valves have the highest pressure requirement for flow. Hence, the preferential microfluidic flow direction will be towards other capillary burst valves. Therefore, no flow towards the thermal activated valves is expected, indicating isolated fluid collection upon valve activation. Human study was also conducted to show the difference between the traditional collection method and the programmed time-controlled sweat collection method. The human study demonstrates improved sweat analyte data (sweat volume, pH, lactate, and cortisol) obtained from the traditional sweat collection method to a programmed time sweat collection device. The human study results also show an indication of a correlation between sweat rate and sweat lactate against aerobic and anaerobic exercises. Our approach can also be integrated with past and current advanced microfluidic systems and other chemical sensing modalities such as colorimetric and electrochemical measurement of sweat analytes that are present in current sweat devices for advanced on-board diagnostics.

5:00 PM EL18.06.52
Real-time Electrostatic Sensors based on Piezoelectric Nanogenerators and Polymer Field Effect Transistors Qun-Gao Chen and Wen-ya Lee; National Taipei University of Technology, Taiwan

With the increased attention in wearable tactile sensing devices. This study demonstrates a self-powered transistor-based tactile sensor based on micropillars made by poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) electrospun nanofibers and a diketopyrrolopyrrole (DPP)-based conjugated polymer. The sensors containing PVDF-HFP-nanofiber-embedded micropillar shows a high sensitivity of 83.54 $VkPa^{-1}$ in a small pressure range (<1 kPa). The micropillar structure can generate a open-circuit voltage of up to 79 V. To collect the signals of static electrical potential in a portable device, we integrate an in-situ monitoring system consisting of a polymer-based transistor-type sensor and Arduino board to detect the changes of static electrical potentials. The transistor-based sensor circuit can gather the electrostatic signals generated by electrospun-nanofiber-embedded pollars and act as an amplifier to increase signals. Moreover, the mobility of the transistor-based sensors can operate in a low voltage of 5 V and show a mobility of 0.15 $cm^2V^{-1}s^{-1}$, the threshold voltage of 0 V, and the on-off ratio of 10^5. This device combined with the microcontroller can wirelessly control the real-time pressure monitoring sensor for tracking human health. This work demonstrate a new device design for wearable electronic circuits.

5:00 PM EL18.06.53
Healable N-type Naphthalenediimide-based Polymer Semiconductors with Dynamic Covalent and Non-covalent Bonding for Field-Effect Transistors Yueh-Chun Huang[1], Wen-ya Lee[1], Tomoya Higashihara[2] and Ho-Hsiu Chou[3]; [1]Department of Chemical Engineering & Biotechnology National Taipei University of Technology, Taiwan; [2]Yamagata University, Japan; [3]National Tsing Hua University, Taiwan

Stretchable semiconductors have been reported over the past decade. However, stretchable electronic devices with remarkable mechanical compliance still present challenges. Therefore, self-healing materials used in semiconductors are crucial for developing stretchable integrated circuits. Their self-healing ability can recover the degradation of devices performance caused by the breaking from mechanical deformation on the polymer semiconductor soft film. In contrast to non-covalent self-healing materials with relatively low mechanical properties and limited stability, we demonstrate a self-healing n-type polymer with multiple interactions, including light- and heat-induced dynamic covalent bonding and hydrogen bonding. The healable NDI-based polymer semiconductor, poly(naphthalene-bithiophene-co-isoindoline-1,3-dione), with maleimide group is blended with a stretchable polyurethane oligomer with conjugates anthracene moieties. Because of Diels-Alder and photochemical chemistry, the self-healed n-type field-effect transistors are achieved. The damaged n-type semiconducting polymer blend can be healed through a double dynamic network of the light-induced [4+4] and thermal-triggered [4+2] cycloaddition linkages. Moreover, the hydrogen bonding and elasticity of polyurethane oligomers assist to recover the electron mobilities of the polymer blend. This work shows that thermal and UV light triggering demonstrate self-healing n-type polymer semiconductors with dynamic covalently bonded double networks and hydrogen bonding. To conclude, these results provide new directions and applications for the development of self-healing materials. To our best knowledge, this work is the first self-healable n-type polymer semiconductor using dynamic covalent bonding.

5:00 PM EL18.06.54
Interfacial Stabilization via a Phase-Switched Bulk Heterojunction for Self-Powered Photodetector and Photovoltaic Applications Jihyun Lim, Min Soo Kim, Woongsik Jang and Dong Hwan Wang; Chung-Ang Univ, Korea (the Republic of)

Non-fullerene acceptor materials (especially Y6) have recently attracted much attention in organic photovoltaics due to their excellent optoelectronic properties that lead to high reproducibility performance.[1] Nevertheless, when fabricating devices based on the PM6:Y6 active layers with high efficiency, the use of chloroform (CF) with a low boiling point is unavoidable,[2] which is a major obstacle for large active-area device fabrication or modularization due to its fast evaporation. Although spin-coating is appropriate at the laboratory level, it is difficult to apply it to produce large active areas. For the first time, we succeeded in introducing a phase-switching process when forming a PM6:Y6 bulk heterojunction using relatively high-boiling chlorobenzene instead of CF. Phase-switching method using soft mold has been considered by advanced technology to overcome limits of the wet coating such as spin coating, which is composed of a deposition of large area and specific region, material loss, and penetration of solvents.[3] A phase-switching process was introduced to a PM6:Y6-based active layer to achieve a uniform surface with preferred Y6 acceptor-domain positioning. By designing the wetting coefficient-based process to fit the surface properties of a small-molecule Y6 acceptor-based bulk heterojunction, a highly reproducible phase-switched active layer was successfully formed over an area of 2.25 cm^2.[4] It improved charge transport ability and suppressed surface defects owing to a molecular orientation favorable for efficient charge separation and transport.[5] Furthermore, adding chloronaphthalene additive induced the domain growth of Y6 acceptors with dense molecular packing, enhancing the phase-switching process's effects. Uniformly distributed performance in the phase-switched active layer via the phase-switching process was demonstrated in fabricated large active-area devices. Furthermore, the process was utilized in a PM6:Y6-based self-powered photodetector, which improved detectivity owing to the suppression of the dark current density. Therefore, the phase-switching process is an important technology for forming high-quality thin films composed of small-molecule acceptors for efficient self-powered photodetector and photovoltaic applications.

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5:00 PM EL18.06.55
Micron-sized GaN Domains Grown by Thru-Hole Epitaxy over Reduced Graphene Oxide and Directly Grown Graphene as Building Blocks for Flexible Devices Hyunkyu Lee, Gyuseock Ko, Jae Hun Kim, Jong Woo Ha, Hyung Beom Kim, Hyeonoh Jo, Hansol Kim, Jieun Yang and Chinkyo Kim; Kyung Hee University, Korea (the Republic of)

With the increased demand for high-performance micro-LED devices, it becomes more crucial to reduce the density of threading dislocations, suppress leakage currents on the side walls, and improve the transferability of individual devices as their size is required to be decreased. Recently, thru-hole epitaxy, similar to conventional epitaxial lateral overgrowth but with a 2D material, containing extremely small openings, as a mask was reported to be one of the intriguing candidates for this purpose. For this growth method to be more controllably utilized to produce micron-sized domains as building blocks for flexible devices, however, there are some issues to be resolved such as the control of size, distribution, and density of thru-holes in 2D material. In this study, we carried out the thru-hole epitaxy of GaN on a graphene-coated *patterned* sapphire substrate to make position-controlled micron-sized domains, which can be utilized as platforms for individual micro LEDs. The advantage of thru-hole epitaxy over conventional epitaxial lateral growth is that the opening area of the substrate can be as narrow as several nanometers in such a way that the density of threading dislocations in each domain can be significantly reduced as well as those domains can be readily detached by a thermal release tape. Coating the substrate with graphene was made possible either by directly growing graphene or reducing sprayed graphene oxide. In contrast with transferred graphene, either reduction of sprayed GO films or direct growth of graphene allowed us to better control the hole density and distribution of graphene. The GaN domains grown on graphene-coated sapphire substrates were found to be well aligned with the underlying substrates and readily exfoliated by a thermal release tape. AFM topography and TEM analysis were utilized to characterize the existence, distribution, and position of thru-holes, which were responsible for the reduction of threading dislocation density and the easy detachment of GaN domains.

5:00 PM EL18.06.56
Selective Assembly of Monolayer Two-dimensional Single Crystalline Metal Nanosheets via Ultrasonochemical process Seungyeon Kim, Ho Kwang Choi, Young-Seok Song and Tae-Wook Kim; Jeonbuk National University, Korea (the Republic of)

The ultrasonication process has been widely used as a representative cleaning method to remove undesired particles or residues on substrates for the fabrication of electronic devices or as a dispersing method for the particles in a desired solvent. Recently, ultrasonochemistry was introduced to enable the formation of a thin film in a solution by attaching nano-sized metal spherical particles on a ceramic or polymer substrate. However, there were negligible reports on conductive thin films by using monolayer assembly of giant two-dimensional (2D) single crystalline metallic nanosheets.
In this study, giant 2D single-crystalline nanosheets were assembled on a substrate by an ultrasonic deposition method that enables the formation of a uniform and monolayer assembled metallic film. We have demonstrated the various monolayer copper nanosheets film with different surface coverages via ultrasonochemical process. According to the surface properties of the substrate, concentrations of the nanosheets solution, processing time, and the polarity of the solvent, the degree of surface coverage of the 2D metal nanosheet on a substrate is systematically controlled. Especially, we achieved max. 88 % of surface coverage of copper nanosheets on a glass substrate, exhibiting ~ 65 ohm/sq of sheet resistance value. Also, it was possible to form monolayer assembled metal sheets on the surface of complexed 3D structures. Additionally, we demonstrated simultaneous patterning of the Cu nanosheet films by controlling the surface energy of the selected area of the substrate. From the above results, we identified that the ultrasonchemical process is useful for large-scale assemble of conductive fillers on both 2D and 3D substrates. Our monolayer assembled 2D metal nanosheet film is applicable for the promising functional conductive films.

5:00 PM EL18.06.57
Optical Memory Transistor—From Fabrication to Characterization Lizhi Yan[1] and Paddy K. L. Chan[1,2]; [1]The University of Hong Kong, Hong Kong; [2]Advanced Biomedical Instrumentation Centre, Hong Kong Science Park, Hong Kong

Optical memory transistor (OMT) is a emerging branch of the memory transistors, which involves optical signals in the programing or erasing process. Memory transistor is a promising candidate for the next generation memory devices towards in-sensor neuromorphic computing applications. In this study, we developed nonvolatile optical memory transistor by using 2,9-Diphenyl-dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (2,9-Dph-DNTT) organic semiconductor as the active layer. The fabricated OMT is based on the intrinsic optical memory property of the semiconductor layer. Compare with traditional memory transistors, this can simplify the fabrication process without functionalizing the dielectric layer or the embedding charge trapping sites as the floating gate. By combining with the high-k dielectric material Al_2O_3, the memory transistor can operate at a low voltage during optical-electrical programming and electrical erasing process (less than 4V). Additionally, the transistor shows a field effect mobility up to 3 $cm^2V^{-1}s^{-1}$ and excellent data retention for more than 12 hours with a current ratio higher than 10^4 between the two binary states, which is a promising value for the OMT.
In this talk, the mechanism of the optical-electrical memory phenomenon will be discussed in detailed. With the characterization methods such as TGA/DSC, X-ray diffraction, Kelvin probe force microscope, conductive atomic force microscope and etc, we confirmed that the effective charge trapping centers introduced by the metastable nanosprouts structure of the organic active layer are corresponding directly to the memory performance. At last, a demonstration of converting 2D information array to 3D information array will be introduced, with the large tunability of the OMT memory performance introduced by the substrate temperature difference in the evaporation process (larger than one order), we fabricated memory transistors array with patterned memory performance pixels. Then the 2D information array can be converted into 3D information array with the additional dimensionality of the pixel memory performance difference.

5:00 PM EL18.06.58
Poisson Effect-Assisted Replication Lithography for Repetitive Fabrication of 3D Microstructures Minsu Kim, Dokyung Kyeong, Han Jun Park, Gain Lee and Moon Kyu Kwak; Kyungpook National University, Korea (the Republic of)

It has become possible to manufacture complex three-dimensional structures easily with additive manufacturing technology. The production of submicron structures has also become possible through the development of a multi-photon polymerization lithography system. However, due to the slow manufacturing speed and the need for expensive equipment, the actual application of micro-scale 3D printing has been limited to the production of small prototypes and laboratory-scale samples.
Meanwhile, with the development of an imprint-based microstructure replication system, large-scale and continuous fabrication processes for the mass production of functional microstructures are becoming possible. Although there is a limit to the structure that can be fabricated with the conventional imprint processes, the productivity of imprint-based microfabrication is relatively superior to that of 3D printing systems.
In this study, a 3D microstructure replication method is proposed and demonstrated with the assist of the Poisson effect. A soft stamp mold replicated from the original mold fabricated by a two-photon polymerization 3D printing system is pressurized to form the intended 3D structural cavity. After resin polymerization, the pressure is removed to release the cured 3D structure from the mold cavity. By using the imprinting and 3D printing hybrid method proposed in this study, it is possible to replicate 3D microstructures that cannot be replicated with the conventional imprinting method. It might also be applied to large-scale fabrication, repetitive replication, and continuous fabrication of 3D microstructure surfaces, which were greatly limited by the existing 3D printing system.
The original master mold was fabricated with a 2PP 3D printing system considering the intended deformation. From the master mold, the soft mold was replicated using elastomeric materials showing sufficient lateral deformation from the Poisson effect. After applying resin for the replication on the prepared soft mold, normal pressure was applied to the soft mold to induce lateral deformation. The resin was cured into the intended 3D microstructure in the cavity.
The replication quality of the resultant microstructure was investigated according to the normal strain of the soft mold. It is confirmed that various

elastomeric materials can be used for the preparation of the soft mold if the material shows sufficient lateral deformation from the Poisson effect. In addition, it is also confirmed that various resin materials, heat- or UV-curable, are available for the 3D microstructure replication including hard PUA, soft PUA, NOA, PDMS, and PFPE.
The hybrid fabrication method demonstrated in this work is expected to significantly improve the productivity of the 3D microstructure surface simply by applying additional pressure in the conventional soft-lithographic imprint process.

5:00 PM EL18.06.60
Intrinsically Stretchable and Non-Halogenated Solvent Processed Polymer Solar Cells Enabled by Hydrophilic Spacer-Incorporating Polymers Chulhee Lim, Jinwoo Lee, Sun-Woo Lee, Yeonji Jeon, Seungjin Lee, Taek-Soo Kim, Jung-Yong Lee and Bumjoon Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

A new series of P_Ds with oligo ethylene glycol-based flexible spacer (OEG-FS) is developed and demonstrate efficient PSCs with high power conversion efficiency (PCE) of 17.74% processed by hydrocarbon-solvent (toluene) process. This hydrophilic FS alleviates excessive backbone rigidity of the polymer donors (P_Ds), while retaining sufficient aggregation in toluene. Also, the FS enhances P_D/SMA interfacial interactions and improves the blend morphology, affording efficient charge generation and mechanical stress dissipation. Therefore, the resulting PSCs with FS incorporated P_D showed superior PCE (17.74%) and crack-onset strain (10.50%) values, outperforming the PSCs without the FS (PCE = 15.7% and COS = 2.99%). More importantly, we develop intrinsically stretchable PSCs (IS-PSCs) with the OEG-FS containing P_D, accomplishing the best performances in terms of both PCE (12.05%) and stretchability (retaining 80% of the initial PCE after 22% strained). This work provides a simple and effective strategy to design P_Ds for the efficient, green-solvent processed, and mechanically robust PSCs.

5:00 PM EL18.06.61
Stretchable-Gradient Interface of Flexible and Stretchable Electronics for Wearable Health Monitoring Sunju Kang and Sunkook Kim; Sungkyunkwan University, Korea (the Republic of)

With the rapid development of wearable electronics, the robust interface of flexible and stretchable electronics is also demanded. Currently, flexible printed circuit boards (FPCBs) and stretchable physiological monitoring sensors are assembled by a conventional anisotropic conductive film (ACF) bonding technique. However, the interface can still be prone to delamination issues under repeated external strains subjected to human body movements. Here, a stretchable-gradient interconnect, a novel design and fabrication for integrating the FPCB and stretchable temperature sensor, is reported. The interconnect is designed to have adequate stretchability from the FPCB to the stretchable temperature sensor, establishing a stable transition of internal mechanical stress compliances. In addition, we performed electrical and mechanical stability tests of the proposed body temperature monitoring system with the stretchable-gradient interconnect by applying the device to the wrist with a high bending angle in the human body, and the results show a linear response and high robustness properties over multiple strain tests. This approach enables extended opportunities to develop FPCB-compatible on-skin stretchable sensors with high accuracy and robust mechanical properties.

5:00 PM EL18.06.62
A Single Microtip Shape Memory Polymer Surface with Reversible Dry Adhesion for Transfer Printing Junhyung Kim and Seok Kim; Pohang University of Science and Technology, Korea (the Republic of)

Transfer printing enables a deterministic assembly of micro-scale heterogeneous materials (herein called ‘inks’) fabricated from mother substrates using a polymeric stamp with reversible dry adhesion. During transfer printing, the strong adhesion between stamp and ink allows for the retrieval of the ink from the mother substrate and the weak adhesion in between allows for the release of it to the desired target substrate.
A shape memory polymer (SMP), one of the polymeric materials for transfer printing has a dynamic variation of rigidity upon thermal stimuli. This characteristic divides SMP into two states across the glass transition temperature (T_g): glassy state (under T_g) and rubbery state (over T_g). In the rubbery state where SMP is heated, SMP can freely change its shape. Then, the glassy state SMP after cooling under T_g keeps its deformed shape, and the adhesion of SMP increases dramatically. Thereafter, SMP may recovers its permanent shape to lose its strong adhesion when reheated over T_g.
Employing these characteristics of SMP, a single microtip surface is designed as a polymeric stamp with extreme adhesion reversibility. The transfer printing procedure using a single microtip SMP surface consists of flattening, picking up, and placing. The flattening process changes the microtip to be with a flat region, and thus transparent, which allows precise alignments. Then, an elaborate vertical approach is implemented using a custom mechanical stage. Here, the flattened surface helps easy and conformal contact with an ink depending on the shape of the ink. Once forming a conformal contact, the SMP surface is cooled and generates substantially strong adhesion (20.5 atm) because of the drastic rigidity change. For placing an ink onto the desired target substrate, the deformed microtip SMP surface is reheated over T_g in order to recover its original shape, which makes a point contact with an ink. Since the point contact causes approximately zero adhesion in viscoelastic materials, precise placing is possible.
To demonstrate its outstanding transfer printing ability, the adhesion tests for an single microtip SMP surface to pick up and place are conducted. Also it was shown that the single tip SMP surface can freely manipulate inks regardless of their 3 dimensional shapes. This transfer printing strategy using a single microtip SMP surface presents the highly desired potential for the assembly of microelectromechanical system (MEMS) and other device-level architectures.

5:00 PM EL18.06.63
***In Situ* Patterning Method of Hydrogel for *In Vivo* Applications** Minjeong Kim[1,2] and Dae-Hyeong Kim[1,2]; [1]Seoul National University, Korea (the Republic of); [2]Institute of Basic Science, Korea (the Republic of)

Despite recent advances in hydrogel applications for bioelectronics and tissue engineering, especially for implantable use, their advanced applications as functional devices are still largely limited without a patterned structure. Several *in vitro* patterning methods for hydrogel have been developed. Still, for implantable use of patterned hydrogel devices, the incision surgery that could be a significant burden to the patient should be accompanied. Here, we present a novel patterning methodology that enables *in-situ* patterning of the hydrogel *in vivo* through the minimally-invasive administration. The *in-situ* patterning method could be deployed based on the distinctive properties of the hydrogel such as appropriate mechanical strength, facile solute diffusion, and various crosslinking mechanisms. Also, with the filler integration, we successfully demonstrated the *in-situ* fabrication and operation of the hydrogel device and the hydrogel tissue scaffold, showing the feasibility, generality, and practicality of the method. This patterning method would facilitate the implantable use of the structural hydrogels by presenting a novel administration method.

5:00 PM EL18.06.64
Integration of Conductive Nanocomposites and Nanomembranes for High-Performance Stretchable Conductor Hye Jin Kim[1,2], Dongjun Jung[1,2], Sung-Hyuk Sunwoo[1], Sonwoo Jung[2] and Dae-Hyeong Kim[1,2,2]; [1]Center for Nanoparticle Research, Institute for Basic Science (IBS), Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)

Stretchable metallic nanocomposites have been viable material candidates for high-performance soft bio-interfacing electrodes. However, it is still challenging to fabricate a stretchable metallic nanocomposite that features outstanding charge transfer capability and low impedance as well as high conductivity and mechanical stability. Here, we present a material strategy for a stretchable conductor that meets such requirements by integrating stretchable conductive nanocomposites with stretchable conductive nanomembranes. The silver nanowires (Ag NWs) nanomembrane fabricated by the float assembly method is integrated with the Ag NWs nanocomposite prepared by the drop casting method. The compactly assembled NWs in the nanomembrane maximize conductivity by reinforcing the percolation networks of the nanocomposite. Moreover, the nanomembrane lowers impedance by allowing efficient charge transfer to the target tissue through the exposed NWs. After their integration, a high conductivity of ~ 35,700 S cm^{-1} is obtained, and the impedance is decreased by ~88.9% (at 1000 Hz) in comparison to the original Ag NWs-based nanocomposite (i.e., without integration of the nanomembrane). The soft bioelectrode using the stretchable conductor successfully records electrograms from the rat heart, recognizes various arrhythmic events, and applies feedback pacing.

5:00 PM EL18.06.65
Core-Shell Structured Liquid Metal-Nanocomposite Microfiber for Minimally-Invasive Implantable Bioelectronics Seonghyeon Nam[1,2] and Dae-Hyeong Kim[1,2,3]; [1]Center for Nanoparticle Research, Institute for Basic Science (IBS), Korea (the Republic of); [2]School of Chemical and Biological Engineering, Seoul National University, Korea (the Republic of); [3]Department of Materials Science and Engineering, Seoul National University, Korea (the Republic of)

Stretchable conductive fibers have attracted great interest for their distinctive advantages in biomedical electronics. Among them, due to the high electrical conductivity, excellent stretchability, and strain-insensitivity, liquid metal-based fibers have been highlighted as promising material candidates. However, practical biomedical application of liquid metal-based fibers, especially for implantable electronics, has been limited mainly owing to the leakage of toxic metal ions and poor electrochemical property. Here, we present core-shell structured microfiber consisting of a liquid metal alloy as a core and Ag-Au nanowire composite as a shell, along with its minimally-invasive implantation strategy. The proposed microfiber is intrinsically soft, stretchable, biocompatible, and thin, which is ideally applicable to organ interfaces. By solidifying the liquid metal core, such a thin microfiber becomes rigid enough to pierce the skin and can be deployed into the organ by minimally-invasive procedure. Moreover, functionalization of the microfiber by introducing additional micro/nanoparticles into the nanocomposite surface facilitates either lowering impedance or sensing biochemical, showing its broad applicability for strain-insensitive electrophysiological sensor, electrical stimulator, and electrochemical sensor. The microfiber is implanted on the heart and stomach in rodents by the freezing method and performs high-quality biosignal recording and electrical stimulation, offering the capability for a promising platform as implantable bioelectrodes.

5:00 PM EL18.06.67
4D Nanocellulose Printed Circuit Boards Jonathan D. Yuen, Joyce C. Breger and Jonathan A. Yuen; Naval Research Laboratory, United States

Due the nascency of 4D printing, integration of electronic capabilities into 4D printed structures presents opportunities barely explored. We demonstrate microbially-grown, nanocellulose-based, flexible printed circuit boards (PCBs) that can self-fold from flattened 2D forms into a variety of 3D forms - thereby creating 4D nanocellulose PCBs. This can be achieved by printing an SU8 layer on a nanocellulose PCB affixed on rigid surface, and then inducing a strain between the SU8 layer and nanocellulose. When the PCB is selectively cut and then released, the PCB will flex and fold into a 3D shape. This process allows for complexity in both form and electronic capability that has not been previously demonstrated, of which we will present various examples, including kirigami-based patterns.

5:00 PM EL18.06.68
No hysteresis TIPS-pentacene:polystyrene Blend-Based Organic Field Effect Transistor by Extruded Direct Ink Writing and the Application in Resistive Load Inverter Circuit Huiwen Bai, Yi Yang, Richard M. Voyles and Robert A. Nawrocki; Purdue University, United States

As low-cost, low-temperature, large-area, and easy-to-process electronic devices, organic field effect transistors (OFETs) have gained tremendous research interest.[1] Compared to organic semiconductors (OSCs) made with traditional vacuum or photolithography methods,[2] the solution-processed OSCs are promising due to their lower fabrication costs, larger area, and higher feasibility for customization. Over the past few decades, various solution-based fabrication methods for OSCs, such as spin-coating, dip-coating, drop-casting, zone casting, spray-coating, inkjet printing, and roll-to-roll printing, have been investigated.[3] When it comes to distinguished printing methods in the industry, inkjet printing is the most commonly used because its droplet volume can reach the femtoliter range to reduce the destructive effect of solvents and significantly improve the printing resolution. However, inkjet printing can only print low-viscosity materials and limit the utility of printable materials. Furthermore, the so-called coffee ring effect appears when the suspension's concentration is low, resulting in the non-uniform distribution of particles. As an alternative method, the extrusion-based Direct Ink Writing (DIW), due to its low energetic extrusion, can produce a smooth printing surface.[5] In addition, the extrusion-based DIW is considered a simple, adaptable, and low-cost method that is applicable in ambient conditions with moisture and oxygen.[6] Besides supporting a broad range of depositable feedstock materials, such as polymers, alloys and ceramic materials, extrusion-based DIW is also less likely to clog the printing nozzles compared with inkjet printing.[7] These advantages of extrusion-based DIW can facilitate the large-scale production of organic electronics through the automation of industrial process.
We report on fabricating solution-processed bottom-gate/top-contact OFETs with motor-controlled extrusion-based DIW printed semiconductor layer, which is believed to be the first such demonstration.[8] Based on the blend solution of an organic semiconductor, 6,13-bis (triisopropylsilylethinyl) pentacene:polystyrene (TIPS-pentacene:PS), we printed p-type OFETs using extrusion-based DIW method at different in-situ annealing temperatures. We found that the organic semiconductor deposited at 25 degree displayed the best performance with maximum mobility of 0.14 cm^{-2} V^{-1} s^{-1}, I_{ON}/I_{OFF} ratio of 2.7×10^3, threshold voltage of 0.14 V, and minimal hysteresis. The X-ray diffraction spectra and polarized optical microscopic images of the TIPS-pentacene:PS films revealed the changes of crystallinity and thermal cracks at different in-situ annealing temperatures. Static characteristics and long-term stability of resistive load inverters are reported. In addition, bending test was conducted of an OFET under three different bending radii. The pre-bent and post-bent characteristics of the OFET are analysed in this study.

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5:00 PM EL18.06.69

Influence of Channel Thickness on the Electrical Property and the Stability of Amorphous SiZnSnO Thin-Film Transistor Ji Ye Lee[1], Ji Won Kim[2] and Sang Yeol Lee[2]; [1]Korea University, Korea (the Republic of); [2]Gachon University, Korea (the Republic of)

Transparent amorphous oxide semiconductors based thin film transistors (TFTs) are suitable for flexible displays, such as rollable and foldable displays. The electrical property and the stability of amorphous SiZnSnO (a-SZTO) TFTs depending on the channel thickness will be investigated, by using temperature stress (TS) and negative bias temperature stress (NBTS). Also, the Debye length of a-SZTO TFT will be calculated by observing the thickness effect on the performance of TFTs, and the change in the effective carrier concentration will be confirmed. As the channel thickness increases, the threshold voltage (V_{TH}) of a-SZTO will shift in the negative direction. This is mainly due to the increase of carrier concentration. During TS and NBTS, the threshold voltage shift (ΔV_{TH}) will increase steadily, as increasing channel thickness. These results can be explained by the total trap density (N_T) increase due to the increase of bulk trap density (N_{Bulk}) in a-SZTO channel layer.

5:00 PM EL18.06.70
Stretchable Display with Negative Poisson's Ratio Using an Auxetic Structure Beomgil Ha and Byung Yang Lee; Korea University, Korea (the Republic of)

Many studies on stretchable devices that form electrodes on flexible substrates have been reported recently. In this study, a flexible substrate with negative Poisson's ratio characteristics was fabricated to solve problems such as image distortion and electrode deterioration due to Poisson's ratio of existing flexible devices. A flexible substrate was used for the substrate, and a stretchable substrate was completed by inserting a frame having an auxetic structure to realize a negative Poisson's ratio in a sandwich structure. The result of this study is that the Poisson's ratio can be controlled by inserting an auxetic structure into the substrate, thereby minimizing the mechanical strain that occurs when the substrate is stretched. As a result, a flexible substrate with a horizontal elongation of more than 30% and a Poisson's ratio close to zero was obtained. Additionally, LEDs were added on the substrate to realize a display without image distortion when stretched. The development of stretchable substrates with auxetic structures and displays using them can contribute to the development of the stretchable display market in the future.

5:00 PM EL18.06.71
Recoverable, Flexible and Stretchable Liquid Metal Based Electrodes Dong Jin Han and Byung Yang Lee; Korea University, Korea (the Republic of)

With the development of new devices such as wearable devices, soft robots, biomedical devices, and flexible display applications, the need for flexible electrodes or electrodes with little resistance change during tension is increasing. However, many of the obstacles of flexible or stretchable electrodes are large resistance changes or problems with large-area use. In this study, we developed a flexible electrode with little change in resistance even in a tensile state of up to 300% by focusing on increasing the conductivity of the electrode by adding copper and iron nanoparticles to the liquid metal. We have developed an elastic electrode that can be restored in case of damage. Electrodes were connected to LEDs to verify their ability to operate under tension and recover in case of damage.
Keyword: Liquid metal, Nanoparticles, Tensile, Flexible, Recovery

SESSION EL18.07: Bioelectronics
Session Chairs: Ho-Hsiu Chou and Weichen Wang
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3018

8:15 AM EL18.07.01
Ambipolar Transcap Based on Graphene Acid Films Applied on an Impedimetric Biosensor Rafael C. Hensel[1,2], Biagio Di Vizio[2], Jijin Yang[2], Francesco Sedona[2], Mauro Sambi[2], Stefano Agnoli[2], Andrea Cester[2], Osvaldo N. Oliveira Jr.[1] and Stefano Casalini[2]; [1]University of São Paulo, Brazil; [2]University of Padua, Italy

The ever-increasing demand for portable electronic devices has brought the need for smaller and more efficient energy storage systems. In this context, transcaps are attractive because they combine the electronic features of a field-effect transistor (FET) and a supercapacitor.[1] Apart from the high efficiency of storing/delivering charge within a few seconds, its charging process controls the channel conductivity. Here, our transcap is composed of a coplanar electrolyte-gated FET on Si/SiO_2.[2] Source and drain are based on interdigitated electrodes (IDEs), which were covered by drop-cast films of graphene acid (GA).[3] GA shares the same wet processability of graphene oxide (GO) due to its stability in aqueous dispersions, but with the advantage of exploiting its satisfactory conductivity, thereby avoiding any reduction step. Moreover, the gate electrode was coated by GA to increase its surface area. The systematic investigation of the current-voltage characteristic in 0.1M NaCl showed that this layout presents ambipolar charge transport. The galvanostatic charge-discharge demonstrated that the delivered energy and power are up to 17.5 mWh/kg and 7.7 W/kg, respectively. This versatile layout was successfully implemented in paper fluidics, demonstrating that it can be applied even to real-time monitoring of an aqueous flux, thereby exploiting both p-type and n-type conduction. Another advantage of GA is its high concentration of carboxyl groups (three times higher than GO),[3] which turns GA promising for biosensing, also improving the adsorption of antibodies on carboxylic acid groups. Proof-of-principle experiments showed the feasibility of implementing the GA-covered IDEs on an impedimetric biosensor to detect cancer biomarkers. Therefore the versatile processability of such devices turns them suitable to be further exploited on portable flexible electronics and sensing applications.

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Acknowledgments
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8:30 AM EL18.07.02
Stretchable Multichannel Polymeric Electrode Array for Large-area and Chronic Surface Electromyographic Signal Recording
Vittorio Mottini and Jinxing Li; Michigan State University, United States

Electromyography (EMG) is a technique employed in clinical and research settings for recording and monitoring the electrical activity produced by skeletal muscles. Conventional EMG recordings are performed with microneedle electrodes implanted in the muscle. To reduce the invasiveness of the technique, surface electromyography (sEMG) is employed. However, a remaining challenge is performing long-term and large-area sEMG recordings while maintaining inter- and intra-patient signal reproducibility. We developed a new stretchable, multichannel, and high-density electrode array based on a novel intrinsically stretchable conductive material based on conductive polymer PEDOT. The new material, combined with scalable laser-based fabrication techniques, allows for low-impedance, stretchable (1500% stretchability), and large-area sEMG monitoring.
Moreover, thanks to the excellent conformality of the device to the skin, the electrodes can record chronic sEMG signals with high signal-to-noise ratios and low motion artifacts and noise for more than 24 hours. This device will allow clinicians to monitor neuromuscular diseases' progression chronically, non-invasively, and accurately.<div id="accel-snackbar" style="left: 50%; transform: translate(-50%, 0px); top: 50px;"> </div>

8:45 AM *EL18.07.03
Flexible Bioelectronic Systems for Treating Pain John A. Rogers; Northwestern University, United States

Managing pain represents an essential aspect of patient care. Current approaches rely primarily on opioids, which present significant risks of addiction and various other adverse side effects. The increasing societal burdens associated with opioids motivates the development of non-addictive alternatives. Engineering-based approaches that leverage implantable electronic devices to eliminate pain in an on-demand fashion have significant potential. This talk summarizes two such technologies, both built in flexible/stretchable forms using bioresorbable electronic materials and targeted for the elimination of post-operative pain over a timescale relevant to the recovery process. The first uses high voltage electrical stimulation; the second relies on local cooling. Both schemes allow for reversible blocking of pain signals in specific targeted peripheral nerves, in a manner that avoids drawbacks of previous technologies based on similar biological mechanisms. The advanced materials aspects, the device designs, and the animal model validation studies will be discussed.

9:15 AM EL18.07.04
Wireless Smart Bandage with Integrated Sensors and Stimulators for Advanced Wound Care and Accelerated Healing Yuanwen Jiang; University of Pennsylvania, United States

Chronic non-healing wounds represent a significant healthcare burden, with more than 6 million individuals affected in the United States alone. A chronic wound is defined as a wound that has failed to heal by 8-12 weeks and is unable to restore function and anatomical integrity to the affected site. These wounds are associated with loss of function and mobility, increased social stress and isolation, depression and anxiety, prolonged hospitalization, and overall increased morbidity and mortality. In addition, management of chronic wounds has been estimated to exceed $25 billion annually. While interventions exist, such as growth factors, extracellular matrix, engineered skin, and negative pressure wound therapy, these treatments are only moderately effective. Current standard-of-care wound dressings are passive and do not actively respond to variations in the wound environment. 'Smart' bandages based on wearable devices hold great potential in advancing treatment of chronic wounds. However, there has been limited development in incorporating both sensors and stimulators for real-time physiological monitoring and active wound care.

For improved therapeutic outcomes, an ideal smart bandage platform needs to meet the following requirements. First, it needs to be mechanically flexible and wirelessly operated to avoid any undesired tethering and discomfort caused by conventional rigid, battery powered devices. Next, it should integrate both sensing and stimulation modalities for autonomous, closed-loop wound management. Finally, it should have on-demand skin adhesion with a tight interface for robust signal transduction and energy delivery during operation, while providing easy detachment to avoid secondary skin damage during device removal.

To address these requirements, we developed a miniaturized flexible printed circuit board (FPCB) capable of dual channel continuous sensing of wound impedance and temperature, as well as delivering programmed electrical cues for accelerated wound healing. To ensure efficient signal exchange and energy delivery between the circuits and the soft skin tissue, we designed a low-impedance and adhesive hydrogel electrode based on electronic-ionic dual conducting polymers. Compared to well-established ionically conducting hydrogels, our dual-conducting hydrogel has lower impedance across the entire frequency domain, giving rise to more efficient charge injection during stimulation. To mitigate secondary skin damage when peeling off the adhesive electrodes, we introduced a thermally controlled reversible phase transition mechanism to the hydrogel backbone and achieved two orders of magnitude lower adhesion at elevated temperature when compared to the normal skin temperature. Using multiple pre-clinical animal models, we found that our smart bandage could continuously monitor skin physiological signals and deliver directional electrical cues, leading to accelerated wound closure, increased neovascularization, and enhanced dermal recovery. Finally, the wireless nature of our smart bandage allowed us to utilize complex animal models, such as parabiosis, to investigate the possible underlying mechanisms behind the observed effect of electrical stimulation. Our data suggests that the beneficial wound healing outcomes could be attributed to the activation of pro-regenerative wound healing genes.

9:30 AM *EL18.07.05
Functional Materials and Devices for Emerging Bioelectronic Interfaces Luisa Petti, Martina Aurora Costa Angeli, Pietro Ibba, Manuela Ciocca and Paolo Lugli; Free University of Bozen-Bolzano, Italy

Thanks to the extraordinary advances recently experienced in the field of materials, manufacturing processes, device designs and architectures, and system integration, it is now possible to realize electronic devices featuring not only standard electrical properties, but also more unique and novel capabilities, such as flexibility, stretchability, twistability, or biocompatibility and biodegradability. Smart functional devices which can ubiquitously conform to complex 3D surfaces, dissolute and degrade in relevant environments, and/or be interfaced with biological systems are extremely important to develop environmental sensors, on-body wearable, or even implantable devices, as well as sustainable precision agriculture solutions. In the realization of all these systems, printing technologies play a key role offering advantages such as cost-effectiveness, large-area scalability, as well as availability of a wide range of sustainable substrates and materials. Very recently, bio-printing is gaining increasingly attention, especially for the realization of bio-derived sustainable devices, as well as bioelectronic interfaces to be used in regenerative medicine and tissue engineering, as well for advanced bio-hybrid devices.

Here, our most recent work on printed (and bio-printed) materials and devices for emerging bioelectronic interfaces – spanning from wearable devices to plant bio-hybrids - will be discussed.
First, we present how printed physical, chemical, and self-powered sensors can be utilized for wearable sports and rehabilitation applications. Specifically, we present (i) the development and validation of printed textile-based strain sensors able to monitor the breathing rate during different activities (ii) the design and fabrication of flexible electrolyte gated field-effect transistors functionalized with an ion-selective membrane for the detection of ammonium in

sweat, and (iii) the development of wearable and soft triboelectric pressure sensors for real-time pulse monitoring and gait analysis.
Next, we move from human wearables to plant wearables, demonstrating how bioimpedance methods can be employed for an effective monitoring of the health status of plants, thanks to the combination of customized printed electrodes, portable impedance analyzers, and ad-hoc developed machine learning classification algorithms.
Subsequently, we show how plants (in particular Arabidopsis thaliana plants) can be interfaced with conjugated polymer nanoparticles (CP-NPs) for a bio-engineered control of photosynthesis and thus plant growth. We show that the roots length of Arabidopsis thaliana plants grown in a medium mixed with CP-NPs yield a 45% increase (as compared to the controls, grown in the absence of CP-NPs) after 9 days of germination.
Finally, we also show how CP-NPs can be mixed with hydrogels to bio-print light-sensitive 3D cell scaffolds for applications in bio-photonics and light-control of living cells.

10:00 AM BREAK

10:30 AM *EL18.07.06
Tissue-Mimicking Neural Interface Yuxin Liu; National University of Singapore, Singapore

Despite the advancement of neurotechnology, the mismatch between the soft and developing neural tissue and rigid electronics causes adverse immune response, motion artifact and tissue constraint. I will share our recent works on high-density neural electronics, soft neural interfaces that can accommodate biomechanical motion in dynamically moving tissues, and morphing electronic that is shape-shifting and self-adapting with growing neural organoid in vitro and growing nerve tissue in vivo.

11:00 AM EL18.07.07
Achieving Tissue-Level Softness on Stretchable Electronics Through a Generalizable Soft Interlayer Design Yang Li, Nan Li, Yahao Dai and Sihong Wang; The University of Chicago, United States

Stretchable electronics are promising tools for biomedical diagnosis and biological studies because of their high stretchability which can accommodate deformation and promote intimate contact with the human body. However, most existing stretchable electronic devices are relying on electrically functional materials with high Young's modulus in the range of GPa. On one hand, low-modulus substrate/matrix (e.g., hydrogels and ultrasoft silicones) cannot be integrated with high-modulus functional materials to reduce the effective modulus of the entire device, because the modulus mismatch induced unstable interfaces and cracks propagation in the functional layers. On the other hand, building stretchable electronics with conventional high-modulus elastomers still causes 4 orders of magnitude higher in modulus than the soft bio-tissues, which impedes forming the stable interfacing with soft, dynamic living tissues. Here, we present a generalizable soft-interlayer design that, when added between the functional layer and the substrate, can effectively solve the challenge of using existing stretchable electronic materials to build tissue-level-modulus devices (e.g., transistors, active matrix, sensors), while achieving high stretchability. With a soft interlayer of intermediate modulus, the lower modulus mismatch and inherently formed tough bonding at the interfaces synergistically improve the stretchability of functional materials on ultrasoft substrates. High-modulus conductive materials such as carbon nanotubes (CNTs), silver nanowires (AgNWs), and PEDOT: PSS composites are developed into stretchable interconnections with both high stretchability and ultra-low modulus when integrated with ultrasoft silicone substrate using different soft interlayers. Also, a transistor device with an ultralow modulus of 6.7 kPa and stretchability up to 100% is successfully demonstrated on a thin hydrogel substrate through the soft interlayer design. Furthermore, using the laser-based selective etching of the soft interlayer, a 5x5 transistor array device fabricated on the patterned soft interlayer with hydrogel substrate can even achieve a lower modulus of 3.6 kPa, which is 3 orders of magnitude softer than previously reported stretchable transistor arrays on SEBS substrate. Benefiting from the tissue-like softness, our ultrasoft stretchable devices can form more stable and imperceptible contact with dynamic, soft nonzero Gaussian surfaces (e.g., organ surfaces) as compared to the conventional devices with the modulus in the range of MPa range.

11:15 AM EL18.07.09
Flexible and Biocompatible Pectin-Graphene Thin Film Sensor Arrays for Ultra-High Sensitivity Temperature Sensing Ezekiel Hsieh[1] and SungWoo Nam[2]; [1]University of Illinois at Urbana-Champaign, United States; [2]University of California, Irvine, United States

Pectin films have recently emerged as a promising artificial membrane material for wearable sensing, human-robot interactions, and prostheses owing to their mechanical flexibility and extremely high temperature sensitivity. These films are composed of poly-galacturonic acid chains crosslinked via their carboxyl groups by Ca^{2+} ions, resulting in optically transparent thin films exhibiting temperature dependent ionic conductivity. Previous studies have demonstrated pectin film-based temperature sensor arrays with temperature sensitivities several orders of magnitude higher than traditional semiconductor temperature sensors over a wide functional range relevant to human activities (0 – 45 °C). However, though prior works have established the basic working mechanisms of pectin temperature sensor arrays, flexible and wearable device configurations based on pectin films have not yet been realized. Here, we demonstrate a pectin film design with patterned graphene electrodes in a sandwich configuration across the thickness of the films. This enables not only mechanical flexibility but also individual interrogation of each pixel, greatly reduces the input voltage requirements for measuring the temperature-dependent ionic conductivity, and improves the sensor response time. We additionally leverage the optical and infrared transparency of graphene to result in fully optically transparent devices. The resulting pectin-graphene arrays are also biocompatible and mechanically flexible offering unique opportunities for prosthetic and wearable applications where rigid semiconductor-based temperature sensors would be inadequate. The extremely high temperature sensitivity enables not only surface contact temperature sensing but infrared and convective sensing of warm objects in the vicinity of the sensor. We evaluated these arrays for wearable applications as transparent bandages capable of continuously monitoring skin temperature for wound healing with limited spatial resolution but extremely high temperature sensitivity. We have additionally investigated the use of these arrays for electronic skins in human robot interactions, capable of detecting human contact without requiring force-feedback sensing. Altogether, these flexible pectin-graphene thin film sensor arrays demonstrate a uniquely advantageous means for thin film flexible temperature sensing.

11:30 AM EL18.07.10
Cold Atmospheric Plasma Deposition of Conductive Antibacterial Coatings for Wearable Devices Ulisses Heredia, Sina Nejati, Akshay Krishnakumar and Rahim Rahimi; Purdue University, United States

Silver-based antibacterial coatings are extensively used in the medical industry to prevent the transmission of infectious deceases caused by harmful bacteria. Despite the well-known antibacterial properties of silver nanoparticles, their poor adhesion to target substrates severely decreases the lifetime and efficacy of silver-based antibacterial coatings. Moreover, in traditional coating techniques such as dip coating, the amount and distribution of silver compounds are difficult to control. As a result, the safe use of medical devices is compromised due to a limited antibacterial effect (low silver amount) or a lack of biocompatibility (high silver amount). Therefore, silver-based antibacterial coatings with long-lasting action and optimized silver concentration are highly desirable. Currently, cold atmospheric plasma deposition (CAP) has emerged as an eco-friendly alternative to produce silver-based coatings with customized long-lasting antibacterial properties. In CAP, silver-based antibacterial coatings are produced by the concurrent formation of a polymer matrix and the synthesis of silver nanoparticles. The resulting highly crosslinked polymer matrix provides a strong fixation of the embedded silver nanoparticles thus, extending their sustained release. Here, we demonstrate the direct deposition of antibacterial Polypyrrole-silver nanocomposites by cold atmospheric plasma deposition. The silver content of antibacterial coatings was controlled by the amount of silver nitrate used as a precursor (0.5wt%, 1.0wt%, 2wt%, and 4wt%). The antibacterial properties of polypyrrole-silver nanocomposites were verified through the inhibition zone and contact-killing test showing a good bactericidal effect against *Escherichia coli* and *Staphylococcus epidermidis*. As proof of concept, polypyrrole-silver coatings are directly deposited on carbon-based textiles and used in wearable electrodes with antifouling properties.

SESSION EL18.08: Mixed-Conducting Polymers and Devices
Session Chairs: Jonathan Rivnay and Sihong Wang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3018

1:45 PM *EL18.08.01
Molecularly Hybridized Conduction in Conjugated Polymers Towards Next-Generation Iono-Electronic Devices Aristide Gumyusenge; Massachusetts Institute of Technology, United States

The implementation of smart body-machine interfaces is attractive for both healthcare applications and future consumer products. Fusing the body and machines, however, requires electronic hardware with i) excellent mechanical compliance, ii) operational stability in physiological environments, iii) reliable harnessing, discerning, amplification, and transduction of physiological information, and iv) ability to adapt or learn from physiological surroundings and execute tasks accordingly. For this highly demanding task, iono-electronics, where a semiconductor responds to incoming ions and undergoes a property change (electronic, optical, mechanical) which is in turn detected or utilized for a specific application are promising candidates. Though conjugated polymers have shown to be ideal conductors for such applications, only a few mixed conductors are studied to date and a one-material-fits-all bottleneck continues to hamper rapid advancements. The challenge lies in the lack of a cross-disciplinary design approach of high-performance materials. Establishing the needed balance between the two antagonistic modes of transport (ion permeability and electronic charge transport) to yield high performance devices has not only become an exciting field of fundamental research, but also a conduit towards advanced electronics. My lab at MIT (the laboratory of organic materials for smart electronics, OMSE Lab) employs molecular design to meet performance requirements in polymer-based iono-electronics. In this talk, I will share our ongoing efforts in designing novel semiconductors with varying degrees of ion-responsiveness and the scope of applications enabled by molecular tuning. We utilize copolymerization as a facile route to yield a library of mixed conductors enabling a variety of applications ranging from rapidly switching electrochemical transistors to high-fidelity artificial synapses. We have shown that by systematically tethering polar side groups onto known excellent electron conductors, we can probe the contribution from both ionic and electronic conduction to the resulting device performance and determine suitable applications. Lastly, my talk will introduce how we are utilizing these novel conductors to design redox-active nanocomposites combining biocompatibility, electrochemical sensitivity, and neuromorphic signal processing capabilities towards high performance bio-electronics.

2:15 PM *EL18.08.02
High-Performance, Printed and Low-Power Complementary Electrochemical Transistor Circuits for Sustainable IoT Applications Magnus Berggren; Linkoping University, Sweden

The realization of electrochemical transistor circuits is reported, targeting an array of different IoT applications. Future IoT circuit technology must be robust, manufactured using easy and sustainable production techniques and must also include materials that are eco-friendly with a minimal CO_2 footprint. This talk will emphasize the material, manufacturing and power consumption properties from application performance and sustainability points of view.

2:45 PM BREAK

3:30 PM *EL18.08.05
Soft Mixed Conductors Towards Bioelectronics with Unconventional Form Factors Jonathan Rivnay; Northwestern University, United States

Direct measurement and stimulation of ionic, biomolecular, cellular, and tissue-scale activity is a staple of bioelectronic diagnosis and/or therapy. Such bi-directional interfacing can be enhanced by a unique set of properties imparted by organic electronic materials. These materials, based on conjugated polymers, can be adapted for use in biological settings and show significant molecular-level interaction with their local environment, readily swell, and provide soft, seamless mechanical matching with tissue. At the same time, their swelling and mixed conduction allows for enhanced ionic-electronic coupling for transduction of biosignals. Such properties stress the importance of bulk transport processes, and serve to enable new capabilities, device concepts, and form factors relevant for, for example, electroactive scaffolds and bioactive constructs to modulate tissue state and/or cell fate. In this talk, I will demonstrate how molecular design and processing can be leveraged to achieve soft, conductive composites that are amenable to 3D printing, for example by micro-scale continuous liquid interface processes. Particle-based active materials can be readily tuned, integrated into process flows, and post-processed to achieve scalable soft, flexible, and stretchable electronics. New materials design will continue to fill critical need gaps for challenging problems in bio-electronic interfacing, regenerative engineering, and soft robotics.

4:00 PM EL18.08.06
Adhesive Semiconducting Polymers and Electrochemical Transistors for Conformable Biointerfacing Nan Li and Sihong Wang; University of Chicago, United States

Integrating bioelectronics with living biological tissues to interrogate and improve health status represents an important avenue for realizing human-machine interfaces. Semiconducting polymers-based transistors (e.g., organic electrochemical transistors (OECTs)) as an advanced sensing device, are highly desired for direct electrical biointerfacing due to their low operation voltage, high sensitivity and signal-to-noise ratio. We previously demonstrated a universal and facile approach for imparting conjugated polymers with a range of functional properties including direct photopatterning and biochemical sensing. To interface with wet and dynamically moving tissues, for example, heart, brain, or sciatic nerve, conventional suturing causes tissue/device damage and cannot achieve good conformability; having the adhesive property will ease the attachment process and help achieve a conformable contact and high spatial sensing resolution. However, the use of a separate adhesive layer between the semiconducting channel and tissue can cause increased interfacial impedance. Thus, developing an intrinsically adhesive active interfacing layer will significantly improve the devices' conformability on tissue surfaces and signal acquisition sensitivity. So far, however, to the best of our knowledge, none of the existing high-performance p/n-type semiconducting polymers are adhesive owing to a number of challenges, which pose significant challenges for using OECTs to achieve conformable electrical interfacing with wet and dynamically moving biotissues.

In this talk, I will present the development of an intrinsically adhesive semiconducting polymer by creating a rationally designed polymer network with interpenetrating semiconducting polymers and adhesive brush polymers to realize both high normalized maximum transconductance (~100 siemens per centimeter) and good adhesion on wet biotissues (interfacial toughness ~35 joules per square centimeter). Benefiting from the brush polymer design, the semiconducting polymer network possesses soft and viscoelastic mechanical properties (Young's modulus ~10 kilopascal) similar to biotissues, moderate water absorption (30 %), controllable swelling (<10 %), and abundant tissue-reactive groups (-COOH and -NHS), which synergically contribute to the adhesion on wet tissue surfaces. In addition, the semiconducting material shows abrasion-resistance and high stretchability above 100 % strain, which lead to the robust electrical performance. Also, the material presents good biocompatibility owing to low mechanical strain. Furthermore, enabled by the compatibility of the adhesive polymer with solution processing and vacuum deposition procedures, we fabricated an intrinsically adhesive and stretchable OECT with the adhesive semiconducting polymer as the active channel and gate and demonstrated its use for monitoring electrophysiological signals consistently and reliably on wet heart surfaces under perturbation scenarios.

4:15 PM EL18.08.07
Beyond 10 MHz/V High Speed All-Vertical Electrochemical Transistor Jung Woo Moon, Dong Gue Roe, Soo Young Cho, Yonghyun A. Kwon, InCheol Kwak, Seonkwon Kim, Seonmi Eom and Jeong Ho Cho; Yonsei University, Korea (the Republic of)

Organic electrochemical transistors (OECTs) have emerged as promising candidates for next-generation biosensing device due to their remarkable transconductance, low threshold voltage and good bio-compatibility. However, OECTs had to have a slow driving speed due to its unique operating principle, which have been pointed out as a disadvantage of OECTs. We propose another approach for overcoming this obstacle. Moreover, since most OECTs perform electrolyte gating, gating with Ag/AgCl reference electrode is common, therefore scalability was often not good. An all-vertical OECT architecture enable outstanding fast operating speed, and also enables to expansion of large-area and high-density OECTs. Simple approach for implementing the patterned Ag/AgCl reference electrode could be an answer for the scalability. As a result, 14 MHz/V operation frequency was yielded, which is the highest value for OECTs reported to date.

4:30 PM EL18.08.08
3D-printed OECT for Flexible Complementary Circuits Matteo Massetti; Linkoping University, Sweden

Silicon-based (Si) complementary metal-oxide-semiconductor (CMOS) field-effect transistors have been one of the main components in the field of the integrated circuit (IC) since the 1980s, mostly due to their low power consumption. For this reason, Si-based CMOS devices have been researched for Internet of Things (IoT) applications, acting as low-power sensors (e.g., motion, light, temperature). In the last decades, there have been a growing interest in developing flexible and soft IoT modules, capable of conforming to different shapes and eventually even placed on skin/inside the body, acting as smart biological sensors.
For this kind of applications, the perfect candidate is represented by organic electrochemical transistors (OECT). Indeed, OETCs typically operate with < 1 V and possess high transconductance, exploiting a mixed ionic-electronic semiconducting polymer as an active material and a highly ionically conducting electrolyte.
Here, we report the development of functional inks for 3D printing a flexible complementary OECT-based circuit. The electrical connections are 3D printed using carbon/silver-based flexible blends. The channel area is defined using 3D-printable green alcohol-based formulations of a n/p-type organic semiconducting materials. Finally, we print a PDMS formulation to insulate the electrical connections and define the channel area. These printed OECTs show excellent electrical and mechanical properties. In addition, we demonstrate the possibility of exploring alternative geometries to improve the circuit integration into smaller footprints as well as demonstrating low power consumption and operational voltage.
These fully 3D-printed inverters thus represent an interesting step towards the development of conformable, and wearable devices for IoT applications. In addition, the low operation voltage (<1V) offers the possibility of having self-powered devices (e.g. by light, heat, wireless power), thus paving the way to battery-free wearable electronics.

4:45 PM EL18.08.09
Self-Healable Printed Electronic Cryogels for Bioelectronics and Plant Monitoring Eloise Bihar[1], Elliot Strand[1], Megan N. Renny[1], Catherine Crichton[1], Ignacy Bonter[2], Jim Haseloff[2], Robert Mcleod[1] and Gregory L. Whiting[1]; [1]University of Colorado-Boulder, United States; [2]University of Cambridge, United Kingdom

Biocompatible cryogel scaffolds are of great interest in the field of biomedical research and translational medicine. Cryogels are traditionally used for the encapsulation of therapeutic or biological agents such as small molecule drugs, proteins, or biomolecules. Amongst them, Poly(vinyl alcohol) (PVA) is a good candidate for a novel gelling agent due to its self-healing properties, mechanical tunability, and biocompatibility. In this work, we present a novel method for integrating printed electronic materials with biocompatible PVA-based cryogels to form hydrogel bioelectronic devices. The electronic gels can be customized to offer various functionalities, including supercapacitors, electrodes, and Organic Electrochemical Transistors (OECT). These highly stretchable cryogel-based devices exhibit high conductivity (up to 350 S cm^{-1}), high transconductance (in the mS range), and high capacitance (up to 4.2 mF g^{-1}), as well as high stretchability (up to 330% strain), and self-healing properties. The biocompatible functionalized gel-based electrodes and transistors were successfully implanted in plant tissue. Data recording the ionic activity was collected for over two months with minimal scar tissue in tomato stems. These cryogel-based electronics are excellent candidates for tissue engineering scaffolds, biosensing, and drug-eluting systems.

SESSION EL18.09: Poster Session II
Session Chairs: Ho-Hsiu Chou, Francisco Molina-Lopez and Sihong Wang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL18.09.01
Photosensitisation of Inkjet-Printed Graphene with Stable All-Inorganic Perovskite Nanocrystals Jonathan S. Austin[1], Nathan D. Cotttam[1], Jonathan H. Gosling[1,1], Chengxi Zhang[2], Feiran Wang[1], Tyler James[1], Peter Beton[1], Yundong Zhou[3], Gustavo F. Trindade[3], Christopher Tuck[1], Richard Hague[1], Oleg Makarovsky[1] and Lyudmila Turyanska[1]; [1]The University of Nottingham, United Kingdom; [2]Shanghai University, China; [3]National Physical Laboratory, United Kingdom

Photodetectors based on low-dimensional materials are promising candidates for next generation optoelectronic devices and over the past decade the photoresponsivity of these devices has improved drastically due to material innovations [1]. All-inorganic perovskite nanocrystals (NCs) have been of particular interest owing to their high absorption cross-sections, long carrier diffusion lengths, tunable optical properties, and improved stability compared to other perovskite materials [2,3]. This stability enables the use of new manufacturing methods, specifically inkjet printing, which offers a promising route for scalable fabrication of devices with a high degree of design freedom and opportunities for device fabrication on flexible substrates [3-5].

Here we report a novel formulation of all-inorganic $CsPbBr_3$ and $CsPb(Br/I)_3$ NC inks for inkjet printing thin films over large areas and demonstrate high precision fabrication of complex photoluminescent patterns on rigid and flexible substrates. These films are used to photosensitise chemical vapour deposition (CVD) grown graphene transistors increasing their photoresponsivity to 10^7 A/W in the VIS-UV range [6], which is greater than that of any other inkjet-printed device recorded in the literature ($R = 10^4$ A/W [7]). We also fabricated fully printed photodetectors by incorporating inkjet-printed graphene (iGr) and printed Au electrodes. The fully printed $CsPb(Br/I)_3$/iGr photodetector displayed a maximum responsivity of 10 A/W [6], which to our knowledge is the largest responsivity reported for this type of device ($R = 10^{-1}$ A/W [8]). The performance of these devices is analysed and explained using modelling of charge transport through functionalised graphene and graphene networks [5] and explained by slow carrier dynamics governed by complex charging processes [9]. For reduced manufacturing complexity, we formulated and printed a hybrid ink containing both iGr and $CsPbX_3$ NCs (iGr-$CsPbX_3$) to produce photodetectors in a single deposition step on rigid and flexible substrates. In these detectors a single hybrid iGr-$CsPbX_3$ film acts as both photosensitive and conductive layer and achieved a maximum responsivity of 10^{-2} A/W, with negligible change in conductivity up to 200 bending cycles [6]. This work demonstrates successful integration of low-dimensional materials with additive manufacturing technologies and highlights its potential for scalable and customisable production of optoelectronic devices on rigid and flexible substrates.

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5:00 PM EL18.09.02

Contact Resistance of Low-Voltage n-Channel Organic Thin-Film Transistors Based on Three Different Organic Semiconductors Sabrina Steffens[1], Tobias Wollandt[1], James Borchert[2], Ute Zschieschang[1], Benjamin A. Günther[3], Lutz A. Gade[3], Bettina V. Lotsch[1] and Hagen Klauk[1]; [1]Max Planck Institute for Solid State Research, Germany; [2]Universität Göttingen, Germany; [3]Universität Heidelberg, Germany

Transistors based on organic semiconductors provide the possibility of fabricating electronic circuits and systems on flexible polymeric substrates, owing to the low process temperature of organic semiconductors. For mobile systems that can be used in wearable electronics and in diagnostic devices directly attached to the human body, an extremely low power consumption is a critical requirement. From a circuit-design perspective, the most effective approach to minimize the power consumption of digital electronic circuits is to combine p-channel and n-channel field-effect transistors in a complementary circuit design.

While the performance and stability of p-channel organic thin-film transistors (TFTs) are already sufficient for certain applications, the performance and stability of n-channel organic TFTs are still comparatively poor. This is partially due to the fact that in n-channel organic transistors, charge transport takes place in the lowest unoccupied molecular orbital (LUMO), whose energy must fall within a relatively narrow region between approximately -4.0 to -4.5 eV to allow efficient charge exchange with the source/drain contacts while providing sufficient stability. Organic semiconductors that fulfill this requirement include π-conjugated systems with strong electron-withdrawing substituents either attached to or incorporated into the molecular backbone.

Here, we compare the performance of low-voltage n-channel organic TFTs based on three promising small-molecule semiconductors having LUMO energies between approximately -4.0 to -4.5 eV, namely N,N'-bis(2,2,3,3,4,4,4-fluorobutyl)-(1,7 & 1,6)-dicyano-perylene-tetracarboxylic diimide (ActivInk N1100; Angew. Chem. Int. Ed. 43, 6363, 2004), 2,9-bis(heptafluoropropyl)-4,7,11,14-tetrabromo-1,3,8,10-tetraazaperopyrene (TAPP-Br_4; Adv. Funct. Mater. 23, 3866, 2013) and diphenylethyl-3,4,9,10-benzo[de]isoquinolino[1,8-gh]quinolinetetracarboxylic diimide (PhC_2-BQQDI; Sci. Adv. 6, eaaz0632, 2020). The TFTs were fabricated on flexible polyethylene naphthalate (PEN) substrates or on silicon substrates using a hybrid gate dielectric composed of a thin, plasma-grown aluminum oxide layer and an *n*-tetradecylphosphonic acid self-assembled monolayer. TFTs were fabricated either in the inverted staggered (bottom-gate, top-contact) or the inverted coplanar (bottom-gate, bottom-contact) device architecture, using gold for the source and drain contacts. In the coplanar TFTs, the surface of the source and drain contacts was functionalized with a chemisorbed monolayer of one of four different thiols, namely 4-methylbenzenethiol (MeTP), 4-(methylsulfanyl)-thiophenol (MeSTP), 4-methoxythiophenol (MeOTP) and benzyl mercaptane (BM) to improve the charge exchange between the contacts and the semiconductor. The semiconductors were deposited by thermal sublimation in vacuum. All electrical measurements were performed in ambient air

For each of the three semiconductors, the TFTs fabricated in the coplanar device architecture were found to have a smaller contact resistance (measured using the transmission line method) than the staggered TFTs; this finding is consistent with results reported previously for low-voltage p-channel organic TFTs (Nature Commun. 10, 1119, 2019). Regardless of the semiconductor, the best TFT performance was obtained by functionalizing the contacts with MeSTP. In addition, PhC_2-BQQDI and N1100 were found to provide smaller contact resistance and larger effective carrier mobility than TAPP-Br_4. Flexible coplanar PhC_2-BQQDI TFTs with MeSTP-functionalized contacts have an intrinsic channel mobility up to 0.6 cm^2/Vs, an on/off current ratio up to 10^6, a subthreshold slope as small as 100 mV/decade, and a contact resistance as small as 90 Ohm-cm (a record for n-channel organic TFTs). These results are important in view of the realization of low-voltage organic complementary circuits for low-power flexible electronics applications.

5:00 PM EL18.09.03

Highly Efficient Ternary Near-Infrared Organic Photodetectors for Biometric Monitoring Chih-Ping Chen; Ming Chi University of Technology, Taiwan

Near-Infrared (NIR) small molecule acceptor with the absorption of up to wavelength of 1000nm attracted much attention for organic photodetectors (OPD) and the biometric application. We evaluate the IEICO-4F as third component for PffBT4T-2OD: $PC_{71}BM$ based OPD to having efficient NIR response and greatly suppressing leakage current at reverse bias. By variation of the blend ratios and thickness (250-600nm), we realized an NIR OPD with ultralow dark current density (J_D=9.43 nA cm^{-2}) with an ultrahigh detectivity (D^*= 2.7 $\times 10^{12}$ Jones (850 nm)). Furthermore, the OPD shows consistent response, good reproducibility, and stability with a frequency of 0.5 MHz (f_{-3dB}) and ultrafast rise/fall response (560ns and 230ns at –2 V) under 850nm LED light. We demonstrated highly sensitive devices with photoresponse covering from the ultraviolet to near-infrared regions. The inferior compatibility originating from the intermolecular interaction between PffBT4T-2OD and IEICO-4F allowed manipulate the degree of phase donor and acceptor separation for well-defined phase segregation, leading to efficient charge separation, transport, and collection in ternary blends. We demonstrated the transmissive pulse oximetry by integrated our OPD and the LED and precisely calculated and collected the pulse oximetry.

5:00 PM EL18.09.04
Direct Printing of Suspended Metal Oxides Nanowires on MEMS Chip as Gas Sensor Yu Liu[1,2], Hongjun Liu[2], Xiaoyi Zeng[2], Zijun Chen[2], Xing Cheng[2] and Ji Tae Kim[1]; [1]The University of Hong Kong, China; [2]Southern University of Science and Technology, China

Semiconducting metal oxides(MOs) are prevalently used in gas sensors thanks to its unique charge transport mechanism being sensitive to surrounding gas molecules. [1] To enhance the performance of the chemiresistor-type gas sensor, both the composition and structure of the sensing materials need to be optimized. [2] One-dimensional MOs nanowires(NWs), comparing to the conventional thick films, have exhibited outstanding gas sensing performance such as lower detection limit and shorter response time.[3] Currently, various synthesis methods of MOs NWs have been developed including hydrothermal, chemical vapor deposition, electrochemical deposition, and electrospinning, etc. However, the current existing methods fail to deliver precise point-to-point fabrication, which makes the integration of multiple gas sensing materials rather challenging. In addition, with the existing NWs synthesis technology, the fabrication of gas sensing NWs on a suspended heater membrane of the Micro-Electro-Mechanical System(MEMS) chip is complicated.[4]
Here, inspired by the printing electronics, we present an alternative approach to fabricating freeform MOs NWs directly on the MEMS heater chip. The method exploits a nano-pipette filled with the ink containing polymer binder and metal precursors to print a preliminary composite wire with hundreds of nanometers in diameter and suspended arch architecture on micrometer-scale MEMS electrode pairs via a precise displacement and positioning system. After calcination, polycrystalline metal oxide NWs are successfully obtained. By optimizing the type or quantity of metal precursors in the ink, or adding precursors of noble metals such as gold, silver, platinum, and palladium, abounding MOs-based composite NWs are fabricated for diverse gas sensing. In addition, through such a point-to-point direct printing technology, various semiconducting metal oxides NWs can be assembled in a micron-scale region with high integration density, excellent precision, and nano-scale characteristics, which largely reduces power consumption and improves sensing performance. Furthermore, it also offers us a promising and straightforward process for multi-oxides material-based “E-nose” device fabrication.
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5:00 PM EL18.09.05
A Pen-on-Paper Graphene Oxide-Based Nanocomposite for Multitype Strain Sensing Zengsheng Weng and Fangxin Zou; The Hong Kong Polytechnic University, Hong Kong

Flexible strain sensors that exploit nanotechnologies to achieve superior performances have become increasingly indispensable in a number of high-value-added applications, such as human body monitoring, structural health monitoring and human-machine interaction. For real-world implementations, it is utterly important to fabricate sensors that, on one hand, possess high sensitivities, and on other hand, are customizable and convenient to install.

Recently, the pen-on-paper (PoP) approach – a fundamental printing technique that makes use of ubiquitous and portable raw materials – demonstrates the potential to meet the installation requirements of flexible strain sensors in real-world applications. Moreover, many modified graphene-based nanofillers have been shown to exhibit high sensitivities to microscopic deformations. Owing to their long-term stable dispersibility in solutions, modified graphene-based nanofillers are considered high suitable ingredients for PoP inks. On this basis, a PoP ink was prepared from graphene oxide (GO) in this work, and the ink was used to fabricate a flexible GO/paper strain sensor that can capture multiple types of deformations (i.e., in-plane tension, in-plane compression and out-of-plane pressure).

To prepare a GO ink, graphene was first oxidized by the Hummers’ method to a certain degree of oxidation and then put into an ordinary ink pen, together with polymer dispersants including phenolic resin and amphoteric polyacrylamide. GO/paper sensor specimens were fabricated by using the ink pen to mark on printing paper. The dimensions of the sensor specimens are fully customizable. The ink demonstrates an excellent writability even when a piece of paper is in bent state. Furthermore, even if an ink is left unused for several months, sensor specimens that are fabricated from it would exhibit a similar sensing capacity to those that are fabricated from a freshly prepare ink.

The sensitivities of the GO/paper sensor to in-plane tensile strain and in-plane compressive strain were evaluated by subjecting sensor specimens to bending. Within 1% strain, the gauge factors were found to be 121 (tension) and 103 (compression). Thanks to the 3D structure of GO, the GO/paper sensor is also able to capture out-of-plane pressure, exhibiting a sensitivity of 0.34 kPa^{-1} within pressure range of 2-7 kPa. To simulate real-world implementations, sensor specimens were attached onto aluminum alloy substrates to monitor the tensile strain, compressive strain and pressure applied onto the substrates. The real-world practicality of the GO/paper sensor was further demonstrated through a number of applications, including gesture recognition, eye movement and intraocular pressure monitoring, and aerodynamic pressure measurement.

Through the abovementioned experiments, it was observed that the sensitivity of the GO/paper sensor to tensile and compressive strain is inversely proportional to the degree of oxidation of the GO used. From material characterization results, it was found that as the degree of oxidation of the GO in a sensor specimen increases, the energy band gap and the distances between the GO particles would increase, while the number of layers and the size of the GO particles would decrease. The result of these changes would be the damaging of the conductive network in the sensor specimen and the weakening of the tunneling effect across the GO particles, leading to a reduction in sensitivity.

To summarize, this work introduces a flexible GO/paper strain sensor fabricated by the PoP approach. The sensor demonstrates high sensitivities to various types of real-world deformations, including in-plane tension, in-plane compression and out-of-plane pressure. Moreover, the GO ink prepared possesses an outstanding long-term stability. Last but not least, the inverse relationship between sensitivity and the degree of oxidation of GO was discussed.

5:00 PM EL18.09.06
Printed Memristors for Memory, Computing and Hardware Security Hongrong Hu[1], Alexander Scholz[1], Liang Yang[1], Gabriel Cadilha Marques[1], Florian Feist[1], Eva Blasco[2], Christopher Barner-Kowollik[3], Martin Wegener[1] and Jasmin Aghassi-Hagmann[1]; [1]Karlsruher Instituts für Technologie, Germany; [2]Universität Heidelberg, Germany; [3]Queensland University of Technology, Australia

Memristors are two-terminal electronic devices whose resistance can be changed upon the application of an electrical field. The device could be potentially used for non-volatile memory, novel computing paradigms, and hardware security. Currently, most of the reported memristors are fabricated by traditional thin film techniques such as vacuum deposition methods, photolithography, or CMOS-compatible processes. Additive manufacturing techniques like inkjet or laser printing have only recently been demonstrated to be feasible for memristor fabrication. This has the advantage of efficient material usage, cost-effectiveness, and rapid prototyping capability.

We demonstrate three types of memristors fabricated either by inkjet printing or laser printing. The first device is a fully inkjet-printed symmetric Ag/ZnO/Ag structure which shows digital resistive switching. Our utilized ZnO precursor ink is water-based and requires a post-deposition annealing step. The fully inkjet-printed memristor exhibits excellent parameters such as a high R_{off}/R_{on} ratio of 10^7, a long retention time of over 10^4 seconds, good endurance, and almost forming-free characteristics, which are advantageous for non-volatile memory applications. The second device is partially inkjet-printed and based on Ag/WO_{3-x}/Au. The device itself can be probed dynamically by applying a bias to exhibit digital resistive switching, caused by conductive filaments, or it can be operated as an analog resistive switching device without forming a conducting filament. The analog resistive switching properties are utilized to mimic the behavior of a biological synapse or neuron. This includes short-term plasticity, metaplasticity, and integration of several input signals. The third presented device is a fully laser-printed memristor formed by Ag and Pt as the electrodes and ZnO as the active layer. The semiconductor ZnO is converted from a novel precursor ink through local laser-induced hydrothermal synthesis. In addition, the memristors are integrated into a 6×6 fully-laser printed crossbar structure and successfully utilized for physical unclonable function (PUF) implementation.

In summary, we have demonstrated inkjet-printed and laser-printed memristors fabricated in a facile, rapid, and material-efficient approach. The introduced printed memristors show excellent device performance and are hence promising candidates for applications in non-volatile memory, neuromorphic computing, and hardware security.

5:00 PM EL18.09.07
Formation of NiSi by Pulsed Laser Annealing on Contact Resistance Reduction and its Applications on Flexible Inverter and 6T-SRAM Yu Chieh Hsu[1], Yan Yu Chen[1], Jia-Min Shieh[2], Wen-Hsien Huang[2], Chang-Hong Shen[2] and Yu-Lun Chueh[1]; [1]National Tsing Hua University, Taiwan; [2]Taiwan Semiconductor Research Institute, Taiwan

With the proper selection of metal silicide, contact resistance can be effectively reduced between the source/drain (S/D) and connected metal. The addition of metal silicide at any connection region can also raise the on/off ratio and improve the performance of electric devices. In this work, we applied the pulsed laser annealing (PLA) method to form nickel silicide (NiSi) between S/D metal and the top connecting metal. Three different kinds of laser wavelengths, including 355 nm (ultraviolet laser), 532 nm (green laser) and 1064 nm (infrared laser), were used to compare the results of NiSi formation in these laser annealing processes. NiSi phase with low sheet resistance was formed by an ultraviolet laser annealing process without damaging the polyimide (PI) substrate. After integrating the PLA NiSi onto the S/D region, the on/off ratio increased at least 3 times and the field effect mobility increased by 50%. The contact resistance was lowered from 21 kΩ to 8.5 kΩ after integration. Furthermore, the voltage gain of the CMOS inverter was also improved by 30%, making it have a faster switching speed. For the 6T-SRAM part, the static noise margin (SNM) of 6T-SRAM is elevated from 0.82V to 1V at V_{dd} = 4V. This work shows the achievability of using the PLA process to synthesize low thermal budget NiSi on the flexible substrate and the successful integration provides a new route to improve the performance of flexible 6T-SRAM devices. Better performance of the devices can ameliorate the application and function of wearable electronics, which will be an important part of the IoTs generation in the future.

5:00 PM EL18.09.08
Thiol-ene Chemistry in the Dielectric Layer Manipulating Polymer-based Devices from Transistors to Non-volatile Memory Devices Chang-Jing Liu and Wen-ya Lee; Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taiwan

Stretchable electronic materials with a high dielectric constant are promising for low-voltage-driven devices. This work demonstrates a stretchable dielectric layer using poly (acrylonitrile-co-butadiene) (NBR), a higher dielectric constant for the dielectric layer. The stretchable dielectric layer is cross-linked using the thiol-ene reaction between the double bond and the thiol functional groups. It has also been found that the chemical structure of thiol functional groups is capable of determining the device's memory characteristics. The CN triple bond in the NBR polymer structure is highly polarized, thus leading to a high capacitance. The highest capacitance can reach 60 nF/cm^2, and the dielectric constant can reach 14.6. Moreover, the mobility can approach 2.87 cm^{2}V^{-1}s^{-1}, the on-off ratio reaches 10^6, and the threshold voltage is 0 V. In addition, by observing the hysteresis characteristic of the device, it can be found that the memory windows of the crosslinked NBR dielectric showed a large window of 3.14 V under a voltage program voltage of -5 V. This results indicates that the crosslinking density can affect charge retention capability of the devices. The memory characteristics and synaptic behavior of devices have also been achieved using cross-linked NBR-based transistors. This work provides new insight into designing neuromorphic devices for the next generation of artificial intelligence.

5:00 PM EL18.09.09
Photocurable Stretchable Silver Nanocomposite Electrodes Pei-Tun Liao, Wan-Yi Lai and Wen-ya Lee; Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taiwan

Stretchable conductive electrodes are an essential component to transport electronic current without degradation, even under large deformation. To achieve reasonable electronic properties in soft electronics, it is necessary to transmit electronic signals through stretchable conductive materials to avoid loss of signal under strains. However, it is challenging to obtain stretchable electrodes with high stretchability (100%) and conductivity (>10^6 S/cm). Silver nanowire (AgNWs) is a great one-dimension candidate for a stretchable and conductive electrode due to their excellent electrical characteristics. The purpose of our research is to prepare a stretchable silver nanocomposite using AgNWs by modifying silver nanowires with polyisoprene via thiol-ene chemistry. The nanocomposite decreases the contact resistance to achieve high conductivity and low sheet resistance. Furthermore, Adding polyisoprene can effectively improve stretchability. The photo-cured stretchable electrodes show great solvent resistance under various organic solvents. The great solvent resistance makes the stretchable electrode patternable. Currently, our stretchable electrode patterning has been successfully developed to below 20 μm, and the sheet resistance can be controlled below 0.8 Ω sq^{-1} under 100% strain. This work successfully demonstrates photo-patternable stretchable electrodes with low resistance and high stretchability.

5:00 PM EL18.09.10
Morphological Investigation of High Performance Bulk Heterojunction Active Layer to Probe the Origin of Device Instability Haoyu Zhao, Nathaniel L. Prine, Guorong Ma, Andrew Bates and Xiaodan Gu; The University of Southern Mississippi, United States

The performance of conjugated polymer-based organic photovoltaic device relies on the bulk heterojunction morphology of the electron donor and acceptor blend. The morphology including the average domain size, crystallinity, and phase purity of donor/acceptor blend determines the device performance. Although the power conversion efficiency (PCE) is above 18%, the origin of the instable performance over longer times remains poorly understood. In this work, we conducted multiple characterization techniques to explore the dynamic, temperature-dependent morphology of a state-of-the-art donor polymer (PM6) blended with a non-fullerene small-molecule acceptor (Y6). Particularly, we focused on the thermal analysis of the donor and acceptor using fast scanning calorimetry (Flash DSC) to understand the crystallization kinetics. Combined with the assistance of atomic-force microscopy paired with infrared microscopy (AFM-IR) and X-ray scattering, we concluded the origin of PCE loss can be attributed to the severe phase separation caused by acceptor diffusional crystallization. The pure Y6 showed crystallization dominates the process at 110 °C. And the isothermal crystallization of donor further accelerated for Y6 in the blend. As the blend is maintained at elevated temperatures, the crystallization of the Y6 domains was observed to induce phase separation with donors, as evidenced by the AFM-IR characterizations. Finally, we systematically examined the impacts of operational conditions (temperature and time) on the blend film morphology, which could suggest a pathway to suppress the crystallization to improve the device stability in future.

5:00 PM EL18.09.11
Chemical Activation of Commodity Plastics for Patterned Deposition of Flexible Electronics Jessica Wagner[1], Jared Fletcher[1] and Stephen A. Morin[1,2,2]; [1]University of Nebraska - Lincoln, United States; [2]University of Nebraska–Lincoln, United States

A low-cost and scalable procedure for the deposition of electronic materials onto thin polymeric substrates would be useful to the fabrication of flexible circuits. Traditional fabrication methods such as photolithography and laser-direct structuring are expensive, require long processing steps, and are not readily scalable to 3-dimensional components or flexible polymeric substrates. While electroless deposition is an ideal method for bridging the gap from 2D to 3D fabrication, metal delamination of the deposited films remains a significant problem. We have developed a general approach to increase the adhesion of metal films to commodity plastic substrates using a metal-chelating polymer, polyethyleneimine, in conjunction with patterned electroless deposition. When combined with flexible microfluidic reactors for deposition of different metals and materials (conducting, semi-conducting, etc.), a procedure (microfluidic-directed material deposition or mDMD) for entirely solution-based manufacturing of flexible and non-planar electronics can be realized. We demonstrated the durability of these traces using adhesion tests and mechanical deformations and illustrated the functionality of these metals in simple electronic circuits and electrochemical devices. The ability to deposit different types of materials following the reported procedure allows for the fabrication of flexible circuits with a diversity of functionalities (e.g., optoelectronic, potentiometric, etc). mDMD is compatible with a diverse array of plastics (e.g., PC, PET, PP), metals (e.g., copper, nickel, silver, and gold), and, through the use of chemical bath deposition procedures, semiconductors (e.g., metal chalcogenides and oxides) with properties applicable to flexible electronics, sensors, and electrochemical devices.

5:00 PM EL18.09.12
Flexible Adhesive-based Multilayer Antenna Using Press Patterning at Room Temperature for Electronic Applications Min-Seok Jeon[1], Jae-Hoon Lee[1], Jeong-Ryul Kim[2] and Duk-Hee Kim[3]; [1]Korea Testing Laboratory, Korea (the Republic of); [2]ICH Co., Ltd., Korea (the Republic of); [3]APC Co., Ltd., Korea (the Republic of)

Flexible electronics have attracted significant research attention due to their distinct features and emerging applications in numerous fields such as, flexible displays, implantable sensors, wearable medical devices, and energy storage systems, among other applications. One of the current and future challenges in electronics is to develop suitable multifunctional materials which can address simultaneously several parameters such as flexibility, lightweight, conductivity, environmental impact, and production cost. Adhesive polymer electronics (multiply patterned laminates without lithography and etching process) forms a new and high-potential technological field, which may pave a way for many novel electronic applications and products. In this presentation, a new distinct fabrication method was applied to make flexible and adhesive patterned multilayer antenna using just press patterning at room temperature. This process needs no etching steps and gives no environmental wastes. In addition, several process steps can be reduced and, therefore, cost competitiveness can be improved very much. Overall structure is composed of multi polyimide film, metal film, adhesive and liner film. The patterned structure can be made only pressing at room temperature. Dielectric properties of the antenna were measured in the range of 6 to 10GHz. Precise cross-sectional structures, interfaces, and defects were analyzed by SEM, EDX, and ion beam polishing. Mechanical and thermal durability tests were performed to demonstrate possibility to several fields of wearable electronic applications. Failure analysis was compared between test antenna with different structures on the basis of physics-of-failure. Overall reliability of the antennas was evaluated by the results of durability test and failure analysis.

[Acknowledgement]
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5:00 PM EL18.09.13
Direct Metal Printing of 3D Electronic Components and Circuits Using MetalJet Negar Gilani, Nesma Aboulkhair, Marco Simonelli, Mark East and Richard Hague; University of Nottingham, United Kingdom

Printed electronics have been the focus of increasing attention in the past decade due to their wide range of diverse applications, including soft robotics, actuators, wearable electronics, biomedical applications, and human-machine interfaces. Considerable research has been devoted to nanoparticle-based inkjet printing as a large-scale fabrication method of such devices, and tremendous advances have been obtained. However, there are still process-related challenges to be addressed, including nozzle clogging, ink formulation, nanoparticle synthesis, drying, and sintering of the nanoparticles. Furthermore, higher electrical resistivity than the corresponding bulk metal, poor adhesion of printed traces to the substrate, and the coffee ring effect are common quality-related challenges associated with the process.

Drop-on-demand Metal Jetting (DoD-MJ is an emerging Additive Manufacturing technology that has the potential to fabricate 3D electronic components and flexible electronics whilst overcoming the challenges mentioned above. The metal jetting approach consists of dispensing and depositing individually-controlled droplets of molten metal onto a substrate at precise locations. DoD-MJ processes are classified based on the droplet generation actuation method. MagnetoHydroDynamic (MHD) actuators are the most advanced devices to date that have overcome the challenges of producing high-temperature droplets at high rates. One of the main advantages of DoD-MJ over inkjet printing is its simplified fabrication approach. This simplicity is granted by a wide availability of potential feedstock material, no residual impurities, and the elimination of the need for pre-processing and post-print processing.

MetalJet, the MHD-based system used in this study, has the capacity to produce molten micro-droplets (60–90 µm) at temperatures up to 2000 °C to form single and multi-material objects at frequencies up to 2 kHz. The work presented here reports that interface formation at the droplet substrate during the deposition of molten droplets embeds them into the substrate to obtain an acceptable level of adhesion. Moreover, strong metallurgical droplet-droplet bonding was obtained through remelting the interfaces. Consequently, the electrical resistivity of printed structures was comparable to that of the corresponding bulk metal. Overall, the work paves the way for the fabrication of next-generation electronics.

5:00 PM EL18.09.14
A Generalized Model for Thin Film Transistors on a Substrate of Arbitrary Geometry Shirsopratim Chattopadhyay[1] and John Labram[2]; [1]Oregon State University, United States; [2]University College London, United Kingdom

Flexible electronics is an emerging and rapidly blossoming technology that makes cheap, compact, light-weight devices with exotic form factors realizable. It's expected to usher in a paradigm shift in diverse real-world applications of paramount importance, from medical technology to robotics to industrial Internet of Things (IoT).
While a lot of research has been done on developing novel materials and manufacturing techniques for these devices, a comprehensive mathematical model to describe their behavior remains elusive. With the traditional Gradual Channel Approximation used for linear, flat thin film transistors (TFTs) still being the standard approach. This approximation will be invalid when the curvature of these devices becomes comparable to device dimensions. It's vital to develop the mathematics that encapsulates this behavior before flexible electronics becomes fully commercial, as it forms the building block for further integrated circuit (IC) design with flexible TFTs.
While there have been works on modelling the effect of physical stress due to deformation, such as those arising from bending and shear, on the electrical characteristics of TFTs, the effect of geometry itself is something seldom considered. In this work, we borrow on ideas from Differential Geometry and Point Set Topology to analytically develop a mathematical model that would predict electrical characteristics given the device geometry. We show that our model accurately predicts the expected behavior for a traditional linear TFT, as well as those on the surface of a cylinder and a sphere. It's expected that the proposed model will guide future design and fabrication of ultrathin film chips and circuits. For flexible electronics to be commercially viable, it must be predictable under all circumstances.

5:00 PM EL18.09.15
Extraordinary Mechanical Properties of Inorganic Double Helical van der Waals Crystal Nan Wang, Jiangbin Wu, Hefei Liu, Xinghao Huang, Hung-Yu Chen, Jiahui Ma, Hangbo Zhao and Han Wang; University of Southern California, United States

Tin indium phosphate (SnIP) is a quasi-one-dimensional inorganic double helical van der Waals semiconductor consisting of two atomic helical chains twining around each other along the axis of the helix at the atomic scale. Here, we experimentally discovered the extraordinary mechanical properties of SnIP. Confirmed through both nanomechanical bending measurements and the Brillouin scattering spectroscopy, this unique double helical structure possesses the smallest Young's modulus (~13.6 GPa) among any known stable inorganic materials and is even comparable with many polymers. Furthermore, the relatively easy slippage between neighboring double helices coupled through van der Waals interactions resulted in a surprisingly large elastic (>27%) and plastic (>60%) bending strain, conferring SnIP the highest flexibility and deformability among all known semiconducting materials. This discovery represents a major breakthrough in materials science that not only sets new records for key mechanical properties of inorganic materials, but also advances the understanding of this unique class of double helical van der Waals crystals with application potentials in a broad range of nanomechanics and nanoelectronics disciplines.

5:00 PM EL18.09.16
Iontronic Pressure Sensor Based on Modulation of Electrical-Double-Layer Kota Inoue[1], Kazumoto Miwa[2], Sunao Shimizu[2], Shimpei Ono[2] and Hiroki Ota[1]; [1]Yokohama National University, Japan; [2]Central Research Institute of Electric Power Industry, Japan

An iontronic pressure sensor that uses modulation of electrical charges in the electrical-double-layer(EDL) due to pressure was demonstrated in this study. In recent years, tactile sensors using various pressure-sensitive materials such as piezoresistive, capacitive, piezoelectric, and friction types have been developed to detect a wide range of pressures for applications in artificial joints, robots, and wearable devices. Among pressure sensors, the capacitive type is being commercialized at the product level as touch screens and biometric authentication in smartphones and PCs, taking advantage of its features such as high sensitivity, low power consumption, and fast response time. In particular, capacitive pressure sensors using EDLs of iontronic thin films are capable of excellent sensing over a wide range and with high resolution. Ionic liquids (ILs), which are commonly used as materials for iontronic thin films, have high electrical conductivity, electrochemical stability, and thermal stability. Gelation of ILs in the liquid state to form ionotropic thin films provides structural stability and reduces the risk of ILs leakage. The principle of conventional iontronics based pressure sensors is that the capacitance of the EDL is directly proportional to the contact area between electrodes and surfaces of the iontronic thin film. In other words, it is necessary for external pressure to cause mechanical deformation of the iontronic thin film in order for sensing. Therefore, to use iontronic thin films as pressure sensitive materials, microfabrication and fine patterning processes are required. Even as a pressure sensor, having a fine pattern remains a challenge in terms of structural stability.
In this study, we confirm that EDLs at the interface between iontronic thin films composed of ionic liquids and polymers and metal electrodes are modulated by the physical addition of pressure. This phenomenon is not due to mechanical deformation of the ionic liquid thin film, but to an increase in the charge of the EDL due to the application of pressure. Using this mechanism, IL-based iontronic thin films can function as deformation-independent pressure sensors. In this study, IL gel thin films fabricated without patterning were used as iontronic thin films. In addition, the signal was amplified by an electrical-double-layer transistor (EDLT). Iontronic thin film was applied as the gate insulating layer of the EDLT and the EDL modulation due to pressure was output as modulation of current value. Organic semiconductor material was selected as the channel material of the EDLT, and at low voltage the channel can be controlled by EDLs generated by IL gels. The use of a transistor as a signal amplifier also facilitated the use of a pressure sensor matrix. The pressure sensor matrix is important for pressure mapping, and this device is useful for applications in artificial joints, robots, and wearable devices. This research uses the new concept of ion modulation in EDLs, which expands the possibilities of devices using EDLs.

5:00 PM EL18.09.18
Lubricant-Infused Gravure Printing Plate for Conductive Pattern Printing Hsuan-Chin Lu and Ying-Chih Liao; National Taiwan University, Taiwan

The development of printing technologies to fabricate conductive patterns on flexible and stretchable substrates has gained much attention in recent years due to the pursuit of high-performance healthcare and communication applications. Among various printing methods, gravure printing is a high-speed, low-cost printing method capable of fabricating high-resolution patterns on the scale of microns. The successful printing of high-quality features depends heavily on the ink transfer ratio from the printing plate to the target substrate. In our previous study, the mechanisms of liquid transfer were investigated and we demonstrated that a lubricant-infused surface can provide fast contact line slippage to enable total liquid transfer between flat plates. In this study, PDMS-based gravure printing plates with porous microstructures are fabricated, which can help retain lubricating oils and improve the longevity of the lubricating layer by oil effusion to the surface. Different methods are utilized to fabricate the porous microstructures, and the effects of pore size, porosity and morphology on the transfer ratio are investigated. The mechanical properties and durability of the printing plates are also investigated to prove the applicability of using this method for practical applications. Finally, modified conductive ink is used to print conductive patterns onto a polymer substrate to demonstrate the potential for creating flexible or stretchable electronics.

5:00 PM EL18.09.19
Generation of Additional Logic States in Molecular-Switch Embedded Anti-Ambipolar Transistor for Realizing Multi-Valued Logic System Chan So, Dae Sung Chung, Seong Hoon Yu and Syed Zahid Hassan; Postech, Korea (the Republic of)

Developing logic circuit systems that have high data throughput levels and mechanical flexibility is becoming more and more important with expanding market of AI and autonomous driving. It is known that the organic thin film transistor can meet the above conditions. However, organic thin film transistors have weaknesses in high-temperature processes and fine patterning. Therefore, there is a limit to increasing the speed of data process by improving the degree of integration. As an alternative to solving this problem, a logic (MVL) system has been proposed. The traditional logic inverter system can perform 2^n processing operations, but the triangular logic inverter system can process 3^n processing operations, which is about 160% more efficient than the traditional logic inverter.

The mechanism of multi-valued logic system is described below. If n-type semiconductor and p-type semiconductor are in lateral contact, the current graph will show the effects like 'union' in the sets. On the other hand, if two semiconductors contact in vertical way, the current graph will show the effects of 'intersection'. Interestingly, in the case of one semiconductor gets over the other at lateral contact to create both lateral and vertical contacts, both effects happen and an additional middle logic state could be generated. This heterojunction, which is called anti-ambipolar, changes the sign of the slope of the drain electrode current value in a specific voltage range. However, as we are planning to make higher level of base, you need a very complex structure. Therefore, a new strategy is needed to implement a high-base logic system. Accordingly, we tried to introduce molecular switch to develop MVL circuits.

As a result, diarylethene, a molecular switch that can change its structure by light, was able to successfully decrease the current level of embedded organic polymer. In the electric field condition, charge carriers move from one electrode to the other. When UV light is irradiated to DAE, the HOMO level of DAE rises as the molecule becomes closed form. Then UV irradiation causes them to be trapped in the HOMO of DAE, which leads to the reduction of overall current level and make additional middle logic state. The reduced current and the shift of NTC range allow us to distinguish different states.

In this work, We demonstrated anti-ambipolar transistor(AAT) and MVL system that used it. Most of DAEs were successfully co-deposited with organic semi-conductor(DNTT). It is believed that molecular switch that has less sterically hindered characteristics obtained better drain current and mobility due to securing free volume for molecular switching.

5:00 PM EL18.09.20
Strain Insensitive Pressure Sensor Integrated on Selectively Photo-crosslinkable Substrate Hyon-Gyu Park, Hayeong Park, Minsung Kim and Joon Hak Oh; Seoul National University, Korea (the Republic of)

Soft, stretchable, and wearable electronic devices have been studied for their potential use in various applications that cannot be achieved with conventional rigid devices. Stretchable electronics, as an advanced technology for flexible devices, have great potential to be used in various wearable devices and sensors, regarding human skins or tissue's stretchable property. However, it is still insufficient for commercial use due to lack of durability and performance.
A common method of manufacturing stretchable electronic devices is to design all constituent materials to be stretchable. Another approach is to design the substrate so that the strain is concentrated on the interconnects and strain-free or limited strain on the unit area. The former approach can provide high integration, but there is a limit to making all elements of a device stretchable. While stretchable substrates (SEBS or PDMS) can be stretched up to 100%, it is very challenging for other elements such as electrodes and active layers to be stretched along the substrate. Even an organic semiconductor that can be significantly stretchable than an inorganic material, it is not easy to withstand deformation of more than tens of %. The latter approach, "rigid island" structure allows the integration of existing rigid electronic components with-out deformation. In particular, the development of stretchable printed interconnects has made it possible to successfully integrate active electronic devices located on rigid polymer islands into stretchable devices.
Herein, we introduce a simple method to fabricate a photo-crosslinkable, transparent elastomer substrate for stretchable electronics and its application to physical sensors. Acrylate based substrate was formed with copolymers. With photo-initiator, acrylate functional group can be crosslinked by UV irradiation and by adjusting the amount of crosslinker, we could control its crosslinking density and modulus. The modulus of substrate increased to 8900%. Additional crosslinking provided 38000% higher modulus than that prior to UV irradiation. The substrate can be selectively crosslinked by exposure to UV light in order to form a rigid region using a patterned mask. Rigid island pattern shape and size can be designed without restraint owing to its simple crosslinking mechanism. 20 mm pattern of rigid/soft area pattern was stretched 100% to confirm its stretching property, rigid region was only stretched 30% while soft area was stretched 210%.
Rigid island structures with repetitive rigid-soft-rigid systems can facilitate the development of capacitive strain/pressure sensor by forming electrodes only on the rigid islands. Rigid island can work as a dielectric layer of the capacitor, sensor sensitivity to strain and pressure are dependent to modulus of the rigid island. We designed pressure insensitive strain sensor (PISS) and strain insensitive pressure sensor (SIPS) by this system. For SIPS, electrospun dielectric layer was introduced to increase pressure sensitivity while maintaining low strain sensitivity.

5:00 PM EL18.09.23
Solution Deposition and Photonic Curing of Hybrid Transparent Conducting Electrodes Robert T. Piper, Gary G. Turner, Justin C. Bonner, Weijie Xu and Julia Hsu; The University of Texas at Dallas, United States

Development is still needed to improve flexible transparent conductive electrodes (TCE), the starting point for many optoelectronic devices, such as LEDs, photovoltaics, and touch-sensitive screens, which are the backbones of many modern technologies. PET/ITO is a common TCE but is made with slow vacuum deposition and thermal annealing processes, which are not compatible with high-speed roll-to-roll (R2R) manufacturing. Because of the limited thermal budget, ITO films must be thicker on PET than on glass substrates to maintain similar sheet resistance (R_{sh}), resulting in lower ITO transmittance. Many solution deposition techniques can already achieve high R2R web speeds > 10 m/min. However, post-deposition thermal annealing of sol-gel TCE precursors requires high temperature (> 300°C) for a long time (> 30 min), leading to either a reduction in R2R web speed or implementation of long, high-energy-consuming ovens. In addition, plastics have higher coefficients of thermal expansion than oxides, resulting in mechanical failures when thermally annealed at high temperatures. A promising alternative to thermal annealing that is R2R compatible is photonic curing. Photonic curing is a photoirradiation process during which a xenon flash lamp emits high-intensity, broadband (200 – 1000 nm) light upon a sample in discreet pulses lasting micro or milliseconds. Light impinging on the sample is absorbed by the film and converted into heat depending on its optical absorption, which drives material transformations: crystallization, phase change, or sol-gel conversion. Because photonic curing uses high-intensity, low-energy light to anneal materials, high-temperature processing can be performed on plastic substrates, which do not absorb a significant amount of light, without damaging them. Photonic curing requires simultaneous optimization of multiple parameters, which will be explored in this work: pulse voltage, pulse length, number of micro-pulses, duty cycle, number of pulses, repetition rate, and radiant exposure.

In this work, a hybrid TCE material is solution deposited and photonic cured on PET substrates. The hybrid TCE consists of a transparent conducting oxide made from sol-gel precursors and a metal network—silver nanowires (AgNW), metal grid traces (MG), or a combination of both. The metal network enhances electrical conductivity without sacrificing optical transmittance. AgNWs and MGs significantly affect the photonic curing process because they absorb light which leads to heating within the material stack. This additional light absorption may enhance the sol-gel oxide conversion during photonic curing. The conversion of the sol-gel metal oxide was tested using a weak acid etch. To evaluate the hybrid TCE performance, we measure sheet resistance (R_{sh}) and average optical transmittance from 400 to 700 nm (T_{avg}) to calculate the figure of merit (FOM) [1]. The preliminary results on spin-coated films show the best-performing hybrid TCE made by photonic curing AgNW and IZO composite films achieves $R_{sh} = 16 \pm 4$ Ω/sq, $T_{avg} = 78 \pm 2\%$, with a FOM

= 90 ± 14. This TCE already outperforms some commercially available PET/ITO products, which have FOM ranging from 24 to 110. To transition to R2R processing, we employ blade-coating to deposit the hybrid TCE materials. The blade-coating and photonic curing processes will be optimized together to produce high FOM hybrid TCE films. Finally, perovskite solar cell devices will be fabricated on these hybrid TCEs and compared to devices made on commercially available PET/ITO.

[1] A. Anand, M. M. Islam, R. Meitzner, U. S. Schubert, and H. Hoppe, *Adv. Energy Mater.*, vol. 11, no. 26, 2021, doi: 10.1002/aenm.202100875.

5:00 PM EL18.09.24
Low-Temperature Heat Treatment Schemes for Particle-Free Reactive Silver Inks Steven DiGregorio, Subbarao Raikar and Owen Hildreth; Colorado School of Mines, United States

Printed electronics afford greater flexibility, fewer processing steps, and less material waste over other electronic manufacturing techniques. Printed electronics often rely on particle-based metal inks that have the downside of high processing temperatures. Even low-temperature silver pastes require temperatures above 200 °C, making them incompatible with some polymers used in flexible electronics. Reactive inks are particle-free conductive inks that can achieve highly conductive metal layers at temperatures as low as 60 °C. Reactive inks contain metal complexes that reduce to metallic films upon printing. The underlying reduction mechanisms are crucial for designing high-performance inks but are not well understood for reactive inks with self-reducing functions. This work investigates the interplay between thermal and evaporative reduction mechanisms in self-reducing reactive silver inks to understand their impact on film morphology and electrical resistivity. We also investigate the bending durability of films with different morphologies to demonstrate the applicability of reactive inks for flexible electronics.

5:00 PM EL18.09.26
Mold-Free Fabrication of Highly Sensitive Pressure Sensors Using oCVD PEDOT and 3D Printed Microstructured Substrates Jinwook Baek, Mitesh Mylvaganan, Yujie Shan, Huachao Mao and Sunghwan Lee; Purdue University, United States

Recent advances in 3D printing have demonstrated splendid promises in next-generation high performance sensor applications due to freedom of design, cost-effectiveness, and rapid prototyping. In this work, we showcase a new manufacturing paradigm to exclude conventional mold-dependent manufacturing of pressure sensors, which requires a series of complex and expensive patterning processes such as mask aligning, photolithography, and etching. Our mold-free fabrication leverages high resolution 3D printed multiscale microstructures as substrate and a gas-phase conformal polymer coating technique to complete the mold-free sensing platform. Micropatterning through a cutting-edge 3D printer enables one to fabricate a non-trivial structure with complex geometry and customized shapes. The array of dome and spike structures with a controlled spike density was applied for a substrate, ensuring a high surface area. For uniform coating on the microstructured surface, oxidative chemical vapor deposition (oCVD) is leveraged to deposit a highly conformal and conductive electrode, poly(3,4-ethylenedioxythiophene) (PEDOT) at low temperature (< 120 °C). The fabricated pressure sensor reacts sensitively to various ranges of pressures depending on the density of the spike and shows high response ($I/I_0 > 10^4$) even pressures under 1 kPa. The mechanism of the high performance achieved was verified through the finite element analysis, which allowed us to identify a correlation between surface structure and sensor characteristics. Our unique findings are expected to be of significant relevance to the technology that requires higher sensing capability, scalability, and facile adjustment of sensor geometry in a cost-effective manufacturing manner.

5:00 PM EL18.09.27
Engineering Soft, Elastic and Conductive Polymers for Stretchable Electronics Using Ionic Compatibilization My Linh Le, Intanon Lapkriengkri, Cassidy Tran, Phong H. Nguyen, Rachel A. Segalman, Christopher M. Bates and Michael L. Chabinyc; University of California, Santa Barbara, United States

Designing a material that is soft, elastic and conductive for stretchable electronics has remained a major challenge due to the tradeoff between conductivity and mechanical flexibility caused by the high stiffness of conventional conductive materials. In this study, we show that ionic interactions provide an effective pathway to obtain materials with appreciable conductivity and flexibility, while also eliminating many synthetic and processing complications in commonly employed strategies. In particular, a conjugated polyelectrolyte (CPE) was blended with a bottlebrush polymeric ionic liquid (BPIL) whose side chains are oppositely charged. In this design, the CPE provides electrical conductivity, while the BPIL offers a super-soft elastomer matrix for mechanical flexibility. Due to the strong electrostatic attraction between the oppositely charged pendant side chains of the CPE and the BPIL, phase separation was effectively suppressed and the polymers formed a homogeneous blend. The resulting material has a Young's modulus of 100 kPa, lying well within the range of soft tissues moduli (25 kPa to 140MPa), and is highly stretchable with a tensile strain to break of 400% and an ultimate tensile strength of 800 kPa. Once electronically doped with a strong acid, this polymer blend has an electronic conductivity that was ~ 0.1 S/cm, a comparable value to that of as-cast commercial PEDOT:PSS. Lastly, the ionic interactions physically crosslinked the polymers, forming a network that strained elastically up to 40% strain without any added crosslinkers.

5:00 PM EL18.09.29
Flexible Hydrogen Sensors Based on Pd-decorated Graphene Microchannels with Low Power Consumption Yeonhoo Kim[1], Taehoon Kim[2], Tae Hyung Lee[2], Yong Seok Choi[2], Seungwoo Song[1], Ansoon Kim[1], Byung Hee Hong[2] and Ho Won Jang[2]; [1]Korea Research Institute of Standards and Science, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)

Hydrogen is a promising future energy source since it is clean, non-toxic, and renewable but explosive over a wide range, from 4 to 74 percent in ambient air. For this reason, the detection of hydrogen gas at an early stage is of great importance in varied research fields such as hydrogen storage systems, fuel cells, and water splitting. Although semiconducting metal oxides have been extensively explored for sensing applications, metal oxides are not suitable for flexible electronics. On the contrary, two-dimensional(2D) materials including graphene are promising alternatives to conventional sensing materials since they are entirely flexible and transparent. To modify the sensing characteristics of pristine 2D materials, various methods such as functionalization, composites, and noble metal decoration have been studied. Among the methods, noble metal decoration is one of the most facile methods to tune the sensing properties of 2D materials.

In this work, we decorated palladium nanoparticles on graphene microchannels with electron beam evaporation to enhance the hydrogen sensitivity of the graphene layers. As the graphene layers are patterned with microchannels, the self-heating effect is induced by current crowding in the narrow electrical path. The self-heating effect enables to detect hydrogen gas at room temperature, which lowers power consumption by not using external heaters. The apparent temperature of the microchannel is characterized by an infrared camera. The hydrogen sensors exhibit good linearity, high sensitivity, and selectivity in a wide range of hydrogen gas concentrations from 1 to 50 ppm. The theoretical detection limit is calculated to be ~241 ppb. Moreover, the flexible sensors show stable sensing performance under mechanical bending strain. The ultralow detection limit and stability of the sensors broaden the potential use of Pd-decorated graphene microchannels for next-generation flexible/wearable applications.

5:00 PM EL18.09.30

Mechanically Stable Flexible Organic Photovoltaics with Silver Nanomesh for Indoor Applications Jae Won Kim[1], Sung-il Chung[2] and Jin Young Kim[1]; [1]Ulsan National Institute of Science and Technology, Korea (the Republic of); [2]Korea Electrotechnology Research Institute, Korea (the Republic of)

Improved performance of flexible organic solar cells (FOSCs) was achieved by developing the performance of organic solar cells (OSCs). OSCs are promising candidates as energy sources for low-power supply systems such as the Internet of Things (IoT) under indoor lighting environments. To apply FOSCs to flexible or wearable applications, they must be mechanically stable. In this study, we fabricated FOSCs with silver nanomesh (AgNM) as the bottom transparent conductive electrode (TCE). Instead of ITO, AgNMs were prepared using three pitches of 25, 50, and 100 µm with a square pattern, using a polyethylene terephthalate (PET) substrate. Notably, the device using AgNMs with a pitch of 25 µm exhibited a power conversion efficiency (PCE) of 14.93% under 1 sun illumination and 17.91% under 1000 lux of LED light conditions. Flexible devices using AgNMs maintained over 92% of their initial PCE under 1 sun illumination (PCE decreased to 12.98% from 14.04%) and over 92% when tested under 1000 lux of LED light illumination (PCE decreased to 16.57% from 17.91%) after 1000 instances of bending. These results demonstrate the advantages of using AgNMs as an alternative TCE under both 1 sun and indoor lightning environments and are promising candidates for flexible applications.

5:00 PM EL18.09.31
Flexible Device Applicable High Mobility InGaZnO/polyimide Thin Film Transistor at Low Temperature Using Interfacial Defect Control Min Jung Kim[1], Hyunmin Hong[1], Shin Dong Yeob[2], Dong-Joon Yi[2], Na Young Choi[2], Si yeon Choi[2], Kwangsik Jeong[2] and Kwun-bum Chung[2]; [1]Dongguk university, Korea (the Republic of); [2]Dongguk University, Korea (the Republic of)

Polyimide (PI) is currently used in various fields, such as substrate, passivation, gate insulator (GI), because PI can be fabricated in the condition of low temperature (~ Room temperature), low cost, large area deposition. Many research have reported PI which has high dielectric (≥ 2) constant and withstand high temperatures (~ 300 °C). In the case of a device using a soft insulating film such as PI, the fabrication method is limited according to the characteristics of PI. In the case of organic thin film transistor (OTFT), in which PI is mainly used as a gate insulator, the carrier mobility of organic semiconductor films is strongly influenced by the crystallinity, molecular packing structures of the organic thin films and charge traps at the gate dielectric/semiconductor interface. Even if certain molecular organic semiconductors can form various molecular packing structures by changing film formation process, the OTFT fabrication has very low reproducibility. It is difficult to analyze and control the composition and defect states in the semiconductor/GI interface of OTFT compared to inorganic device, because polymer materials are mainly used. The operation of the TFT device is affected by a channel formation in the active/GI interface. The analysis of the grain boundary, crystallinity, and defect states in the interface must be supported to adjust the device characteristics according to the purpose. In this study, we suggest a low-temperature ($\leq$100 °C) fabrication method of high mobility (> 10 cm^2/Vs) oxide thin film transistors using 6FDA-MDA as a gate insulator with Al_2O_3 buffer layer and analysis of the qualitative/quantitative defect sites in the interface between PI and IGZO layer. Spectroscopic ellipsometry (SE) and x-ray photoelectron spectroscopy (XPS) are used to the analyze qualitative physical properties of the interface, for example fermi level in the band gap, thickness, composition. Quantitative defect state analysis according to the defect activation energy of the IGZO channel region was conducted by photo induced current transient spectroscopy (PICTS). The improvement of device reliability, especially for PBS seems to be due to the decrease in the deep level defect states in the interface, which is related to the trend of change in composition in the interface due to the application of buffer layer. We applied the optimum fabrication condition to the flexible device with parylene/PET substrate and conducted a bending test to confirm the stability of the device over 1000 times.

5:00 PM EL18.09.32
Fully Spray-Coated Triboelectric Devices for Ubiquitous Smart Objects Shujia Xu[1,1] and Wenzhuo Wu[1,1,2]; [1]Purdue University, United States; [2]Regenstrief Center for Healthcare Engineering, United States

Triboelectric nanogenerator (TENG) has been widely explored for self-powered wearable sensors. Progresses in novel material for high-output TENG have attracted tremendous attention. However, simultaneous consideration of materials system design and manufacturing process receive limited attention. Manufacture and encapsulation techniques feasible for large-scale fabrication in combination with functional materials systems need to be co-developed. Spray coating is an attractive method for large-scale deposition of ink-based materials. Here, we demonstrate fully sprayed TENG on ubiquitous surfaces using ink-based functional materials. Several functional inks compatible with spray coating are formulated to fabricate flexible TENGs for applications such as human pulse monitoring, human-machine interaction, and energy harvesting. Such flexible sensors could also be sprayed and integrated on arbitrary surfaces (e.g., living plants) for deriving ubiquitous smart objects.

5:00 PM EL18.09.33
Novel High-k Fluorocarbon Ultrathin Films for Passivation of Two-Dimensional Nanomaterials Anh V. Hoang, Viet Dongquoc, Phan Thi Kim Uyen, Jeong-A Jo and Eui-Tae Kim; Chungnam National University, Korea (the Republic of)

Two-dimensional (2D) layered materials, such as graphene and transition metal dichalcogenides, have been extensively studied beyond their applications of bulk Si and compound semiconductor technologies as potential semiconductor platforms. However, their excellent electrical performance, including the carrier mobility, are significantly degraded by molecular adsorption from the environment. High-k oxide dielectric capping layers, such as Al_2O_3 and HfO_2, have been applied to suppress Coulomb scattering by shielding the surface from ambient molecules and phonon dispersion, thereby, significantly enhancing the mobility of 2D field-effect transistors (FETs). However, the oxide films not only more often introduce interface trapping defects at the dielectric/2D interface, but also are brittle, so that they cannot be applicable in flexible devices. In this presentation, we report passivation effects of amorphous high-k fluorocarbon (FC) films on graphene FETs. The organic based FC films were deposited on metal-catalytic Si/SiO_2 substrates by using inductively coupled plasma chemical vapor deposition and were subsequently transferred on graphene FETs. Amorphous FC films with high k values more than 30 significantly improved the mobility of graphene FETs, surpassing the corresponding graphene FETs passivated by atomic- layer-deposited Al_2O_3 film. We will further discuss passivation effects of FC films, including long-term stability and density functional theory calculations.

Keywords: Amorphous fluorocarbon, gate dielectrics, graphene, field-effect transistors
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5:00 PM EL18.09.35
3D Printed Triboelectric Smart Skin Mo Lv, Shujia Xu and Wenzhuo Wu; Purdue University, United States

This research presents a novel electrical sensor device, namely 3D printed triboelectric smart skin. The mechanical energy harvesting device and sensor is demonstrated to be stretchable and wearable. Tribo-negative material Polydimethylsiloxane (PDMS) matrix is selected as the dielectric layer with embedded fluidic electrode carbon grease. Triboelectrication and electrical induction are exploited for sensing subtle movements such as heart pulse and large joint movements from human bodies. The device has been investigated through design optimization process with an enhanced mechanical performance. This work demonstrates the device's capability to monitor the human's health status by detecting the heart pulse from the wrist and neck respectively, as well as identifying speech patterns through detecting the vibrations from human voice cord.

5:00 PM EL18.09.36
Morphology Reversal of a Non-Fullerene Acceptor Via Surface Controlled Decal-Printing Technique for Efficient Photo-Conversion and Detection in Organic Optoelectronic Device Minsoo Kim, Dong Hwan Wang and Woongsik Jang; Chung-Ang Univ, Korea (the Republic of)

Recently, the dry film transfer process using polymer mold has been attracted by advanced technology to overcome the limitation of the conventional wet coating process such as spin or dip coating. To demonstrate the transfer process, the soft polymer mold as process mediator is key factor. Polydimethylsiloxane (PDMS) is widely introduced to transfer the thin films previously, but it is difficult to adopt in the organic solvent filed due to the poor chemical resistance. To alternate this, polyurethane acrylate (PUA) material is introduced having proper physical and chemical property to the organic solvent such as chlorobenzene (CB) which is extensively used in organic optoelectronic devices. In this study, a novel thin film transfer technique is highlighted, named decal-printing process, using the surface controlled PUA mediator by introduced hydrophilic 2-hydroxyethyl methacrylate (2-HEMA) as reactive diluent.[2] By controlling the adhesion of the mediator based-on wetting coefficient theory, the decal-printing process is successfully demonstrated by transferring the organic photoactive layer composed of the polymer donor, poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b′]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2-6-diyl)] (PTB7-Th) and narrow bandgap non-fullerene acceptor (NFA), 2,2′-[[4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b′]dithiophene-2,7-diyl]bis[[4-[(2-ethylhexyl)oxy]-5,2-thiophenediyl]methylidyne(5,6-difluoro-3-oxo-1H-indene-2,1(3H)-diylidene)]]bis[propanedinitrile] (IEICO-4F).[3] This process induces a sharp morphology of the thin film, prevents damage to the underlying layer by suppressing the solvent penetration because of this technique enable to dry-transfer process. Both photovoltaic cells and photodetectors prepared by the decal-printed photoactive layers containing fluorinated NFAs showed higher performance (power conversion efficiency = 10.69% and specific detectivity = 1.27×10^{12} A cm Hz$^{1/2}$ W^{-1}, respectively) than those of devices prepared by the conventional spin-coating process owing to morphology reversal and smoother interface that led to suppressed internal resistance and enhanced charge flow in normal structure. Thus, the reproducible decal-printing process using a customized elastomeric polymer mediator is an important thin film fomration technique for efficient next-generation organic optoelectronic materials.[4]

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5:00 PM EL18.09.37
Low Effective Modulus Buckled Crack-Based Sensor for Human Respiration Monitoring Gunhee Lee[1], Jingoo Lee[2], Taewi Kim[2], Inyong Park[1], Sang Bok Kim[1], Dae Hoon Park[1] and Bangwoo Han[1]; [1]Korea Institute of Machinery and Materials, Korea (the Republic of); [2]Ajou University, Korea (the Republic of)

Among the various wearable devices for monitoring various human bio-signals (e.g., human motion monitoring, health care monitoring) being developed, the strain sensor is one of the representatives means for measuring mechanical bio-signals. In order to effectively utilize the strain sensor as a wearable monitoring device, it should satisfy high sensitivity, long-term durability, fast response characteristics, and high flexibility. However, it remains a challenge to accurately detect deformations caused by small stresses with high sensitivity due to the stiffness of the sensor itself. In general, the strain sensor expresses the sensitivity as the magnitude of the signal change with respect to the strain. In the case of soft objects such as human skin, even if an ultra-sensitive strain sensor is used, it cannot detect the deformation properly because the deformation of the skin cannot deform the sensor if the sensor itself is too stiff. To solve this problem, strain sensors made of low-modulus materials can be used, but these generally have low sensitivity and high hysteresis, making accurate measurements difficult. Herein, we proposed a buckled crack-based sensor consisting of thin metal films and polymer-based substrates to deal with these abovementioned problems. The crack-based sensor with a buckling structure sensitively responds to skin deformation and has a strain range of up to 80%. The buckled crack-based sensor possesses high sensitivity (gauge factor (GF) ≈ 250), long-term stability (>10,000 cycles), and low mechanical stiffness during stretching. As the human health monitoring system application, the buckled crack-based sensor successfully demonstrated to measure human respiration rate and depth, as well as the volume of inhalation and exhalation.

5:00 PM EL18.09.38
Breathable Pixelated Stretchable Sensor for Profiling Respiration Air Flow Jaehyun Kim, Yebin Park, Wonjeong Suh, Dongbeom Kim and Unyong Jeong; Pohang University of Science and Technology, Korea (the Republic of)

Due to the air pollution and the pandemic outbreak, the need of quantitative pulmonary monitoring has been greatly increasing. Although a large number of deformable sensors have been developed for wearable healthcare, deformable sensors for monitoring the respiratory patterns have rarely been investigated. Herein, we introduce an air-permeable stretchable pixelated thin film pressure sensor that can be integrated on a commercial face mask. The sensor can provide 2D profiles of the air flow and pressure distribution during inhaling and exhaling. This study presents that a CNT-polymer coating layer deposited on the electrospun microfiber is viscoplastic. The localized viscoplastic piezoresistive patterns enable the strain-independent pressure sensing performance so that respiratory pressure distribution on the pixelated sensor can be quantitatively obtained without being affected by deformation of the sensor. The wearable sensor is expected to monitor temporary breathing disorders and help prediction of pulmonary diseases.

5:00 PM EL18.09.39
Oxygen Vacancy Concentration Controlled Sol-gel Processed Y_2O_3 Resistive Random Access Memory by Al Doping Process HaeIn Kim and Jaewon Jang; Kyungpook National University, Korea (the Republic of)

In this work, we investigated the effect of Al doping on the switching behavior of sol-gel processed Ag/Y_2O_3/ITO RRAM devices. High-quality pure metal oxide layers can be simply deposited via sol-gel process. Their chemical, structural, and electrical properties can be easily tuned by adjusting the precursor component ratio. Moreover, the liquid phase precursor solution can be used for large-area applications, such as in dip-coating, printing techniques, and spin-coating.
Too much oxygen vacancies in the insulating layers of RRAM devices may degrade nonvolatile memory characteristics and increase the leakage current, thereby reducing HRS/LRS ratio. To overcome this issue, we doped Y_2O_3 layer with Al and observed the change of memory characteristics while adjusting Al doping concentration. Undoped RRAM devices exhibited relatively poor endurance characteristics of approximately 30 switching cycles with a small resistive window (~10). But, 50 % Al-doped RRAM devices showed more than 200 switching cycles with a decent resistive window (>10^2). In addition, it was confirmed that as the doping concentration of Al increased, the oxygen vacancy ratio decreased and the lattice oxygen ratio increased in the XPS measurement. These results confirm that appropriate concentration of Al doping can reduce excessive oxygen vacancies and thus improve the nonvolatile memory characteristics of Y_2O_3-based RRAM devices.

5:00 PM EL18.09.40

Crosslinking Organic–Inorganic Hybrid Dielectric with Azide-functionalized Ligand for High-Performance Solution-Processed Oxide Thin Film Transistors Juhyeok Lee, Syed Zahid Hassan, Sangjun Lee, Hye Ryun Sim and Dae Sung Chung; Pohang University of Science and Technology (POSTECH), Korea (the Republic of)

Owing to the global development in IoT technology, interest in metal-oxide semiconductor-based circuits with low standby power consumption, particularly in thin-film transistor (TFT) materials capable of low-cost solution processing, has been rapidly increasing. Notably, most of the high electron mobility oxide TFTs were based on high-*k* inorganic gate dielectrics. Compared with conventional SiO_2, high-*k* oxides such as HfO_2, ZrO_2, and Al_2O_3 are ideal candidates for realizing a high-capacitance dielectric layer capable of low-voltage driving and high density of charge accumulation. However, these high-k inorganic dielectric layers are hindered by 1) expensive deposition equipment and high process temperature for vacuum deposition, and 2) imperfect inorganic purity and porous morphology for solution deposition. Therefore, the development of a solution-processed high-*k* dielectric layer with a high dielectric strength is urgently required. A possible strategy to strengthen the dielectric properties of solution-processed high-*k* oxides is to realize an organic-inorganic hybrid dielectric layer, which typically comprises nanocomposites of polymer and high-*k* oxide nanoparticles (NPs) combining high permittivity of the inorganic NPs and high breakdown strength, mechanical flexibility, and easy processability of the polymer dielectrics. However, existing hybrid dielectric layers have not shown this synergistic effect and yielded only marginal performances, particularly for oxide TFTs.
The aforementioned synergetic effects can be achieved only when the complementary organic and inorganic constituents are well mixed. In reality, owing to the different surface energies of organic and inorganic inclusions, the thin-film morphology of hybrid dielectrics often has the limitations of air voids and low thin-film density, thereby resulting in a high leakage current and consequently a low on/off ratio of the resulting TFT. Furthermore, owing to the thermodynamic instability of the mixed binary phase, the hybrid dielectric layer can lack long-term operational stability. Therefore, it is challenging to simultaneously realize a high-*k* and high dielectric strength from a hybrid dielectric layer.
In this study, we attempted to achieve an organic–inorganic hybrid dielectric layer with a covalently networked morphology between organic and inorganic inclusions for high-performance solution-processed oxide TFTs. We propose a method for chemically crosslinking zirconia NPs and PMMA with functionalized azide ligands, which show higher crosslinking efficiency with a minimized amount. However, simply mixing azide molecules with ZrO_2 NPs and PMMA cannot guarantee crosslinking between inorganic and organic phases; nitrene generated from azide can react with alkyl CH or π-conjugated aromatic groups; therefore, crosslinking is limited only between PMMAs and not between the ZrO_2 NPs and PMMA. Therefore, we newly synthesized azide-functionalized acetylacetonate, functioning as a 1) ligand of ZrO_2 NP in post sol-gel synthesis and 2) crosslinking agent between ZrO_2 NP and PMMA. From the optimized processing conditions, we obtained an excellent dielectric strength of over 4.0 MV cm^{-1}, a high-*k* of ~14, and a low surface energy of 38 mN m^{-1}. We demonstrated the fabrication of exceptionally high-performance, hysteresis-free n-type solution-processed oxide TFTs comprising an In_2O_3/ZnO double layer as an active channel with an electron mobility of over 50 $cm^2\ V^{-1}\ s^{-1}$, on/off ratio of ~10^7, subthreshold swing of 108 mV dec^{-1}, and outstanding bias stability. From temperature-dependent *I–V* analyses combined with charge transport mechanism analyses, we demonstrated that the proposed hybrid dielectric layer provides percolation-limited charge transport for the In_2O_3/ZnO double layer under field-effect conditions.

5:00 PM EL18.09.42
The Effect of Thickness and Oxygen Vacancies on the Performance of Sol-Gel Based Y_2O_3 RRAM Kyoungdu Kim and Jaewon Jang; School of Electronics and Electrical Engineering, Korea (the Republic of)

It is widely known that the admirably pure materials such as metal oxide can be easily obtained by solution-gelation (sol-gel) method. Also, it is remarkable that we are readily able to manufacture the metal oxide-based devices and measure their characteristics simply using several steps. Moreover, using water-based metal-oxide precursors such as an ink is beneficial for mass-production desired in the industry due to the high throughput, low-cost manufacturing, and simple process. Also, these inks can be used for a number of techniques such as direct writing printing (non-contact), transfer printing (direct-contact), inkjet printing, and aerosol-jet and spray printing.
In this experiment, a solution-gelation (sol-gel) processed Y_2O_3 resistive random-access memory (RRAM) devices which showed bipolar characteristics were fabricated. The chemical, structural, and electrical characteristics of the sol-gel based RRAM devices were studied as the liquid-based precursor concentration (0.05 M, 0.2 M, 0.6 M) changed. The Y_2O_3 thickness grow thicker proportionally as the concentration increased. Furthermore, the proportion of oxygen vacancies in Y_2O_3 oxide escalated. The devices which contained minimum oxygen vacancy concentration did not showed bipolar RRAM electrical characteristic. Moreover, the devices with the thickest Y_2O_3 layer exhibited weak resistive switching performance. Among them, the 37 nm thickness of Y_2O_3 layer was an optimal in terms of resistive random access memory properties with low SET voltage (less than 1.5 V) and RESET voltage (-15.0 V). Additionally, the devices presented the longest retention (over 10^3 s), endurance (over 10^2 cycles), and highest ON/OFF ratio (over 10^4).

5:00 PM EL18.09.43
Improved Positive Bias Illumination Stability of Sol-gel Processed SnO_2 Thin-Film Transistor by Depositing Ultra-thin Al Layers Taehun Lee and Jaewon Jang; Kyungpook National University, Korea (the Republic of)

We demonstrate an ultra-thin aluminum layer deposited sol-gel processed SnO_2 thin-film transistors (TFTs) showing high stability performance under bias stress condition. The sol-gel process, one of the printing techniques, is a useful method for depositing metal oxide materials having a high film quality and purity. The properties of deposited film can be simply controlled by adjusting the concentration or other variables of precursor. The advantages of this process allows fabricating metal-oxide layer in large-area applications. Metal Oxide TFTs have gradually alternated silicon based TFTs due to their high field effect electron mobility, simple fabrication process and transparency. Metal Oxide TFTs, Unfortunately, contain electrical instability problems because of oxygen vacancies and defects that are the origin of trap formation. To solve this problem, we deposited an ultra-thin aluminum layer on the active layer of SnO_2 TFTs. In this experiment, we first fabricated pure SnO_2 TFTs via sol-gel process. Then aluminum was thermally evaporated on the prepared device followed by an annealing process at 300°C for 20 minutes. Under the positive bias illumination stress, pure SnO_2 TFTs have a mobility change from 6.27 cm^2/Vs to 5.91 cm^2/Vs and +6.51 V threshold voltage shift. Meanwhile, SnO_2 TFTs with Al deposited layer show the mobility change from 6.03 cm^2/Vs to 5.51 cm^2/Vs and +1.47 V threshold voltage difference. The results reveal that the deposited aluminum layer clearly advanced the positive bias illumination stability. We expect that the ultra-thin aluminum layered SnO_2 TFTs are an excellent candidate for high stability application in transparent electronics.

5:00 PM EL18.09.44
Effect of Photoinitiator Types and Concentrations on the Photocrossliking Density in Acrylate-based UV-curable Inks Bo-Young Kim[1], Subin Jo[1], Jihoon Kim[2], Seong Dae Park[1], Myong Jae Yoo[1] and Hyunseung Yang[1]; [1]Korea Electronics Technology Institute, Korea (the Republic of); [2]Kongju National University, Korea (the Republic of)

The acrylic resin has excellent mechanical and optical properties because it is simple to control the optical properties due to the molecular structure and forms 3-dimensional network structures after photocuring. In addition, the photocuring process has advantages of reducing process time because the curing time is shorter than thermal curing. Recently, the direct printing method using acrylate inks has been applied to manufacturing the printed circuit board for electric devices. [K1] After the manufacturing of circuit using acrylic ink, the chemical process such as etching is performed; for this reason, adhesion properties between ink layer and substrate become a very important factor in manufacturing the printed circuit board. In the case of acrylate inks, the crosslinking density is determined by the type and amount the photoinitiators, the contents of the monomer and oligomer, the UV irradiation time and intensity. In this study, acrylate inks are prepared by varying the type and amount of the photoinitiators, the photo curing behavior and the adhesion properties of acrylate inks[K2] . We confirmed that the photocrosslinking density of the acrylic ink increased as the photoinitiator content increased, also increased the adhesion to the substrate. Finally, acrylic inks with excellent adhesion and etching and stripping was prepared.

5:00 PM EL18.09.45
Intrinsically Stretchable Semiconductor Metallization via Physical Vapor Deposition Method for Skin-Like Electronics MinWoo Jeong[1], Minhyouk Kim[1], Jun Su Kim[1], Tae Uk Nam[1], Ngoc Thanh Phuong Vo[1], Lihua Jin[2], Tae Il Lee[3] and Jin Young Oh[1]; [1]Kyung Hee University, Korea (the Republic of); [2]University of California, Los Angeles, United States; [3]Gachon University, Korea (the Republic of)

Despite the recent application of metallization for stretchable organic thin-film transistor (OTFT), it is challenging in terms of crack-based, limited material and excessive deformation of target materials. Herein, we report a mechanically robust and intrinsically stretchable metallization on an stretchable semiconductor film based on metal-semiconductor intermixing. We deposited noble metals (Ag, Au and Cu) on stretchable semiconductor film and found that vaporized silver forms most continuous intermixing layer during thermal evaporation among three noble metals because of its high diffusivity. The Ag metallized film has a high conductivity (>10^4 S/cm) even under 100% strain stretching and durability that maintains its conductivity without delamination even after 10,000 stretching cycles at 100% strain and several adhesive-tape tests. Furthermore, a native silver oxide (Ag_xO) layer was formed on the interface between stretchable semiconductor film and metallized silver layer to facilitate efficient hole injection and transport, which transcends previously reported stretchable electrodes for OTFTs.

5:00 PM EL18.09.46
Fabrication of Inkjet Printed Tunable BST/P(VDF-TrFE) Dielectrics for Flexible Varactors Tim P. Mach and Joachim R. Binder; Karlsruhe Institute of Technology, Germany

Printed electronics are gaining more attention due to their ability to produce electrical components. For wireless communication, the high-frequency range plays an important role, which makes flexible components such as varactors interesting. Here, the ceramic or polymer dielectric is responsible for the dielectric properties. However, as both come with their own drawbacks, ceramic-polymer composites can be used to combine the excellent dielectric characteristics of ceramics and the easy processibility and flexibility of polymers. Furthermore, to obtain flexible varactors, inkjet printing offers a well-established method for the preparation in a fast and precise manner.
In previous works, an inkjet printed capacitor system consisting of (Ba,Sr)TiO3)/PMMA has already been successfully implemented. However, for varactors, tunability can be achieved in a BST/P(VDF-TrFE) system with the introduction of ferroelectric PVDF based polymers. Herein, printable inks were developed with varying ratio between BST and P(VDF-TrFE) to achieve high tunability and low dielectric losses. Through rheological property and drying temperature adjustments, the so-called coffee stain effect can be prevented. Therefore, thin layers can be realized and characterized on their dielectric properties.

5:00 PM EL18.09.48
Ultrafast, Autonomous Self-healable Electronic Skin with Mechanosensitive Ion Dynamics Elvis K. Boahen[1], Baohai Pan[2], Hyukmin Kweon[1], Joo Sung Kim[1], Hanbin Choi[1], Zhengyang Kong[1], Dong Jun Kim[1], Jin Zhu[3], Wu Bin Ying[1,3], Kyung-Jin Lee[2] and Do Hwan Kim[1]; [1]Hanyang University, Korea (the Republic of); [2]Chungnam National University, Korea (the Republic of); [3]Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

The self-healing properties and mechanosensing capabilities of the human skin has inspired the designs of various self-healing iontronic sensors that respond to pressure, strain, and torsion. Electronic skins based on iontronic materials can be utilized in wide range of applications including wearable technologies, human–machine interfaces, prosthetics, and soft robotics owing to their high noise immunity, exceptional spatial resolution, and excellent response to both static and dynamic stimuli. Conventionally, due to the intrinsic softness of such iontronic materials, they are vulnerable to unexpected mechanical damage, which leads to broken functionalities and limited device longevity. Moreover, the iontronic sensing mechanism most often generates a high initial capacitance due to the limited control of mobile ion dynamics, which results in poor sensitivity. To enhance the control of ion dynamics, previous studies have employed inorganic–based heterogeneous systems to realize ion confinement effect, which resulted in tremendously enhanced device sensitivity. However, the design of such heterogeneous systems can hardly achieve autonomously superior self-healing properties owing to the restricted mobility of polymer chains caused by the slow–moving nanomaterials attached to the polymer. Therefore, designing iontronic systems with simultaneous superior self-healing properties and effective control of ion dynamics, is extremely challenging.
Here, we develop a Cl-functionalized iontronic pressure sensitive material (CLiPS) via the introduction of Cl-functionalized groups (Cl groups) into a polyurethane (PU) matrix, which exhibits not only excellent autonomous self-healing properties but also mechanosensitive ion trap and release mechanism. The design concept involves strategic selection of high chain mobility isophorone diisocyanate and dynamic disulfide bonds to construct the backbone of the PU structure, which are key factors in achieving autonomous self-healing properties of both active matrix and electrodes at room temperature. In addition, with the inclusion of the ionic liquid, a trap and release mechanism is established owing to the ion-dipole interactions between the Cl groups and the ion pairs. On the basis of this unique design approach, we achieved an ultrafast self-healing speed (4.3 µm/min at 25 °C), a high self-healing efficiency (91% within 60 min), and an excellent pressure sensitivity (7.36 kPa^{-1}). Our CLiPS-based device functioned as a pressure-induced tactile sensor to modulate LED brightness, which validates its capability for applications in next-generation wearable technologies and smarter human-machine interfaces.

5:00 PM EL18.09.49
Eco-friendly Transparent Flexible Heater with Metal Mesh Structures Yoonkap Kim and Han-Jung Kim; Gumi Electronics & Information Technology Research Institute, Korea (the Republic of)

Transparent heaters (THs) have been researched with indium tin oxide (ITO) and fluorine-doped tin oxide (FTO) for defrosting and defogging windows, outdoor display panels, and self-heated sensors. However, there is limitation with the ITO and FTO to adapt to flexible and wearable heaters due to their brittleness. Hence, in this study, we proposed a transparent flexible heater (TFH) with copper (Cu) mesh structures fabricated onto poly(vinyl alcohol) (PVA) substrate, which can be dissolved in water, with transfer printing method. The transparent flexible heater exhibited an optical transmittance of ~86% at 550 nm, and reached to ~110 °C with applied voltage of 3V DC. In addition, the thermal response time of the TFH accelerated with a decrease in the thickness of the PVA substrate. In this case, the Cu mesh/PVA-based TFH with a thickness of approximately 75 µm showed fast and effective Joule heating characteristics at a low input voltage (3V DC). Therefore, we expect that the transparent electrode on the PVA substrates considered suitable to develop eco-friendly next-generation electronic devices such as flexible printed circuit boards (PCB) and heater-sensor platforms, flexible actuators and so on.

5:00 PM EL18.09.51

Deformable Tactile Sensor Arrays Integrated with a Frictionless Sensor Interface Enabling Complementary Slip Profiling Yebin Park, Dongbeom Kim, Jaehyun Kim, Wonjeong Suh and Unyong Jeong; Pohang University of Science and Technology, Korea (the Republic of)

To successfully replicate complex human tasks, a robotic hand capable of dexterous object manipulation such as grasping, object reorientation, texture perception, and slip detection is urgently demanded. Among various object manipulation performances, slip detection is the key performance that a dexterous robotic hand should acquire to achieve successful interaction between the object and the robotic hand. In the past decade, numerous artificial tactile sensors for robotic hands have shown vast progress in slip detection and grasping. However, slip detection of these sensors mainly relies on the normal force at the contact position without considering tangential force, which only provides limited slip information. In this work, the deformable ion gel strain sensor array and the piezoresistive pressure sensor array are integrated into a single device to obtain spatial distributions of the tangential shear strain and the normal force at the contact area. The tangential shear strain profile from the ion gel strain sensor array provides a visual representation of various slip occasions, such as translational and rotational slip, through changes in the shape and size of the strain fields. Additionally, the normal force profile from the piezoresistive pressure sensor array allows tracking of contact position and normal force distribution. Moreover, a frictionless interface between sensor arrays was achieved through the use of talc particles. The strain sensor array can accommodate deformation from slip more freely through the frictionless interface, which is crucial for a more accurate shear strain profile. Furthermore, the deformable tactile sensor arrays were attached to the robot gripper to demonstrate effective contact analysis on both translational and rotational slip occasions.

5:00 PM EL18.09.52
Large-Area Vacuum-Filtrated 2D MXene ($Ti_3C_2T_x$) Contacts for Flexible Monolayer Organic Field-Effect Transistors Yifan Guo[1], Keqiao Li[2], Yang Li[2], Baoling Huang[2] and Paddy K. L. Chan[1,3]; [1]The University of Hong Kong, Hong Kong; [2]The Hong Kong University of Science and Technology, Hong Kong; [3]Advanced Biomedical Instrumentation Centre, Hong Kong

High-quality monolayer-based organic field-effect transistors (OFETs) have shown great progress to serve as the building blocks of next-generation flexible electronics. Traditional metal evaporation could cause thermal damage on the organic active layer, thus limiting their electrical performance. MXene ($Ti_3C_2T_x$), a two-dimensional transition metal carbides and nitrides, have high conductivity and compatibility with low-cost solution-processed electrode deposition without inducing thermal damage. By vacuum-filtrated assistance, MXene can achieve lower electrical resistivity due to a tighter layer-by-layer structure compared with other deposition methods. The MXene layer can be patterned by a conformal mask that attached to the printing stamp directly and form a high-resolution electrodes array by direct transfer without a lift-off process. The patterning, deposition of MXene, and subsequent electrodes-transfer are all chemical-free processes, which avoid the chemical damage of the organic active layer and make them extremely suitable for the large-area mass production.

In this work, Meniscus-guided coating is used to grow 2,9-didecyldinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (C_{10}-DNTT) organic semiconductor monolayer on gate dielectric as the active channel, then transferred vacuum-filtrated MXene electrodes (15 µm channel length, which cannot be achieved without photolithography-patterning in previous study) to form the bottom-gate top-contact structure. The $Ti_3C_2T_x$ nanoflakes alignment was improved during the transfer process from cross-sectional SEM and XRD characterization. A subthreshold swing of ~72 mV/decade and field-effect mobility of ~4.2 $cm^2/V/s$ were achieved on high-κ dielectric HfO_2 by decent contact of HfO_2/C_{10}-DNTT/MXene interface, and the I_{ON}/I_{OFF} ratio reached ~10^8. We further fabricated OFETs on an ultra-thin conformal flexible substrate and realized uniform electrical performance. Compared with other MXene contacts, our current work shows comparable mobility with the shortest channel length, which expanded the application range of low-dimensional conductors as the patterning electrodes. We believe this processing approach of the 2D carbon-based MXene is extremely suitable for the layer-by-layer assembly of the next-generation large-area flexible electronics.

5:00 PM EL18.09.54
ZnO Nanorod Decorated Polyvinylidene-MXene Composite Nanofiber for High Electromagnetic Interference Shieling Effectiveness Sol Lee, Minje Kim, Chang geun kim, Viet Anh Cao and Junghyo Nah; Chungnam National University, Korea (the Republic of)

Electromagnetic waves emitted from different wireless devices may adversely affect electronic devices and cause communication faults. To cope with EM pollution, development of high-performance electromagnetic interference shielding materials with lightweight and flexibility is urgently needed. In this study, we developed ZnO nanorod decorated PVDF-MXene composite nanofiber for EMI shielding. To achieve maximum flexibility, polymer nanofiber is used as matrix polymer, and MXene nanoflakes exhibiting excelling EMI SE was incorporated inside the PVDF nanofiber,, forming the composite nanofiber. Additionally, surfactant-coated ZnO nanoparticles (NPs) were mixed in PVDF-MXene composite solution, which was then electrospun to form ZnO NP loaded PVDF-MXene composite nanofiber. During subsequent hydrothermal growth process, ZnO NPs inside the nanofiber are transported toward the surface of the nanofiber, so ZnO NRs start to grow on the outer surface of the nanofiber. Therefore, EMI shielding material developed in this work provides excellent flexibility, superior absorption SE, and increased multiple reflection and scatterings, resulting in high EMI SE (61 dB) and absolute EMI SE (21830 $dB.cm^2/g$). In addition, the oxidation of MXene nanoflakes can be effectively prevented by the encapsulating PVDF nanofiber, maintaining high EMI SE for a long period time. Therefore, the ZnO-decorated PVDF-MXene composite nanofiber introduced in this work has demonstrated high EMI SE, excellent flexibility, and long-term stability.

5:00 PM EL18.09.56
Effect of Gel Electrolyte Mass Fraction on Dye-Sensitized Solar Cell Using Carbon Nanotube Composite-Papers Yi Kou and Takahide Oya; Yokohama National University, Japan

In recent years with the gradual focus on environmental issues, renewable energy sources have gained more and more attention, among which solar energy has gained widespread attention for its wide range and cleanliness, etc. This study investigates the new type of dye sensitized solar cells (DSSC), which are produced by the redox reaction of dyes. The aim of this study is to achieve unique dye sensitized solar cells by using carbon nanotube (CNT) composite papers (CNTCPs) which this study is developing.

Since the CNTs contained in the CNTCP have metallic or semiconducting property, the use of the CNTCP as the cathode and anode of the DSSC has enabled the realization of a paper-DSSC with low cost and reduced environmental pollution. However, in our previous research, the paper-DSSC evaporated and leaked the contained electrolyte after about twenty minutes of operation when using a liquid electrolyte. To extend the life of the paper-DSSC, in this study, the safety and durability of the electrolyte is tried to improve by introducing a gel electrolyte, as follows:

Firstly to make our CNTCPs, we add 48 mg of single-walled CNT and 70 mg of dispersant (Sodium Dodecyl Sulfate) in 36 ml of pure water. Next, this mixed solution is ultrasonically dispersed for 1 hour by using an ultrasonic homogenizer to prepare a CNT dispersion. 1 g of pulp is then blended in 1000 ml of pure water for 1 hour in a blender to obtain the pulp dispersion. The resulting metallic CNT dispersion is mixed with the pulp dispersion and the CNTCP is produced by the modified Japanese washi papermaking method. In the same way, 4 mg of semiconducting CNTs and 36mg of purple sweet potato color are dispersed in 18ml of water. The paper is then mixed with the pulp dispersion to produce a semiconducting CNTCP. The paper is then dried and shaped by heat pressing.

Here, the gel electrolyte is made, the same as the liquid electrolyte used last time, this time still using iodine and potassium iodide as the main materials to carry out the redox reaction. 38.2 mg of iodine and 200 mg of potassium iodide are first dissolved in 20 mg of acetonitrile by heating in a water bath at 60 degrees centigrade, after it is completely dissolved, polyethylene glycol (PEG) was added, after it is dissolved again, the temperature is adjusted to 80 degrees centigrade and PolyVinylidene DiFluoride (PVDF), after all dissolved, the dispersion is placed in an oven at 70 degrees centigrade for 15 to 20 hours, when most of the acetonitrile has evaporated, the electrolyte at this point takes on a viscous liquid form.

The electrolyte is dropped between the two laminated papers just made and when the remainder has evaporated, the electrolyte takes on a gel-like appearance. In our current study, this paper-DSSC was successfully made to generate electricity and extended its lifetime to more than 2 hours by using 1 g PEG and 1 g PVDF, obtaining fill-factor (FF; performance evaluation index) of 0.22 and a photovoltaic conversion efficiency of 6.9×10^{-5}%.

In order to obtain higher photovoltaic conversion efficiency, the concentration ratio of PEG and PVDF is tried to be adjusted this time to compare the effect of this electrolyte on the photovoltaic conversion efficiency of paper-DSSCs at different ratios. Without changing condition for semiconductor electrodes, gel electrolytes with PEG: PVDF of 5:5, 6:4 and 4:6 are added into the paper-DSSCs as trial. As results, we found that changing the ratio of PEG and PVDF tended to affect the photovoltaic conversion efficiency. We are now trying to find the suitable condition for the ratio.

We believe that desired paper-DSSCs with high photovoltaic conversion efficiency and lifetime can be obtained by using carbon nanotube composite paper and our approaches.

5:00 PM EL18.09.57

Recent Progress in X-Ray Scattering Characterizations for Organic Optoelectronic Devices Yu-Wei Su; Feng Chia University, Taiwan

Recent progress in X-ray scattering have provides unique insights into the characterization of polymers in energy applications of photovoltaics and photodiodes. We presented using grazing incidence wide-/small angle X-ray scattering (GIWAXS/GISAXS) to study the bulk-heterojunction morphology of active layers in high-efficient organic photovoltaics (PCE >10%) and photodiodes. The active layer is mainly composed of donor–acceptor type conjugated polymer and n-type fullerene (or non-fullerene) small molecules. The GIWAXS is sensitive to the polymer's crystalline and can determine the crystal structure and the orientation of the crystalline regions. By using GISAXS, the aggregation cluster of conjugated polymer/small molecules can be detected to a length scale range from nanometers to several hundred nanometers.

5:00 PM EL18.09.59

Origin of Layered Herringbone Packing in Polyacenes as Investigated by Stepwise Crystal Structure Optimization Ryota Ono, Kanata Koyama, Satoru Inoue, Seiji Tsuzuki and Tatsuo Hasegawa; The University of Tokyo, Japan

Layered organic semiconductors (OSCs) are useful and suitable for manufacturing thin-film transistor (TFT) device structures. The carrier transport properties in these OSCs are primarily determined by molecular arrangement or crystal structure. It is thus expected that the development of high-performance OSC materials could be highly accelerated, if crystal structure of molecules designed on the desk is known prior to the actual synthesis of the molecules. To achieve this goal, it is essential to understand the origin of structural order found in the known crystals.

Here we investigate the origin of crystal structures for a series of polyacenes, from naphthalene (ring number 2) to hexane (ring number 6), through stepwise quantum chemical optimization approach as to intermolecular arrangements. We simplify and classify intermolecular arrangement parameters by focusing on both layered molecular packing and high crystal symmetry, as is typically observed in layered OSCs. The method allows to achieve highly accurate structure optimization in a short time by utilizing dispersion-corrected density functional theory (DFT) calculations as a technique used for calculating lattice energy. We found that adequate treatments of the variable parameters at each optimization steps lead to reproducing the experimental crystal structures of the compounds. Furthermore, the study revealed that origin of ring number dependence of crystal symmetry and layered crystal structures in polyacenes. We used Gaussian 16 for calculating lattice energy as the sum of intermolecular interaction with B3LYP functional and Grimme's D3 dispersion correction [1]. We first model a simple molecular dimer at an arbitrary relative position that assumes glide reflection symmetry with parallel and unslipped molecular long axes; the dimer is utilized as a fundamental unit for architecting monomolecular layers. First-step lattice energy minimization for the intralayer molecular arrangements allows to obtain regular layered herringbone packing through optimizing the intermolecular dihedral (or herringbone) angle. Then we take slipping or twisting structure into account and search for locally stable layered structure. Finally, we calculate interlayer interaction and search for stable layer arrangement. Through these steps, we can optimize intralayer and interlayer arrangement and gain probable and physically reasonable crystal structure. We optimized molecular arrangement of a series of polyacene molecules by this method, and successfully reproduced the structures of the respective compounds, including their polymorphs. Based on the results, we discuss the origin of the variation in these molecular packing structures in terms of the change of intermolecular twisting structure resulting from the increase of the number of benzene rings.

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5:00 PM EL18.09.61

Liquid Metal Incorporated Devices Toward Multifunctional Soft and Stretchable Electronics Priyanuj Bhuyan, Yuwen Wei and Sungjune Park; Jeonbuk National University, Korea (the Republic of)

In the past decade, liquid metals, especially gallium and its alloys, have surfaced as rapidly emerging cutting-edge functional materials with a view to revolutionize the field of soft and stretchable devices. This special class of materials possesses a handful of fascinating properties. As "liquid" they have low viscosities almost similar to water, along with higher surface tension, negligible vapor pressure and low toxicity; and as "metal" they possess high electrical and thermal conductivity, and transition from their liquid phase to solid phase and vice versa is easily attainable through nucleation and low temperature melting. Effective tuning of these properties and their inclusions in elastomeric materials in various forms via several unconventional techniques can lead to elastomeric metamaterials displaying interesting properties. Herein, we present a compilation of our research works which focuses on liquid metal inclusion in several forms in elastomeric substrates. We shed light on the use of liquid metal in three forms: as bulk injectable electrode material into elastomeric fibers and films, as rheologically modified ink for electrode printing and as micro fillers in elastomeric substrates to amplify electrical properties. Whereas presence of bulk liquid metal as core in 1D fibers and 2D films can render shape memory properties through phase change along with electrical conductivity, solidified gallium wires can be assembled into 3D structures through "room temperature welding" which can be subsequently included in elastomers to realize a 3D fluidic network. The rheology of liquid metal can be tuned to obtain an ink suitable for electrode printing on polymeric films in order to fabricate flexible, ultrasoft and ultrastretchable electronics systems with unhindered electrical and mechanical functionalities. The fluidic nature and low viscosity of liquid metals facilitates their inclusion in elastomeric matrix in the form of micro particles via high shear mixing in order to tune electrical and thermal properties through liquid metal particle inclusions. In short, our compilation provides an insight into conjugating liquid metals in various forms into elastomeric substrates of various physical shapes and mechanical properties via which we were able to design several soft and stretchable systems with specific properties: stretchable 1D fibers and 2D films with shape memory and electrical conductivity, elastomers with 3D fluidic electrode inclusions, flexible, ultrasoft and ultrastretchable sensos with fluidic electrodes and soft devices capable of functioning as healable/reconfigurable waste energy harvesters.

5:00 PM EL18.09.62

GaAs Photovoltaic Arrays Integrated on an Ultrathin Polymer Film Substrate for High Flexibility and a Lightweight Design Sungbum Cho, Dongwuk Jung and Jongho Lee; Gwangju Institute of Science and Technology, Korea (the Republic of)

Ultrathin and lightweight photovoltaics with high efficiency and reliability serve as a convenient untethered power source for new types of electronic devices, such as attachable or implantable electronics, small-scale robots, and many others. However, the extreme mechanical properties of high-performance solar cells and ultrathin films present challenges when handling and processing them to realize ultrathin solar cell arrays. In this paper, we present a highly efficient GaAs photovoltaic array integrated on an ultrathin polymer film (1.4 µm thick). Full processes, including framing, cold-welding, epitaxial lift-off (ELO), and microfabrication, are used realize ultra-flexible and lightweight GaAs photovoltaic arrays. The mechanical characteristics were analyzed via numerical and experimental methods along with demonstrations with electrically functional devices. The power-to-weight ratio (specific power: 5.44 W g^{-1}) is in the highest range, even with single-junction solar cells.

5:00 PM EL18.09.63
Cu_2O Thin-Film Transistor for CMOS Logic Circuit Through the Chemical Reaction During Annealing in N_2 Atmosphere Jae Hak Lee and Youn Sang Kim; Seoul National University, Korea (the Republic of)

Metal oxide semiconductors have been emerging as a semiconductor material for next-generation electronic devices such as switching devices in displays, thin film diodes, solar cells, and Dynamic Random-Access Memory (DRAM) due to several advantages such as low cost, various deposition methods, low processing temperature, and processability on large-area glass substrate. However, it is difficult to construct a low power logic circuit based on Complementary Metal-Oxide-Semiconductor (CMOS) with only n-type metal oxide TFTs, so p-type metal oxide TFTs with good electrical performance is required. Cuprous oxide (Cu_2O) is a potentially promising p-type semiconductor due to the intrinsically good electrical properties such as high hole mobility over 100 cm^2/Vs and the possibility to fabricate devices using conventional semiconductor processes. Despite an intrinsic high hole mobility, Cu_2O TFT has still shown poor electrical performances. Several studies proposed dissociative Cu defects and CuO impurities as the cause of the poor electrical properties of Cu_2O TFTs. First, dissociative Cu (interstitial Cu) defects create a donor-like sub-gap states in the band gap of p-type Cu_2O, causing high off-current. Second, the other considering point is CuO impurities in the Cu_2O thin film, which induce sub-gap states that serve as a hole trapping site above the VBM of Cu_2O because the bandgap of CuO (1.4 eV) is smaller than that of Cu_2O (2.17 eV). Thus, dissociative Cu (interstitial Cu) defects and CuO impurities play a critically detrimental role in the quality of Cu_2O thin film. Dissociative Cu defects cause high off-current and CuO impurities cause low field effect mobility. Therefore, it is essential to reduce dissociative Cu and CuO impurities in order to improve the electrical performance of Cu_2O TFTs.
Here, we demonstrated Cu_2O TFTs with high field effect mobility and low off-current through reduction of CuO impurities and dissociative Cu defects by simply controlling the fabrication conditions without inducing any additional layers or chemical treatments. In the Radio Frequency (RF) sputtering deposition process, a Cu_xO thin film with a high CuO ratio was fabricated by using a mixed gas of Ar and O_2 as working gas. Then, post annealing was performed while flowing N_2 gas. Oxygen added to the working gas during deposition increases the CuO ratio in the copper oxide thin film and consequently reduces dissociative Cu defects. Also, the N_2 atmosphere in annealing plays an important role in reducing Cu_xO to Cu_2O and prevents oxidation to CuO phase. During post annealing, when CuO - CuO transformed to Cu_2O, oxygen is generated, and the generated oxygen oxidized dissociative Cu defects to CuO. The formed CuO also combined with another CuO and transited to Cu_2O. These chemical reactions occur repeatedly and continuously during the annealing process, creating a chain reaction. By XRD and XPS analysis, we confirmed that the fabrication method of Cu_2O thin film combined with controlled deposition and anneal effectively reduces CuO impurities and dissociative Cu defects, the ratio of dissociative Cu defects decreased from 11.3% to 3.1%, which are responsible for the degradation of the electrical properties of Cu_2O TFTs. The fabricated Cu_2O TFTs were showed the field effect mobility of 1.19 ± 0.06 cm^2/Vs, the on/off current ratio of $1.09 \pm 0.06 \times 10^5$. And the Cu_2O TFT device exhibited a Vth shift of 3.31 V under negative bias stress (Vds = -10V, Vgs = -20V, 4000s). As a practical application, we demonstrated CMOS inverter with n-type IGZO TFT and p-type Cu_2O TFT and this device achieved a gain of 14 at V_{DD} = 20 V. Our new fabrication route showed that it was possible to simply fabricate a high-quality Cu_2O thin film, effectively improve the electrical properties of Cu_2O TFTs, and make low-power CMOS logic circuits based on metal oxide semiconductors.

5:00 PM EL18.09.64
Inorganic Nanopillar Arrays Significantly Enhance Optoelectronic Functions, Environmental Stability and Mechanic Robustness of Flexible Perovskite Optoelectronic Devices Zhifeng Huang; The Chinese University of Hong Kong, Hong Kong

One-dimensional (1D) nanostructure arrays can reduce light reflection loss, suppress recombination dynamics, guide charge carrier transport, and relax stress and strain in flexible optoelectronic devices, to improve optoelectronic functions and stability under aging and mechanical bending. However, *in-situ* fabrication of 1D nano-arrays on polymer-based flexible electrodes is challenging, mainly due to degradation of polymer-based electrodes at high temperature of *in-situ* growth.
Here, nanopillar arrays (NaPAs) made of diverse inorganic materials, such as Ti, TiO_2, SnO_x (functioning as electron transporting layers) and NiO_x (serving as hole transporting layers), are deposited onto a flexible electrode by glancing angle deposition (GLAD), to create perovskite solar cells (PSCs) and photodetectors. As-grown NaPAs enhance light transmittance, facilitate light harvesting in perovskite, promote charge carrier transport and collection, and facilitate the formation of large perovskite grains. All these features lead to high efficiency of >20% and >17% for the rigid and flexible PSCs, respectively. No obvious crack nucleation is formed on the NaPAs after 500 bending, resulting in good mechanic robustness and environmental stability of photovoltaic performance. Large-area (1 cm^2) flexible PSCs containing the SnO_2 NaPAs show the champion power conversion efficiency (PCE) of 14.9%, which undergoes only 10% degradation for approximately 800 h storage and 20% degradation by manual bending for around 400 times. Furthermore, compared to the conventional mesoporous counterparts, metallic oxide NaPAs enable the perovskite photodetectors to comprehensively enhance the detection speed, responsivity, and detectivity, and to extend the linear dynamic range.
We devise an advanced technique of low-substrate-temperature GLAD generally adapted to *in-situ* deposition of charge carrier transporting layers made of inorganic NaPAs on flexible electrodes, to significantly enhance optoelectronic performance, mechanic robustness, and environmental stability of flexible optoelectronic devices.

5:00 PM EL18.09.66
In-Depth Study on Molecular Structure-Property Relation for Y6-Based Nonfullerene Acceptors in Organic Photovoltaics Chang Woo Koh[1], Shuran Xu[1], Min Hun Jee[1], Dohun Yuk[2], Jin Young Kim[2], Han Young Woo[1] and Sungnam Park[1]; [1]Korea University, Korea (the Republic of); [2]Ulsan National Institute of Science and Technology, Korea (the Republic of)

Organic photovoltaics (OPVs) have drawn much attention as the next-generation of renewable energy harvesters due to their significant advantages of solution processability, lightweight, mechanical flexibility, semi-transparency, and indoor applicability. Recently, power conversion efficiencies (PCEs) have recently increased to over 20% in tandem devices and over 19% in single cells due to the development of high-performance nonfullerene acceptors (NFAs). Among the NFAs, Y6 is unquestionably a representative benchmark structure with several distinct characteristics, including dominant face-on orientation, high electron mobility, and low energy loss. Y6 has an acceptor-donor-acceptor (A-D-A)-type structure consisting of a

dithieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-e:2′,3′-g] [2,1,3]benzothiadiazole (BTP) core and two electron-accepting 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (INCN-2F) terminal moieties. In particular, an undecyl side chain is substituted at the β-position of the thienothiophene (TTh) moiety (in the Y6 core) to impart solution processibility. However, owing to the complicated synthetic procedure of alkyl-substituted core, further optimizing the molecular structures and industrial scale-up of Y6-based materials are required. Moreover, the bulky side chains on the core of Y6 obstruct core-core intermolecular packing interactions, influencing electronic coupling and charge transport properties.
In this study, three new Y6 derivatives (YBO-2O/-FO/-2F) were synthesized and characterized as an acceptor in OPVs. Compared with Y6, the YBO series have no alkyl chains in the core, and it has been shown that the intermolecular packing properties in the solution processed thin films are significantly improved because of the absence of core alkyl chains. Tighter π-π stacking was confirmed by grazing incidence wide angle X-ray scattering (GIWAXS) and higher electron mobility were also measured by the space charge limited current (SCLC) method with the YBO-2O, YBO-FO, and YBO-2F films compared to Y6 films. From molecular dynamics (MD) simulations, the YBO series were found to preferentially form core-core and terminal-terminal (CC-TT) interactions rather than terminal-terminal (TT) interactions in Y6, which induced dense intermolecular packing for efficient charge transport. The mechanism for dimer formations in solution state is found to be different for YBO series compared to Y6. In the case of YBO series, two molecules initially formed TT dimers as an intermediate state and were subsequently converted into more stable CC-TT dimers. However, in the case of Y6, TT dimers were readily formed and kinetically trapped due to the alkyl chains in the core, and thermodynamically stable CC-TT dimers were relatively slowly formed. Our newly designed YBO series are excellent NFAs in terms of better intermolecular packing, higher electron mobility, and kinetically more favorable aggregation.

5:00 PM EL18.09.68
Effect of Electric Field on Metal Capping Layer of Thin-Film Transistor (TFT) and Its Potential Seo D. Hyo, Sang Yeol Lee and Yoon HongJoon; EMADE.LAB, Korea (the Republic of)

Thin film transistor research has been studied with high mobility and stability to implement high-definition displays and thin film transistor-based electronics, such as neuromorphic devices, multi-value devices and 3D integrated circuits. A metal capping(MC) TFT is a device that meets these needs of the times. The improvement of electrical properties and mobility of TFT will be studied using MC layers on channel layers. It can increase the mobility of TFT by adopting the metal layer on the channel material because the MC material has a relatively lower resistance than that of the channel materials. MC-layer is attributed to form strongly compacted ω-shape current-path by tunneling effect as a result of effective control of the surface potential by low resistance of MC-layer in channel region. In addition, the proposed device structure contributes to the changes in transistor performance when electric field is applied to the MC layer step by step. This could suggest the possibility of the application for contact sensors with high response due to high mobility of MC TFTs.

5:00 PM EL18.09.69
Highly Conductive p-type Transparent Conducting Electrode with Sulfur-Doped Copper Iodide Gahye Kim and Myung-Gil Kim; Sungkyunkwan University, Korea (the Republic of)

Although n-type transparent conductors have been commercialized with high optical transmittance and electrical conductivity, the realization of their p-type counterparts has been a challenging problem. Here, we report the synthesis of a highly conductive transparent p-type sulfur-doped CuI (CuI:S) thin film using a liquid-iodination method with a thiol additive. The CuI:S film shows a remarkably high electrical conductivity of 511 S cm^{-1} with an optical transmittance of greater than 80%. Furthermore, additional hole doping of CuI:S with H_2O_2 treatment improves the electrical conductivity to 596 S cm^{-1}. Consequently, CuI:S exhibits a record-high figure of merit (FOM) value of 63,000 M Ω^{-1} (73,000 M Ω^{-1} with H_2O_2 treatment), which is ~ 370% (~430% with H_2O_2 treatment) higher than the previously reported record-high FOM value. The highly conducting CuI:S electrode is successfully applied as transparent conducting electrodes of the organic light-emitting diode and transparent p-type thin film transistor. The liquid-iodination chemical method with unconventional control of the reaction parameters can be generalized to produce high-quality metal halide thin films, allowing them to be applicable for transparent electronics and optoelectronics.

5:00 PM EL18.09.70
Buckling Instability Control of 1D Nanowire Networks for a Large-Area Stretchable and Transparent Electrode Byoung Soo Kim[1,2], Jeong Gon Son[2] and Sang-Soo Lee[2]; [1]Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)

A commonly used strategy to impose deformability on conductive materials is the prestrain method, in which conductive materials are placed on prestretched elastic substrates and relaxed to create wavy or wrinkled structures. However, 1D metallic nanowire (NW) networks typically result in out-of-plane buckling defects and NW fractures, due to their rigid and brittle nature and nonuniform load transfer to specific points of NW. To resolve these problems, an alternative method is proposed to control the elastic modulus of 1D NW networks through contact with various solvents during compressive strain. Through solvent contact, the interface interactions between the NWs and between the NW and substrate can be controlled, and it is shown that the surface instability of the 1D random network is formed differently from a uniform bilayer film, which also can vary with the modulus of the network. For modulus values lower than the critical point, slippage and rearrangement of NW strands mainly occur and individual strands in the network show an in-plane wavy configuration, which is ideal for structural stretchability. Based on the solvent-assisted prestrain method, letter-sized, large-area stretchable, and transparent electrodes with high transparency and conductivity are achieved, and stretchable and transparent alternating current electroluminescent devices for stretchable display applications are also realized.

SESSION EL18.10: Printed Electronic Materials and Devices
Session Chairs: Ho-Hsiu Chou and Francisco Molina-Lopez
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3018

8:45 AM EL18.10.01
Direct Writing of Elastic Conductors for Three-Dimensional Stretchable Electronics Seungjun Chung; Korea Institute of Science and Technology, Korea (the Republic of)

Skin electronics augment the capability of shareable signals from personal and metabolic activities over communication networks by blurring the physical discontinuity between electronic devices and human skin. With their unique mechanical characteristics, such as lightweight design, softness, and stretchability, skin electronics can be functionalized on various body parts in the form of biosensors, processors, and displays. For high-fidelity operation under these challenging circumstances, the design of skin electronics needs to be tailored elaborately to individuals. However, traditional mask-based lithography primarily optimized for the mass production of standardized, uniform electronics cannot effectively deal with the morphological diversity of the human bodies. Moreover, existing manufacturing processes still lack strategies to implement three-dimensional (3D) structures with soft functional materials such as vertical interconnect accesses (VIAs) and multilayer circuitries that are crucial to the realization of high-performance, multifunctional applications.

Printing technologies have attracted tremendous attention in the realization of customized soft electronics due to their advantages, such as non-vacuum, low-temperature, and non-contact processability. However, most conventional 3D printing processes still deposit one layer at a time, which is unsuitable for complex, filamentary, and omnidirectional wirings (including a z-directional component). In this regard, omnidirectional direct ink writing for self-supporting 3D wirings with elastomer composites has attracted much attention, but the complex composition of their inks that meets apposite rheological properties is a critical bottleneck, resulting in structural collapse and nozzle clogging during extrusion simultaneously. In this presentation, I would like to present our recent results of printing Intrinsically stretchable solid-state elastic conductors into self-supporting 3D geometries. These results promise the design diversity of soft electronics, enabling complex, multifunctional, and tailored human-machine interfaces. Our omnidirectional printing strategies achieve superior viscoelastic properties that provide the structural integrity of printed features, and pseudoplastic and lubrication behaviors that allow great printing stability simultaneously. Freestanding, filamentary, and out-of-plane 3D geometries of intrinsically stretchable conductors are directly written, achieving a minimum feature size <100 µm and excellent stretchability >150%. Particularly, the evaporation of the continuous phase in the emulsion results in microstructured, surface-localized conductive networks, significantly improving their electrical conductivity. To illustrate the feasibility of our approach, we demonstrate skin-mountable electronics that visualize temperature on a matrix-type stretchable display based on omnidirectionally printed elastic interconnects.

9:00 AM EL18.10.04

Universally Applicable Three-Dimensional Photo-Crosslinkers for All-Photopatterned Electronics BongSoo Kim[1], Myeongjae Lee[2], Min Je Kim[3] and Jeong Ho Cho[3]; [1]Ulsan National Institute of Science and Technology, Korea (the Republic of); [2]Korea University, Korea (the Republic of); [3]Yonsei University, Korea (the Republic of)

Fabrication of electronic components at high resolution remains a challenging task for organic electronic devices fabricated entirely through a series of solution processes. We report the all-solution processing of highly integrated arrays of organic thin-film transistors (OTFTs) and logic gates. This processing is performed using newly developed multi-bridge photo-crosslinkers containing 4 or 6 photo-crosslinkable units. Under UV, photo-crosslinkers mixed within solution-processable electronic materials generate a three-dimensional (3D) network of the given host electronic materials. We note that our photo-crosslinkers can produce the 3D network state efficiently even at an unprecedentedly small loading (only 1 or lower wt%), which, in turn, enables preservation of the intrinsic electrical properties of the photo-crosslinked material. Moreover, the crosslinking of electronic component layers allows not only micropatterning of the layers at high resolution (< 5 µm) but also stacking of a given electronic component layer on top of the other layers.[1,2] Furthermore, our efficient photo-crosslinkers enable to produce an ultrathin polymer gate dielectric, the application of which results in excellent hole and electron mobilities of 12.4 and 10.1 $cm^2 V^{-1}s^{-1}$, respectively, from *p*- and *n*-type OTFTs operated at < 3 V.[3] These works demonstrate that the use of photo-crosslinkers paves a new avenue to fabricate future electronic devices.

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9:15 AM EL18.10.05

An N-Type, Stable Electrolyte Gated Organic Transistor Based on a Printed Polymer Fabrizio A. Viola[1,2] and Mario Caironi[2]; [1]Università degli Studi di Cagliari, Italy; [2]Italian Institute of Technology, Italy

Electrolyte-gated organic transistors (EGOTs) have been proven to be one of the most attractive platforms for next-generation biosensors [1], neuromorphic systems [2] and low-voltage electronics [3]. They are particularly indicated for applications where stable operation in aqueous environment and cost-effective manufacturing are required. However, despite a large number of solution processable EGOTs have been reported in literature so far, only few are based on printed semiconductors, with no examples of digitally printed, i.e. inkjet printed, n-type devices, which would easily enable complementary architectures [4].

Therefore, a current challenge is the fabrication of stable n-type EGOTs through large-area, scalable and additive printing techniques for the deposition of the organic semiconductor, facilitating future scale-up and cost-effective process flows. Indeed, through printing techniques such as inkjet, the materials can be deposited in an controllable way over both rigid or flexible substrates with a small production of waste. Moreover, enabling reliable printed n-type EGOT could pave the way for the development of robust complementary electrolyte-gated electronic circuits, which are highly advantageous especially for bioelectronics, for instance as signal amplifiers of weak biopotentials, thanks to their high gain with a very low-power consumption and low-voltage operation.

In this work we propose the first example of a n-type electrolyte gated organic transistor based on an inkjet printed polymer [5].

The proposed device shows a high stability when operated in water and requires only 3 hour of conditioning to produce a stable response, a much faster dynamic than in the case of printed polymers currently tested for p-type EGOTs. The electrical characterization demonstrated a good reproducibility of the device performance, especially in terms of maximum output current, the on/off ratio is above 10^4 and the transconductance is equal to 370 ± 40 uS – when the devices are measured with a Ag/AgCl gate electrode and 0.1 M NaCl as gate electrolyte. Furthermore, as a proof-of-concept, we successfully integrated the proposed printed n-type EGOT with a printed p-type device in an inverter gate able to operate in water for more than 15 hours with a proper inverting behavior and a substantially stable gain. Overall, besides providing a valid and cost-effective technological solution for the fabrication of EGOTs, based on ink-jet printing technique that make possible the integration of n-type and p-type devices, the proposed approach can be a candidate for a plethora of possible use ranging from biosensing, for healthcare or biomedical applications, to complementary circuitry, where reproducibility, high operating stability and low-voltage operation are required.

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9:30 AM EL18.10.06
Flexible Capacitive Pressure Sensors with 3D Printed Lattice Dielectric Layers Arielle E. Berman, Kaiwen Hsiao, Chengyi Xu, Emily Stein, Khuyen Nguyen, Joseph M. DeSimone and Zhenan Bao; Stanford University, United States

Dexterous robotic manipulation and perception requires the sensing of multidirectional forces and combined loadings. With integrated sensor types and a wide variety of possible applications, fabrication techniques can quickly increase in complexity. Additionally, they lack reproducibility and precise control over the microstructure. By utilizing an additive manufacturing process called Continuous Liquid Interface Production (CLIP), three-dimensional lattice elastomeric polyurethane dielectric layers for capacitive sensors can be reliably produced. These different, intricately architectured lattices, called Voronoi, Rhombic, Tetrahedral, and Kagome, cannot be generated with conventional fabrication techniques. The first step towards designing sophisticated capacitive sensors was to characterize the performance of different lattice forms under normal pressure when laminated onto interdigitated electrodes. The impact of altering lattice design parameters, such as volume fraction, strut width, and dielectric thickness, on sensitivity and capacitive response will be discussed in this talk. MicroCT will also be utilized to elucidate the influence of lattice design on the deformation mechanisms and initial capacitance. With this information, rationally designed multifunctional sensors with combined lattice types for anisotropic mechanical properties can be easily printed. CLIP enables simple printing of complex and flexible dielectric layers for fabrication of customizable dielectric layers for capacitive sensors responsive to various external loadings.

9:45 AM EL18.10.07
Biomimetic, Programmable, and Part-by-part Maneuverable Single-body Shape Morphing Film Yongrok Jeong[1,2], Junseong Ahn[1], Ji-Hwan Ha[1,2], Jiwoo Ko[1], Soon-Hyoung Hwang[2], Sohee Jeon[2], Munjeong Bok[2], Jun-Ho Jeong[2] and Inkyu Park[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Korea Institute of Machinery and Materials, Korea (the Republic of)

Recently, shape morphing films (SMFs) have been actively researched owing to their diverse applications such as soft robotics, soft gripper, and healthcare/wearable devices. Recent research about SMF concentrates on improving the morphing complexity, possibly widening the applicable area of the SMF. Their morphing complexity has been achieved by assembling multiple actuation elements in a single system. However, most of them are manually assembled, leading to unreliability in the assembled result, and are unsuitable for complex movements such as the gripping motion of the *Drosera Capensis,* which needs elaborate morphology and a highly ordered structure with multipTon order to resolve this problem, this study proposes a biomimetic, programmable, and part-by-part maneuverable single-body SMF, which may replace the conventional assembly methods.

An electrothermal actuator is adopted as the fundamental principle: multiple layers with diverse coefficients of thermal expansion (CTE) cause bending, originating from the difference in volume change induced by Joule heating. A strain-restricting layer and a strain-inducing layer were required, therefor polyimide and SU-8 with low CTE as the strain-restricting layer, and PDMS with high CTE as the strain-inducing layer, were adopted. Equivalently function to the assembled system, programmability and part-by-part maneuverability should be realized either. Programmability was achieved by a similar mechanism with *Bauhinia variegates*, which morphs by the hygroscopic volume change of overall tissue with restriction by the cellulose fibril structure. Similarly, the temperature-induced volume changes and anisotropy in elastic modulus by SU-8 microwall cause the bending of film in the intended direction. In the case of part-by-part maneuvering, it is achieved by controlling the voltage distribution of the underlying electrothermal heater.

The SU-8 wall pattern was optimized to maximize the bending sensitivity. Four variables (width (w), pitch/width ratio (p/w), height ($t_{\text{SU-8}}$) of the SU-8 micro-wall, and the relative thickness of PDMS concerning that of SU-8 ($t_{\text{PDMS}}/t_{\text{SU-8}}$)) are optimized to maximize the curvature (k) between the initial and heated states. Resultantly, $w = 25$ µm, $p/w = 2$, $t_{\text{SU-8}} = 75$ µm, and $t_{\text{PDMS}}/t_{\text{SU-8}} = 1.5$ was selected. Based on the simulated result, over the NiCr nano-mesh-embedded PI film used as the electrothermal heater, the SU-8 wall with morphology that follows the optimization ($w = 25.1$ µm, $p/w = 1.99$, $t_{\text{SU-8}} = 80$ µm, and $t_{\text{PDMS}}/t_{\text{SU-8}} = 1.28$) was fabricated as SMF.

For characterization, two samples of sizes 1x1 and 5x5 mm^2 were analyzed. The first experiment investigated the change in depends on power density ($P' =$ applied power/area of SMF). The results show a linear relationship between P' and κ for both samples, with a sensitivity ($S = \triangle P'/\triangle\kappa$) of 7.83 cm/W for the 1x1 SMF, and $S = 6.26$ cm/W for the 5x5 SMF. In the second experiment, 10–90% rise time (τ_R) and 90–10% fall time (τ_F) were measured for $P' = 0.6$ W/cm^2. As a result, $\tau_R = 4.08$ s, $\tau_F = 4.09$ s for the SMF, and $\tau_R = 4.91$ s, $\tau_F = 11.11$ s for the SMF were measured. Finally, 1000 cycles of heating/cooling were performed with the 5x5 SMF, and no noticeable irregularity was observed.

Complex movements were demonstrated for two biomimetic applications: artificial inchworm (crawler) and artificial *Drosera capensis* (gripper). In the case of the artificial inchworm, five different motions were demonstrated (pose stabilization: front-to-back flip and back-to-front flip; basic movements: crawl, left turn, and right turn). In the case of the artificial *Drosera capensis*, the insect-gripping motion via hierarchical morphology was demonstrated. The proposed method for the fabrication of a biomimetic, programmable, and part-by-part maneuverable single-body SMF can successfully replace the conventional assembly process and achieve advanced SMF technology by enabling various complex movements toward practical applications.

10:00 AM BREAK

10:30 AM EL18.10.08
Tuning Polymer-Acceptor Backbone Coplanarity and Conformational Rigidity to Achieve High-Performance Printed All-Polymer Solar Cells with Reduced Charge Recombination Yilei Wu and Zhenan Bao; Stanford University, United States

Compared with small-molecule acceptors (SMAs) based polymer solar cells, all-polymer solar cells (all-PSCs) comprising both polymer donor and polymer acceptor offer superior morphological and mechanical stability as well as a broader processing window. However, current performances of all-PSCs are still inferior to those of SMA systems, mainly because of the scarcity of high performing polymer acceptors relative to the diverse SMAs. Herein, we report a high-performance polymer acceptor incorporating intramolecular noncovalent interlocking effect that leads to a more coplanar and rigid molecular conformation compared to the polymer acceptors based on commonly used thiophene-based linkers. As a result, this new polymer shows a better backbone conjugation and tighter interchain π-stacking, leading to all-PSCs with higher charge-transport mobility and reduced energetic disorder. Furthermore, detailed morphology and photophysical investigations reveal that such blend exhibits a good balance between polymer miscibility and domain purity, thus leading to a more suppressed charge recombination and higher current density and fill factor. Overall, a significantly higher efficiency of 15.6% is achieved respect to control system (9.8%). Moreover, a remarkable efficiency of 14% is demonstrated for the solution-sheared All-PSCs under ambient conditions, which is a record-high value for devices made under conditions relevant to the real-life printing technologies. This study reveals the potential of noncovalent interlocking effect to construct polymer acceptors with more coplanar and rigid chain conformation, which are desirable properties to achieve superior All-PSCs.

10:45 AM EL18.10.09
Inkjet Printing Organic Photovoltaics for Contact Lens Applications Tsu-Yu Chou, Tanmay Sinha and Francisco Molina-Lopez; KU Leuven, Belgium

Smart contact lenses (SCL) are considered as a noninvasive platform for health monitoring and diagnosing. We can use SCL to measure eye movements, blood oxygen, or even detect the concentration of glucose for some diabetes patients. However, the space limitation in SCL makes it challenging to power them since current performing batteries are too bulky to be integrated on the lens. We propose inkjet printing (IJP) organic photovoltaic (OPV) cells as an alternative complementary (to small batteries) power supply for SCL. OPVs are good candidates in this application because they involve non-toxic materials that can be processed from solution using green solvents. Moreover, the absorption spectrum of the organic semiconductors used in OPVs matches well the one of indoor lighting, leading to cells with higher power conversion efficiencies (PCEs) than traditional Si solar cells for indoor conditions. The use of IJP is justified because contrary to typical applications of solar cells, the integration of OPVs on SCL does not require high-throughput or large-area deposition. Instead, free patterning with good resolution is a main aspect to pursuit. In our work, we focus on the relation process-morphology-performance of the inkjet-printed active layer. By choosing proper solvents, which takes into consideration the boiling point, surface tension, viscosity and density, we succeed in reducing the coffee-ring effect and in making uniform films. Those improved films will ultimately lead to higher PCE.

11:00 AM *EL18.10.10
Printed and Flexible Carbon Nanotube Based Thermoelectrics Mariano Campoy-Quiles; ICMAB-CSIC, Spain

The conversion of waste heat into electricity using solid state devices, namely thermoelectrics, based on carbon materials has experienced renewed interest in the last decade as these materials are particularly suited for large area and low-temperature operation applications since they are abundant, typically show low-toxicity and are easy to process [1].
In this contribution we will focus on our recent attempts to further extend the sustainability, scalability and range of applications of CNT based thermoelectrics. First, we will describe the use bacteria in environmentally friendly aqueous media to grow large area bacterial nanocellulose (BC) films with an embedded highly dispersed CNT network [2]. The thick films are fully bendable, can conformally wrap around heat sources and are stable above 500 K. The resulting composite films exhibit comparable thermoelectric properties to buckypapers while saving more than 90% of the carbon nanotubes. Interestingly, BC can be enzymatically decomposed, thus completely reclaiming the embedded CNTs once the generator has reached the end of its lifetime. Second, we will show our recent studies on the stability and scalability of CNT based thermoelectrics, starting from CNT salts, [3] and give some examples of potential uses, such as solar thermoelectrics [4].
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11:30 AM EL18.10.11
All-Aerosol-Jet-Printed Highly Sensitive and Selective Polyaniline-Based Ammonia Sensors Tolga Aytug[1], Christine Fisher[2,1], Pooran Joshi[1], Lydia Skoolrood[3,1] and Bruce Warmack[1]; [1]Oak Ridge National Laboratory, United States; [2]The City University of New York, United States; [3]North Carolina State University, United States

Early detection of refrigerant gas leaks, in particular ammonia (NH_3), is crucial to avoid significant economic loss and prevent harmful effects to human health and environment. We report design and scalable fabrication of a low-cost and low-power polyaniline-based NH3 gas sensor on flexible polyimide (PI) substrates using additive manufacturing techniques. The silver interdigitated electrode arrays and conducting polymer films are printed onto PI using a direct-write technology of aerosol-jet printing (AJP). The gas sensing performance of the fabricated devices is evaluated in the analytical early leak detection range of 5–1000 ppm NH_3 in air as a function of both thermal and relative humidity exposures. The sensor exhibits sensitivity down to 5 ppm NH_3 with a sub-ppm detection limit and good repeatability. Application of AJP to print other ink formulations on technological viable platforms will also be discussed.

11:45 AM EL18.10.12
A Transient Printed Soil Decomposition Sensor based on a Biopolymer Composite Conductor Gregory L. Whiting[1], Madhur Atreya[1], Stacie DeSousa[1], John-Baptist Kauzya[1], Evan Williams[1], Austin Hayes[1], Karan Dikshit[1], Jenna Nielson[1], Sara Khorchidian[1], Abigail Palmgren[1], Shangshi Liu[2], Anupam Gopalakrishnan[1], Eloise Bihar[1], Carson Bruns[1], Richard Bardgett[2], John Quinton[3] and Jason C. Neff[1]; [1]University of Colorado Boulder, United States; [2]The University of Manchester, United Kingdom; [3]Lancaster University, United Kingdom

Soil health is one of the key factors in determining the sustainability of global agricultural systems and the stability of natural ecosystems. Microbial decomposition activity plays an important role in soil health; and gaining spatiotemporal insights into this attribute is critical for understanding soil function as well as for managing soils to ensure agricultural supply, stem biodiversity loss, and mitigate climate change. Here, we present a novel approach to monitiroing microbial activity by demonstrating an in-situ electronic soil decomposition sensor that relies on the degradation of a screen-printed conductive composite trace utilizing the biopolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) as a binder. This material responds selectively to microbe-active environments with a continuously varying resistive signal that can be readily instrumented with low-cost electronics to enable wide spatial distribution. In soil, a correlation between sensor response and intensity of microbial decomposition activity is observed and quantified by comparison with respiration rates over 14 days, showing that devices respond predictably to both static conditions and perturbations in general microbial decomposition activity.

SESSION EL18.11: New Concepts in Soft and Polymer Electronics
Session Chairs: Zong-Hong Lin and Sihong Wang
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3018

1:30 PM EL18.11.01
Assessing Edible Semiconductors for Future Edible Electronics Mario Caironi, Alessandro Luzio, Alberto Davide Scaccabarozzi and Elena Feltri; Istituto Italiano di Tecnologia, Italy

Edible Electronics [1] is an emerging field targeting devices and sensors that can be safely ingested without need of supervision nor recollection, and are degraded within the body after performing their function. Final applications are both in the healthcare, in forms of smart pills which are not simply ingestible but are also digestible, and in the food sector, offering safe direct tagging of food. For future edible electronic systems, active circuits will be required, both for logic and control. To this end, one of the main challenges is the development of transistors based on edible semiconductors with sufficient performance to be adopted in such systems. Here we report on our recent progress on reassessing carotenoids semiconductors, mainly beta-carotene, for thin films in transistors. By careful processing and microstructuring of films, a maximum field-effect mobility exceeding 10^{-2} cm^2/Vs was achieved, with reasonable stability in dark-conditions. At the same time, we report on the integration of commonly ingested organic dyes in fully edible transistors architectures. Such results indicate that options for edible semiconductors are available and can be exploited towards first integrated edible logic circuits.

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1:45 PM EL18.11.02
Predictive Design of A Conjugated Polymer's Mechanical Property from its Dynamics Xiaodan Gu; University of Southern Mississippi, United States

Organic semiconducting polymers are promising candidates for stretchable electronics for their mechanical compliance. Donor-Acceptor-type conjugated polymers have been the key driver for the recent boost in device performance. To date, the effect of the conjugated backbone building block on the thermomechanical property of conjugated polymers has not been well understood, despite much work on their influence on the electronic property. In this talk, I will discuss our work on the structure and dynamics study of thin-film thermomechanical property relationship for donor-acceptor polymers with systematically varied donor units on the conjugated polymer. From our previous study, we realized the importance of the Tg on the mechanical property, here, I will discuss our effort to develop a machine-learning model to predict the glass transition temperature and modulus of the polymer. In the end, I will provide some perspective about the accessible range of the modulus and stretchability we can reach.

2:00 PM EL18.11.03
Control of Surface Wrinkling through Compliant Nanostructured Interfaces Kuo-Kang Hung and Ioannis Chasiotis; University of Illinois at Urbana-Champaign, United States

A novel approach for independent control of the wrinkle wavelength and amplitude, with the additional capability for anisotropic wrinkling without the need for multiaxial loading, is presented for applications in flexible electronics. Surface wrinkling occurs due to the mechanical instability induced by the stiffness mismatch between a soft substrate and a stiff film. In a two-layer system comprised of a thick compliant substrate and a thin stiff film, the wrinkle pattern, as described by the wrinkle wavelength, amplitude and orientation, is limited by the material properties and thickness of the two layers. In this work, an interface layer of nanostructures fabricated by Glancing Angle Deposition (GLAD) is introduced to modify the surface wrinkling of polydimethylsiloxane (PDMS) due to a Cu film, thus enabling further control of wrinkling in an otherwise constrained material system. Isotropic (nanospring) and orthotropic (nanochevron) Cu interfaces were GLAD-deposited with different geometric parameters to control the in-plane stiffness of the interface. The isotropic nanospring films provided a novel means to control the scale of wrinkle patterns, namely both the wavelength and the amplitude of surface wrinkles, while maintaining the amplitude-to-wavelength aspect ratio. The anisotropic nanochevron films resulted in anisotropy ratio of ~10 which provided a unique means to modify the wrinkle direction independently of the direction of applied load. The predictions by an experimentally-calibrated analytical model for anisotropic wrinkling were in very good agreement with experiments.

2:15 PM EL18.11.04
Sustainable Future Wearable Devices Through Entirely Recyclable Organic Electronics Kyoseung Sim; Ulsan National Institute of Science and Technology, Korea (the Republic of)

The organic electronic waste produced during the synthesis and disposal of organic electronics is becoming an unavoidable problem for the environment, as a result of the growing interest and efforts being put into developing organic electronics for future technologies such as wearable electronics. Although organic e-waste may pose a risk of genotoxicity and cytotoxicity to both the natural environment and humans, most efforts to reduce the amount of e-waste have concentrated on recycling metallic components. In this study, we present a recyclable organic flexible (ROF) electronic device that may be constructed without the need for spin-coating by employing selective dissolution and closed-loop recycling of the whole process of material recapturing and reusing. Both the ROF electrode and the electronic device maintained their reliable electrical characteristics after being subjected to mechanical bending and having been recycled five times. In addition, ROF transistors and logic gates were manufactured with organic semiconductors and dielectrics, and recycled devices exhibited no significant degradation in performance. In the end, we were successful in creating a sustainable device cycle by rebuilding a variety of ROF electronics solely utilizing components recycled from a variety of working devices. In this work, ROF electronics reveal a potentially fruitful technique for a sustainable system for the future development of wearable electrons.

2:30 PM BREAK

SESSION EL18.12: Soft and Stretchable Electronic Materials
Session Chairs: Ho-Hsiu Chou and Yahao Dai
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3018

3:30 PM EL18.12.01
High-Speed Fabrication of Intrinsically Stretchable Perovskite Optoelectronic Devices on Ubiquitous Substrates (Elastomer, Paper, Textiles, *etc.*) Using Printing and Handwriting Junyi Zhao[1], Zhibin Yu[2] and Chuan Wang[1]; [1]Washington University in St. Louis, United States; [2]Florida State

University, United States

Stretchable optoelectronic devices built on thin elastomer substrates may find a wide range of applications in wearable health monitoring devices, soft robots, deformable displays, and many more. Although considerable efforts and progress have been made to explore the potential of using halide perovskites in high-performance light-emitting diodes (LEDs), existing fabrication techniques based on the rigid substrate cannot meet the growing demand from large-area flexible or stretchable displays. In this work, we report the high-speed fabrication of intrinsically stretchable perovskite LEDs (PeLEDs) printed directly on elastomer thin films, in which every single layer in the device from bottom anode to top cathode is patterned solely using the highly scalable inkjet printing approach. In addition to the elastomer, paper and textiles commonly used in our daily lives also hold great potential as platforms for next-generation flexible and wearable electronics. We have developed a highly versatile, scalable, and eco-friendly handwriting approach that enables multicolor PeLEDs (covering the entire visible spectrum) and perovskite photodetectors (PePDs) (both vertical-photodiode configuration and planar-photoconductor configuration) to be directly drawn onto various unconventional substrates (paper, textiles, plastic, rubber, metal, and three-dimensional objects) in an ultrafast and mask-free manner. This is achieved by daily used ballpoint pens filled with our uniquely formulated inks of conductive polymers, metal nanowires, and perovskite/polymer composite for photoactive layers. One of the greatest challenges associated with implementing optoelectronic devices on paper and textiles is the rough surface morphology of the yarn and fiber networks, which could result in nonuniform printed film thickness and leakage current. To tackle this issue, the ionic polymer was blended into inks to establish localized self-planarization as well as strengthen the composite stretchability. Just like drawing with multicolor pens, by writing the above functional inks layer-by-layer, high-performance perovskite optoelectronic devices can be customized on almost any target substrate within minutes even by untrained individuals. Noted that the entire manufacturing was conducted in ambient conditions without any specific moisture and temperature control. Our simplified device architecture and fabrication strategy dramatically reduce the fabrication time compared to the hours or days required by conventional microfabrication processes. The handwritten PeLEDs exhibit a brightness as high as 15,225 cd/m^2, a current efficiency of 6.65 cd/A, and a turn-on voltage of 2.4 V. The PePDs exhibit an on/off ratio over 10^4, a responsivity of up to 132 mA/W, and a response time of less than 15 ms. Owing to the extraordinary flexibility of each functional layer, the handwritten LEDs on the paper substrate could be bent to a 1 mm extreme curvature radius for over 5000 cycles without decay in performance. This work opens the avenue for perovskite optoelectronics in extremely low-cost and large-area application scenarios such as E-textile, E-paper, smart packaging, and other disposable electronics and wearables.

3:45 PM EL18.12.02

Growth of Transition Metal Oxides and Sulfides on Liquid Metal Core-Shell Particles for Optically Responsive Soft Electronics Wilson Kong[1], Rebecca Chai[2] and Christopher E. Tabor[1]; [1]Air Force Research Laboratory, United States; [2]UES, Inc., United States

Ga-based liquid metals (LM) are gaining significant noteriety as functional soft materials utilized as stretchable conductors, catalytic substrates, and a platform for materials development. Rapid formation of a surface oxide enables core-shell micro or nanoscale particle structures for LMs, further increasing their functional capabilities. However, the utility of these particles are often governed by the properties of the native gallium oxide shell which hinders their potential application space. In particular, the optical properties of eutectic Ga-In alloys (eGaIn) is limited to the UV absorption spectrum[1] compared to other noble metal nanoparticles which absorb light in the IR-Vis range. Transition metal oxides or sulfides are commonly employed as optically responsive materials for flexible electronics and sensing devices[2-4], with absorption frequencies that extend into IR-Vis. Recent research investigated the synthesis of such materials on a LM substrate due to its electron-rich surface[5], opening new opportunities for materials development. Having a synergistic combination of optically responsive coatings, with a soft conductive core can potentially lead to new hybrid materials for the next generation of optically tunable, stretchable electronics and sensors. In this work, we investigate a solution-based method to directly synthesize tungsten oxide/sulfide coatings on eGaIn surface during particle processing. The reactive surface of eGaIn drives the reduction and deposition of these materials from a single precursor, which can be tuned by multiple processing parameters. Specifically, we elucidate factors such as precursor concentration, reactive ion species, and solvent selection that can influence the favorability of tungsten sulfide or oxide growth on eGaIn particles. Additionally, we characterize the compositional and optical properties of these core-shell structures to gain better insight into their structure-property relationships. This method yields a simple and generalizable pathway for producing functional LM particles with tunable optical behavior that show potential usage in soft optoelectronic applications.

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4:00 PM EL18.12.03

Strain Dependency of Charge Transport of Stretchable Conjugated Polymers Kilwon Cho, Seung Hyun Kim and Sein Chung; Pohang University of Science and Technology, Korea (the Republic of)

Semiconducting conjugated polymers (CPs) have attracted considerable interests due to their great potential for application in flexible and stretchable electronics. However, there still remains challenging work to control the strain-induced thin-film properties, such as crystallinity, morphology, and charge transport properties of CPs. We investigated how straining of CP films affect microstructures and electrical properties of organic semiconductor films. Results on photocrosslinking of CPs by a length-modulated azide crosslinker will be discussed. Azide crosslinking selectively controls the microstructure of the amorphous domain to improve stretchability and retain the charge transport properties of CP films. Next, the influence of the backbone rigidity of CPs on thin film's stretchability and charge transport properties will be discussed. Strain-induced alignment and conformational change of polymer chains provide favorable transport pathways for charge carriers in organic thin films.

4:15 PM EL18.12.04

Intrinsically Stretchable and Highly Conductive Self-Doped Polymer Thin Films Tokihiko Shimura[1,2], Minoru Ashizawa[3], Stephen O'Neill[4], Taizo Tominaga[1,2] and Naoji Matsuhisa[2,1]; [1]Keio University, Japan; [2]The University of Tokyo, Japan; [3]Tokyo Institute of Technology, Japan; [4]University of Cambridge, United Kingdom

Soft conducting polymers, which have been prepared mainly with Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), show high conductivity, stretchability, biocompatibility, and transparency, which enables applications in electronic skins of robots and high-quality biological sensing. Although pristine PEDOT:PSS is brittle, additives can significantly enhance the stretchability.[1,2] However, insulating additives can ultimately limit the conductivity or stability under various environments, including high humidity. We hypothesized that self-doped PEDOT (S-PEDOT), which has shown

high conductivity in a recent study,[3] is an ideal system to achieve both high conductivity and stretchability with a single component.
Here, we demonstrate the high stretchability and conductivity of S-PEDOT thin films without any additives. The S-PEDOT thin film on thermoplastic polyurethane (TPU) showed a high stretchability of over 200%, which is significantly better than that of PEDOT:PSS. Our S-PEDOT showed a high conductivity of 100 S/cm alone, as well as an enhanced conductivity of 500 S/cm by the addition of sulfuric acid to the solution. The increased molecular weight through controlling the polymerization condition enabled high conductivity and stretchability. Further details regarding the processing conditions for high conductivity and stretchability will be discussed in the talk. Additionally, the S-PEDOT thin film can be patterned in a high resolution (~tens of micrometer) by nanosecond UV laser ablation. Therefore, the S-PEDOT thin film has sufficient performance to realize various stretchable electronic devices.

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4:30 PM EL18.12.06
Beyond Stretchability: Increasing the Strength, Hardness, and Survivability of Semiconducting Polymers by Crosslinking Alexander Chen[1], Jeremy Hilgar[1], Anton Samoylov[2], Silpa Pazhankave[3], Jordan Bunch[1], Kartik Choudhary[1], Guillermo Esparza[1], Allison Lim[1], Xuyi Luo[4], Hu Chen[5], Rory Runser[1], Iain McCulloch[6], Jianguo Mei[4], Christian Hoover[3], Adam Printz[2], Nathan Romero[1] and Darren J. Lipomi[1]; [1]University of California, San Diego, United States; [2]The University of Arizona, United States; [3]Arizona State University, United States; [4]Purdue University, United States; [5]King Abdullah University of Science and Technology, Saudi Arabia; [6]University of Oxford, United Kingdom

Essentially all research done on the mechanical properties of polymeric semiconductors for organic photovoltaics has had the underlying goal of increasing the "stretchability": that is, the deformability and softness. However, softness is the wrong figure of merit for many applications envisioned for organic semiconductors, including distributed sources of solar energy subject to damage by indentation, scratching, and abrasion. A focus on modulus and fracture strain at the expense of strength, toughness, and elastic range – i.e., properties characteristic of hardness and resilience – leaves many potentially lucrative applications on the table. For example, in organic photovoltaics, applications in which materials can be integrated onto surfaces already modified by human artifacts (e.g., rooftops, roads, and painted surfaces) comprise an enormous potential source of renewable energy. Additionally, the predominant focus on tensile properties fail to account for other forms of mechanical injury these devices will face (e.g., compressive forces). For photovoltaic applications that require high mechanical robustness, the mechanical properties of semiconducting polymers must be optimized to improve their strength, toughness, resilience, and hardness while maintaining their stretchability. Crosslinking is a well-understood technique for tuning the mechanical properties of conventional polymers. In this talk, we discuss our progress in increasing the mechanical robustness of semiconducting polymer films by using a four-armed azide-based crosslinker ("4Bx"). We show that low loadings of 4Bx can be used to improve the strength, toughness, and hardness of semiconducting polymer films, while maintaining their stretchability (i.e., fracture strain). Additionally, low loadings of 4Bx can be used to increase the mechanical robustness of the bulk heterojunction in organic solar cells, resulting in devices with increased survivability and stability (i.e., abrasion resistance, thermal ageing, solvent resistance).

SESSION EL18.13: Poster Session III
Session Chairs: Ho-Hsiu Chou, Francisco Molina-Lopez and Sihong Wang
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL18.13.01
EMI Sheilding Film Design, Fabrication and Characterization Mingxuan Li, Mohammad Mehdi Zarei and Paul Leu; University of Pittsburgh, United States

With the increasing use and complexity of electronic devices and systems, new types of electromagnetic interference (EMI) shielding are needed. The purpose of EMI shielding is to reduce the coupling of electronic components to surrounding radiation, which could reduce the functionality or accuracy of electronic devices or shorten their lifetimes.
In many optoelectronic applications, electromagnetic interference shielding (EMI) is required to protect electronic devices from surrounding radiation while allowing high levels of visible light transmission. Literature has yet to report structures with high transmission (over 92.5%), high EMI shielding efficiency (over 30 dB). We optimize nanophotonic structures for high EMI shielding efficiency (SE) and high visible light transmission using Bayesian optimization. We demonstrate the ability to achieve structures with 41.2 dB SE and 90.8% visible transmission and 35.6 dB SE and 95.1% visible transmission. The results of our work also provide some insight into how to design better optical surfaces.
In addition, we are developing next generation EMI shielding materials. We demonstrate the incorporation of reactive silver inks into PET and textiles. Silver thin films on PET demonstrate 82.6 dB SE in the X band (8 – 12 GHz) and 85.3 dB SE in the Ku band (12-18 GHz). Furthermore, these films maintain performance after repeated bending. Furthermore, we have incorporated these silver inks into knitted textiles and demonstrated 74.8 dB SE in the X band (8-12 GHz) and 76.6 dB SE in the X band (8 – 12 GHz). As prepared silver films do not degrade after 1,000 stretching cycles at 50% strain and maintain EMI SE higher than 70 dB after 300 min washing. This work demonstrates reactive silver ink coated films on different materials for efficient EMI shielding protection that may be used for smart wearable devices, personal medical electronics, and next generation communications.
Microgrid is another structure we explored for transparent EMI shielding. It has the advantage of controllable, scalable and flexible.

5:00 PM EL18.13.02
Achieving High-Mobility Pentacene Thin-Film Transistors by Reducing the Trapping Density Between Insulators and Organic Semiconductors Yunseok Jang, Jeongdai Jo and Seung-Hyun Lee; Korea Institute of Machinery & Materials, Korea (the Republic of)

Organic thin-film transistors (OTFTs) continue to attract much attention as a key driving component of commercial wearable devices such as glasses, watches, wristbands and belts. Wearable devices are also being studied in the direction of electronic skin (e-skin) by fusing various sensors.[1-2] Because e-skin requires effective communication between biological and electrical signals, OTFTs are frequently used to detect target biomolecules and biological signals. For this, it is necessary to develop a high-performance OTFTs, and many studies are in progress.[3]

It is well known that interface control is very important in the fabrication of high-performance OTFTs. Many studies show the importance of treating the dielectric surface to impart improved molecular ordering such as good morphology and molecular alignment. [4] Although these findings are important, we consider that carrier trapping in the channel region formed between the insulator and the organic semiconductor will also be an important parameter. Holes are carriers in p-type organic semiconductors such as pentacene, and this study was conducted considering that holes may be easily captured by hydroxyl groups on the surface of the insulator. Hydroxyl groups may be present due to incomplete crosslinking, as residual hydroxyl groups from the solvent due to incomplete baking after solution-based film formation, or from absorbed water molecules due to exposure to ambient air. [5,6]
To clearly understand these effects, the surface roughness and surface energy of the insulator and the crystal structure were uniformly controlled. In addition, hundreds of nanometers of cured poly(4-vinyl phenol) (PVP) and tens of nanometers of additional layers were used to maintain the same insulating properties and to control the carrier density by adjusting the content of hydroxyl groups. As a result, the charge mobility was increased by 400% by controlling the carrier trapping density. This result shows that control of the carrier density is an important factor in the fabrication of high-performance OTFTs. [7]

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5:00 PM EL18.13.03
Piezoelectric Anisotropy-Induced PVDF Cube Switch with Multiple Responses Hyeongjin Jo, Yujun Song and Ji-Hyeon Song; Dankook University, Korea (the Republic of)

Smart materials, which suggest a way to overcome the limitations of conventional ones, have led researchers and scientists beyond the possibility now. Among those, piezoelectric materials have advantageous properties such as being light-weight and self-powered. This innovative material opened a new chapter of trend in electronics: flexible electronics. Remarkably, PVDF film has been spotlighted among the piezoelectric materials by the scientist due to its flexibility, and biocompatibility. Owing to its properties, it has great potential to be applied in a diversity of fields. Piezoelectric materials have another distinctive characteristic: anisotropy. Due to the anisotropy of the materials, they generate an independent electrical signal in accordance with their own piezo element axis.

In this study, we conceptualize a multi-responsive cube switch by utilizing anisotropy of PVDF film with a structural approach. Since the cube switch is in a 3D structure, the cube exhibits multiple responses simultaneously from its sides with a single stimulus. By diversifying cube planar figures, the amount of electrical potential value from the cube side can be adjusted. When the cube planar figure is in the 2D plane, each section generates an identical voltage as a response to vertical pressure. However, when this cube planar figure is folded and assembled into a 3D structured cube, each side of the cube starts to get individual coordinates in terms of the piezo axis. This dimensional change (from 2D to 3D) and anisotropy of PVDF film allow the cube switch to respond with multiple voltage waveforms with a single force.

As an extended method, we suggest cutting angle variation of planar figures as a method to diversify response from the device. Responses from the vertical sides of the cube are closely related to the cutting angle. The external force which aligns with the piezo definition eventually triggers piezoelectric materials to generate voltage. When the cutting angle starts to deviate from its original direction, the angle between the force direction and piezo definition also departs. Ultimately, the deviation of the force direction from the corresponding piezo axis makes the device generate a different electrical signal. By combining the two methods above (cube planar figure designs and cutting angle variation), we variegate possible cases of response from the device. The design stage and fabrication process of the cube switch is relatively simple and cost-effective than other piezoelectric material-based devices. Simply cutting and folding is enough to make this smart responsive device.

The PVDF cube switch has the potential to be applied to a system where diversity of response is needed, such as a security system. The security system with a lack of cases in passcode patterns is fatal to users. This cube-type switch can compensate for possible problems of the conventional security system. The multi-responsive security system will be highly user-dependent and inimitable by the third party. Also, users may easily designate and variegate the passcodes by adjusting pressing displacements, cube planar designs, and the number of switches in the system.

5:00 PM EL18.13.04
Active-Matrix Electrochemical Display Based on Stable Crosslinked-Silver Nanowires InCheol Kwak, Dong Gue Roe, Soo Young Cho, Yonghyun A. Kwon, Seonkwon Kim, Jung Woo Moon, Seonmi Eom and Jeong Ho Cho; Yonsei University, Korea (the Republic of)

In recent years, advances in technology for flexible optoelectronics have attracted considerable attention. According to the industrial demands, numerous types of research have been devoted to improving the performance of these devices. The transparent electrodes, which are an essential component in flexible optoelectronics, must satisfy the optimum compromise between optical transparency, electrical conductivity, and mechanical flexibility. Silver nanowires (AgNWs) based on percolating networks have been considered the most promising transparent electrodes; because they yield a low sheet resistance at high optical transmittance and high mechanical flexibility with their physical properties attributed to a high-aspect ratio. Moreover, AgNWs have also several advantages of low-cost processing and compatibility with large-area deposition owing to the simple solution process.
Although AgNWs networks possess these outstanding characteristics, it is still a great challenge to utilize AgNWs adequately in integrated electronic devices due to the inherent characteristics of high surface roughness, low work function, instability in the air, and poor adhesion to plastic substrates. Additionally, high-resolution patterning of AgNWs with desired line width and line spacing must be developed to extend the application of complicated optoelectronics. Herein, we report a simple processing method for fabricating high-resolution AgNWs patterns using a solution-processable crosslinking agent. A crosslinker referred to as 2Bx_4EO, which can be dissolved in alcohol solvents is applicable to various materials containing alkyl chains. In this study, patterned AgNWs were obtained by crosslinking polyvinylpyrrolidone from nanowires synthesized by the polyol process. Moreover, the strategy of selective wetting of conductive polymer only onto AgNWs patterns was employed for complementing the inherent characteristics of AgNWs. Furthermore, we demonstrate the application of AgNWs/polymer hybrid conductive films to fabricate organic electrochemical transistors and electrochromic cells.

5:00 PM EL18.13.05

Structural Control of Organic Solar Cells by Photo-Crosslinking Reactions Ryo Suzuki[1,2], Makoto Miyasaka[1], Kyohei Nakano[2], Yuto Ochiai[2], Yumiko Kaji[2] and Keisuke Tajima[2]; [1]Tokyo Denki University, Japan; [2]Riken, Japan

Current organic thin-film solar cells have problems in the precise controls of the nanostructures in thin films which are stable and suitable for the efficient charge generation. In this study, we aim at constructing the ideal mixed donor/acceptor structures with high stability by immobilization of organic semiconductors through photo-crosslinking. Several azide- and diazirine-based crosslinkers with one to four reaction points were synthesized and used as photo-crosslinkers. It has been reported that these photo-crosslinkers do not change the electrical properties of the semiconductor polymers by crosslinking because the photo-generated singlet active species (i.e., nitrene or carbene) insert mainly into the alkyl side chains but do not react with the aromatic rings. We first investigated the immobilization of mixed bulk heterojunction (BHJ) structures by photo-crosslinking. PM6:Y6 was selected as the donor/acceptor materials, and the mixed thin film with 1 wt% crosslinker was irradiated with corresponding UV light for a designated time. The physical properties and the structure of the resulting thin films and their solar cell properties were evaluated. After the light irradiation, the BHJ thin films were washed with chloroform and the absorption spectra of the films were measured. As the result, about 30-90 % of visible light absorption remained relative to the film without irradiation, depending on the irradiation time. These results suggest that the photo-crosslinking reaction insolubilizes PM6 and immobilizes its structure in the BHJ thin films. We evaluated the properties of the organic solar cells with the crosslinked films. It was found that the addition of crosslinkers alone did not change the solar cell performance with the power conversion efficiency of about 14% under the simulated solar light, but photo-crosslinking of the BHJ films resulted in degradation of the photovoltaic properties. We also apply the crosslinkers to the sequentially deposited films of Y6 and PM6 to see the effects of the crosslinking of each layer on the performance. Interestingly, in contrast to the mixed films, the organic solar cells prepared by the sequential depositions in which only the PM6 layer was photo-crosslinked showed no degradation in the photovoltaic performance (PCE 13.8%) that is comparable to those of the BHJ devices. These results give important insight into the morphological control in organic solar cells by using the singlet photo-crosslinkers.

5:00 PM EL18.13.07

Cu-Metal Assisted Chemical Etching that can Fabricate Auxetic Microstructures of Thin Flexible Si Wafer Eunsol Lee, Changsoon Kim and In-Suk Choi; Seoul National University, Korea (the Republic of)

Metal assisted chemical etching (MACE) has attracted considerable attention as an anisotropic Si etching process due to its simplicity and versatility. In this presentation, we introduce copper-based MACE that can substitute for conventional noble metal (Au, Ag, Pt, etc.)-based MACE processes. By systematically controlling the etching parameters, we develop the Cu-MACE process for the first time to tailor the size and depth of anisotropic Si microstructures. Consequently, this led to a cost-effective and simple etching process to fabricate auxetic structured Si membranes that can be used as flexible and deformable substrates for wearable devices.

5:00 PM EL18.13.08

Dry Adhesives Capable of Selective Adhesion Control based on Shape Memory Polymer Han Jun Park, Minsu Kim, Dokyung Kyeong, Ga-in Lee and Moon Kyu Kwak; Kyungpook National University, Korea (the Republic of)

As substrates used in display and semiconductor manufacturing processes become thinner and larger, the demand for ‘transfer printing’ systems for transferring objects with various surface profiles is increasing significantly. High efficiency of this system, carried out with pick-and-place method, requires strong adhesion for ‘pick-up’ and weak adhesion for ‘place’. The so-called 'adhesion switching' is an essential mechanism in the transfer printing systems. Traditionally, this adhesive conversion process used a friction, a vacuum chuck system or interlocking system, and a chemical-based wet adhesive system. However, while these proposed methods can be 'picked up' efficiently and reliably, their use is limited because they require complex equipment and mechanical elements, and the adhesion is not weak enough to 'place'. Various studies have shown that, away from friction, vacuum systems or adhesion by chemicals, 'dry adhesives' provide new pickup possibilities based on Van der Waals interaction. Dry adhesives are rapidly being commercialized in the transfer printing field, attracting attention for their low cost and mechanical durability. In particular, gecko-inspired dry adhesives succeeded in exerting a strong adhesion of more than 20 N/cm^2, developing a massive production system for the manufacture of biomimetic dry adhesives. However, despite their excellent performance, there are some limitations due to the problem of implementing an adhesive removal mechanism for stable detachment when switching adhesion of artificial dry adhesives. Although various attempts have been made to solve these problems, the proposed methods are mainly applied to limited surface roughness such as smooth surfaces. In addition, there is an inefficient cost problem because additional equipment such as a vibration jig or gripper is required.

Shape memory polymers are smart materials with the ability to remember ‘permanent shape’ through ‘shape memory effect’ and to be fixed as ‘temporary shape’ in certain stimuli. Many methods have been suggested to implement a transfer printing system as a mechanism to achieve pick-up by adapting the surface shape to the substrate using SMP's ‘shape memory effect’ and return to its initial shape to remove adhesion. However, it still remains a time-consuming manufacturing process, such as the need to combine multiple materials and a long thermosetting time.

In this work, we report the design of SMP Dry adhesive for a highly reversible thermally active adhesive switch systems using NOA63, a material with a programmable glass transition temperature based on curing conditions. Overcoming the limitations of fabrication time of adhesives introduced previously, we developed an adhesion switch system that can be manufactured very quickly and simply through UV irradiation. The ‘adhesion on mode’ of the fabricated SMP Dry adhesive showed a pull-off strength of about 24 N/cm^2 and could be adapted to various surface topologies. It was also confirmed that the substrate was safely detached by effectively removing the pull-off strength to 1.5 N/cm^2 or less in the 'adhesion-off mode' by the micro-lens pattern formed on the surface. These characteristics of SMP Dry adhesive show strong potential to pick-and-place not only fragile substrates such as wafers and glass, but also various substrates such as micro/nano-scaled semiconductor devices, metals, and plastics. Therefore, it is expected to be applied to an efficient transfer system in a wide range of fields such as display, semiconductor, and robot industries.

5:00 PM EL18.13.09

Sensitive SARS-CoV-2 spike Protein Nano-sensor (CovPNs) based on Gold-nanoparticles Decorated Micropatterned Poly(3,4-Ethylenedioxythiophene) Nanorods and Immobilized with Natural Receptor Angiotensin-Converting Enzyme-2 Syed Atif Ali[1,2,3] and Hsiao-hua Yu[1]; [1]Institute of Chemistry, Academia Sinica, Taiwan; [2]National Yang Ming Chiao Tung University, Taiwan; [3]Taiwan International Graduate Program-Sustainable Chemical Science and Technology, Taiwan

The Carboxyl-functionalized poly(3,4-ethylenedioxythiophene) (EDOTAc) Nanorods were designed into sensitive SARS-CoV-2 Nano-sensor surface (CovPNs) decorated with electrodeposited gold nanoparticles (AuNPs) was found to be highly sensitive. The developed CoVPNs based on electrochemical signals which is good alternative to replace the tests which require lot of time. The structures made into hybrid nanomaterial has shown excellent electrochemical properties. The sensor surface was characterized by electrochemical techniques, SEM, Fluorescence microscopy and XPS. Moreover, morphology of the nanomaterial was characterized by scanning electron microscopy. The results show a linear response for the diluted spike protein of SARS-CoV-2. DPV technique was used for sensing the spike protein on CoVPNs sensor surface which shows that in future the developed surface has potential to be integrated in flexible or wearable immunosensors and transistors for the detection of SARS-CoV-2 spike protein in a short time.

5:00 PM EL18.13.10
Ion Doping Induced Threshold Voltage Control in Electrolyte Gated Transistors Kyung Gook Cho[1], Minsu Kim[1], Kihyon Hong[2] and Keun Hyung Lee[1]; [1]Inha University, Korea (the Republic of); [2]Chungnam National University, Korea (the Republic of)

Ion doping and dedoping phenomena in organic/polymer semiconductors are important for improving the device performance of electrolyte-gated transistors (EGTs) in various iontronic applications including neuromorphic devices, nonvolatile memories, and chemical/bio sensors. In this study, the effects of component ions and their mixtures on the electrical characteristics of the EGTs were systematically investigated utilizing ionic liquid-based solid electrolytes (known as ionogels) as a high capacitance gate dielectric. Electrochemical impedance measurement, secondary ion mass spectrometry (SIMS), and optical absorbance spectroscopy confirmed that anions in the ionogels determined the carrier accumulation in organic *p*-type semiconductors. Accordingly, transistor characteristics such as threshold voltage, subthreshold swing, and charge carrier mobility were dominated by the type of anions because the positive holes are the majority charge carriers. More importantly, a new concept for fine tuning threshold voltage, which is crucial for the determination of power consumption and operational characteristics of logic circuits, was suggested by controlling the molar fractions of binary anions. This new and simple strategy successfully controlled the inversion characteristics of ion-gated inverters. Thus, this study proposes a useful route for tuning the electrical characteristics of EGT-based logic circuits as well as provides an important guideline for material selection in high-performance iontronic thin-film devices.

5:00 PM EL18.13.11
3D Printable Double-Network Solid Polymer Electrolytes for Accurate Motion Monitoring Chae Yoon Lee, Jeong Mu Heo and Keun Hyung Lee; Inha University, Korea (the Republic of)

Solid polymer electrolytes based on ionic liquids, also known as ion gels, have gained significant research interest due to their great features including mechanical robustness, high stretchability, non-volatility, thermal/electrochemical stability, and high ionic conductivity. To increase the durability and reliability of stretchable strain sensors, sensing elements can sustain a wide range of mechanical variation with sufficient mechanical strength. To achieve this, we employed two different polymer networks, or double networks (DN), by using chemically and physically crosslinkable polymer hosts in ionic liquids. The chemically crosslinked network in the DN ionogel provided sufficient adhesiveness between a substrate and the ionogel by incorporating chemical bonds. The physically crosslinked network in the gel offered adequate viscosity for 3D printing. In terms of sensing capability, improving the sensitivity of stretchable sensors is essential for accurate conversion of mechanical deformation. To improve the sensitivity, we designed and fabricated delicate and unique structures by using 3D printing. We designed and patterned gaps in the sensing element that can apart as the sensor stretched, and close as it contracted, which leaded to a large variation in the relative resistance and thus high sensitivity upon deformation. The resulting stretchable strain sensors can precisely detect various motions and convert them into electrical signals.

5:00 PM EL18.13.12
Thermally Stable n-Type Electrolyte Gated Transistors Using High Capacitance Ionogel Dielectrics Su Jung Kim, Dong Hyun Park and Keun Hyung Lee; Inha University, Korea (the Republic of)

Organic electrolyte gated transistors (OEGTs) have gained increasing interest as the principle building unit for printed logic circuits, bioelectronics, and artificial neural networks owing to their outstanding features including low-voltage operation and high transconductance. While OEGTs based on p-type polymer/organic semiconductors are well developed, n-type counterparts still suffer from low performance, thus, precluding the development of all-printed large-area OEGT-based complementary circuits. Most of the recently reports on n-type OEGTs focus on the design and synthesis of high-performance semiconductors and less attention has been made in the electrolyte dielectrics. In these studies, a liquid-state NaCl solution was employed as the dielectric. However, in the case of NaCl solution electrolyte, evaporation of the volatile water prevents long-term stability of the devices even at ambient conditions. In this present study, we fabricated n-type OEGTs using nonvolatile high-capacitance ionogel dielectrics consisting of ionic liquid solidified with 3D polymer networks. Resulting devices operated at low voltages (< 2 V) and exhibited high on/off current ratios (~10^5), which are similar to those of p-type OEGTs. Carrier accumulation and ion doping phenomena in the semiconductor channel were systematically investigated by using impedance spectroscopy, optical absorbance spectroscopy, current relaxation, and cyclic voltammetry. In addition, owing to the non-volatile property of the ionogels, OEGTs maintained their electrical performance even after high temperature annealing as well as long-term operation in ambient conditions. Furthermore, we demonstrated flexible all organic complementary logic circuits by connecting n- and p-type OEGTs.

5:00 PM EL18.13.15
Entangled Hydrogel Staking Layers: Universal Adhesive Material for Soft Electronics Yejin Jo, Yurim Lee and Jungmok Seo; Yonsei University, Korea (the Republic of)

The rapid growth of bioelectronics has stimulated research into soft electronics that integrate electronic devices to human bodies. Soft electronics are commonly composed of rigid electronics interconnected with soft electrode materials having flexibility, elasticity, and Young's modulus similar to that of native tissues to ensure conformal contact with the tissues. Although many materials for interconnecting soft materials to rigid electronics have been reported, there are only a few universal biocompatible bonding techniques have been studied.

Here, we developed a universal adhesive for soft electronics by utilizing layer-by-layer (LbL) stacking of poly(vinyl alcohol) (PVA) and tannic acid (TA) hydrogels. The sub-micron PVA-TA (PT) adhesive allows materials-independent bonding by hydrogel network entanglement in a few minutes mediated by sequential swelling and heat treatment at 130°C using a hair iron. For example, the interfacial toughness of two glued stainless steel and two glued polyimide sheets by PT adhesive was 3.6±0.8 MPa and 0.62±0.09 MPa, respectively. Utilizing hydrogels as a soft electrode materials, the heat treatment process for the integration should be avoided to prevent the deformation and degradation of the hydrogel. The developed PT adhesive allows hydrogels to be bonded without further heat treatments via polymer chain diffusion and entanglement, which occurs when the dried PT glue chain absorbs interfacial water of the adherend hydrogel. We demonstrated applications of PT adhesive for soft electronics through a flexible ionic hydrogel touch panel and a hydrogel strain sensor. A poly(acryl amide) (PAAm)-based ion gel was connected to the controller board with PT adhesive-coated FFC cables to fabricate a flexible touch panel. The connection point between the ion gel and the FFC cable maintained a stable attachment in the vigorous stretching test. The ring-shaped strain sensor is fabricated with poly(acrylic acid) (PAA)-based conductive gel attached to an eco-flex ring by PT adhesive to detect the bending motion of a finger. The conformally contacted strain sensor successfully detects finger-bending motion with 26.1% sensitivity.

5:00 PM EL18.13.16
Strategy to Implement PEDOT:PSS Spin-Coating on the Oxide-Metal-Oxide Electrode for Ink-Jet and Stretchable OLEDs Donghyun Kim, Changmin Lee, Geonwoo Jeong, Dong Hyun Choi, Tae Wook Kim, Sye Hamad Ullah Shah, Hyun Woo Jo, Yeong Beom Kim, Amjad Islam, Keum-Jin Ko and Seung Yoon Ryu; Korea University, Korea (the Republic of)

Organic light-emitting diodes (OLEDs) has emerged as the next-generation display technology due to its many interesting traits, such as high brightness, low power consumption and excellent mechanical flexibility. Although indium tin oxide (ITO) is the most commonly used materials for transparent conducting electrode (TCE) of OLEDs. However, the brittle nature of ITO electrodes and their poor tolerance to external mechanical stress have substantially limited their application in flexible OLEDs. To address this issue, we developed a mechanically robust oxide/metal/oxide (OMO) structured TCE for high performance OLEDs.
In OMO structure, Molybdenum trioxide (MoO_3) with MoO_3/Au/MoO_3(MAM) electrode has proven very useful for this structure. In addition, the solution process of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) can achieve solution process, easily tunable of structure and electrical properties. However, owing to its susceptible nature to water, MoO_3 can damage the entire structure of the MAM electrode. Even though MoO_3/PEDOT:PSS layer could act as hole injection layer, the surface of film could be rough, which results in the instability of OLEDs. Herein, we investigated to maintain the surface morphology of upper MoO_3 electrode for developing the core technology of soluble OLEDs with PEDOT:PSS coated on MAM electrode after UV/ozone(UVO) treatment. Mo receives energy and oxidizes to Mo^{+5} and Mo^{+6}. Through the UVO treatment, the concentration of Mo^{+5}, which acts as an reactor with PEDOT:PSS, decreases and the reaction of MoO_3 with PEDOT:PSS is weakened. Thus, the stable surface morphology could be achieved without affecting the electric and optical properties. The champion OLED device with UVO treatment MAM/PEDOT:PSS TCE achieved the turn-on voltage of 2.66 V and a maximum current efficiency of 105 cd A^{-1} by decreasing energy gap between MoO_3 and TAPC for smooth current injection. This findings shows that OLEDs based on MAM/PEDOT:PSS TCE has the great potential for future display and lighting applications, as well as novel application in soft mechanical electronics.

5:00 PM EL18.13.17
Exploring Reduced Thickness of Au in Oxide-Metal-Oxide (OMO) Electrode for Stretchable Organic Light-emitting Didoes Yeong Beom Kim, Seung Yoon Ryu, Keum-Jin Ko, Amjad Islam, Donghyun Kim, Changmin Lee, Geonwoo Jeong, Dong Hyun Choi, Tae Wook Kim, Hyun Woo Jo and Sye Hamad Ullah Shah; Korea University, Korea (the Republic of)

The challenges for organic light-emitting diodes (OLEDs) with a perfect form factor have led to research into advanced manufacturing processes. Incorporation of OLEDs into wearable, epidermal, and stretchable electronics, with color stability, and high brightness under intensely strained bending/stretching has been of major interest. This interest has led to various studies on electrodes as a replacement of indium tin oxide (ITO). Transparent electrode based on an oxide-metal-oxide (OMO), where a thin metal layer is sandwiched between two dielectric or oxide layers, is similarly a promising candidate. In terms of flexibility and stretchability, a thin and ductile metal layer has the role of resisting fracture since it acts as the crack stopper or retardation on an elastomeric substrate. Therefore, a thin OMO electrode could be proposed for stretchable electronics because of its better hole injection and optical transmittance. However, since the Au electrode greatly affects the transmittance of the device, the thickness should be sufficiently considered. In many studies, it has been reported that noble metals form drivable films from 5 nm or more. When Au or Ag is deposited with a thin thickness (1 ~ 5 nm), island growth occurs and it is difficult to play a role as an electrode. Herein, we demonstrate that the OLEDs can be driven sufficiently even with a 3 nm electrode and can achieve electrode characteristics for flexibility and stetchability. Without lower oxide layer, noble metals grow as islands, however, with oxide buffer layer, grain growth is suppressed with increased surface energy. The ultra-thin Au based tri-layer electrode showed properties that could replace ITO and was helpful for out-coupling of OLEDs. Additionally, we confirmed ultra-thin Au is efficiently worked at various oxide layers (MoO_3, WO_3 and V_2O_5).

5:00 PM EL18.13.18
Scalable and Multifunctional Sensors by Inkjet Printed Graphene Network Feiran Wang, Nathan Cottam, Jonathan S. Austin, Jisun Im, Jonathan H. Gosling, Mark Fromhold, Richard Hague, Christopher Tuck, Oleg Makarovsky and Lyudmila Turyanska; University of Nottingham, United Kingdom

As a novel layered 2D material, graphene has induced a boom in the field of sensor research around the world due to its advantages in mechanical, thermal, and electrical properties.[1] However, the need for high quality mass production, large area fabrication and the homogeneous deposition on various substrates poses a great challenge. We employ inkjet printing as an advanced and convenient fabrication method for achieving comparative effectiveness and multimaterial vertical stacking.[2] A scalable fully inkjet printed graphene multifunctional sensor matrix which integrated humidity, thermal, and pressure sensors was fabricated using two layers of graphene arrays separated by a dielectric layer. The integration of all three sensors into a matrix required that each sensor provide output responses to a specific stimulus without being interfered by other stimuli. The bottom graphene layer can sense the temperature change and the top graphene layer were as the humidity sensing arrays. The dielectric layer sandwiched between two graphene arrays acted as an active layer for the capacitive pressure sensors. The responses have been modelled by inter flake tunnelling of the printed graphene network.[3] Further functionality can be integrated by bringing in additional layers, such as detecting hazardous chemicals and gases. [4] Such multifunctional sensors can be fabricated on flexible substrates such as fabrics and have wide applications in environment monitoring and healthcare devices.

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5:00 PM EL18.13.20
Integration of Electric Circuits into Microprinted Cell Culture Scaffolds for Three-Dimensional Microelectrode Arrays Malte Siegmund[1], Jann Harberts[1], Robert Zierold[1] and Robert H. Blick[1,2]; [1]Universität Hamburg, Germany; [2]University of Wisconsin-Madison, United States Minor Outlying Islands

Microelectrode arrays (MEAs) for non-invasive electrical readout of neurons are a valuable tool for long-term studies of neuronal network signaling on a single-cell level. However, conventional MEAs are traditionally built only in 2D and thus do not represent the three-dimensional network topology of the human brain. Here, we present an approach to equip planar MEAs with 3D microscaffolds featuring circuitry for enabling three-dimensional brain-on-a-chip (BoC) devices with electrical readout on a cellular level. Recently, we presented such microscaffolds prepared by direct laser writing (DLW) for enabling human induced pluripotent stem cell (hiPSC)-derived guided neuronal networks in 3D. Tower-like structures with cavities on the top determined specific locations for neuron settling while interconnecting tunnels confined axonal outgrowth for neuronal network formation. Therefore, changes in the arrangement would reflect onto the formation of the respective networks. However, the electrophysiological readout was limited to individual—and invasive—patch clamp measurements on selected cells from the network.[1],[2] For collective and non-invasive long-term experiments, i.e., *in situ* studying during the cell culture period, this approach for its part needed an addressable extracellular electrical readout system to be implemented into the tailor-made scaffold structure. Herein, we utilized electrodeposition (ED) of gold to form integrated electrodes inside the in this case hollow towers.

Specifically, by printing directly onto electrodes of tailor-made or commercially available MEAs, each tower was individually addressed for ED, and gold was deposited until the vertically growing electrodes filled the entire tower and the gold reached the scaffold cavities. Note, the porosity of the gold can be tuned by changing the deposition rate which allows for optimizing the surface topography to enhance cell coupling to the electrode.[3] The versatile nature of the MEA production as well as the DWL and the ED enables the production of addressable electrodes within the third dimension of almost any shape. Thus, these results take a significant step toward application in analyzing the information transmission within neuronal networks and understanding of underlaying mechanism orchestrating information procession in 3D.[4]

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5:00 PM EL18.13.23
Wide Range Pressure Detection Using Highly Sensitive, Flexible Organic Thin-Film Transistor Sensors Dong Hyun Park, Su Jung Kim and Keun Hyung Lee; Inha university, Korea (the Republic of)

Solidified ionic liquid known as ion gels have been investigated in various applications because of their exceptional material characteristics such as high specific capacitance, outstanding chemical, thermal, and electrochemical stability, non-flammability, negligible vapor pressure, and rubber-like mechanical robustness. Flexible pressure sensors that convert various external mechanical signals can be employed in a wide range of applications including human health monitoring, soft robotics, and artificial intelligence. A variety of sensing mechanisms including piezoelectric, capacitive, and piezoresistive can be used in flexible pressure sensors. Flexible sensors require high sensitivity, a wide sensing range, and a short response time. Capacitive sensors based on ion gels have advantages for being used as flexible pressure sensors because of their stability, fast response, and simple device architectures. However, low sensitivity of the pressure sensors often limits their applicability and practicality. To overcome this issue, we employed organic thin-film transistors and high capacitance ion gels for highly sensitive flexible pressure sensors. By utilizing organic thin-film transistors, weak mechanical stimuli can be amplified into large electrical signals, leading to very high sensitivity. Furthermore, the resulting transistor sensors operated at low voltages below few volts owing to the high capacitance of the ion gel gate dielectrics. In addition, performance of the transistor sensors was enhanced by optimizing the morphology and composition of active layers. As a result, transistor-based pressure sensors can reliably and sensitively convert external mechanical stimuli to electrical signals.

5:00 PM EL18.13.26
Flexible Microfluidic Platform for Heavy Ion Detection Stavros Chatzandroulis[1], Myrto-Kyriaki Filippidou[1], Aris Kanaris[1], Sotiris Ntouskas[1], Evangelos Aslanidis[2], Angeliki Tserepi[1], Georgios Tsekenis[3] and Dimitrios Tsoukalas[2]; [1]NCSR, Greece; [2]National Technical University of Athens, Greece; [3]Biomedical Research Foundation of the Academy of Athens, Greece

Heavy metal ions, such as lead (Pb), cadmium (Cd) and mercury (Hg), are important global environmental threats as they accumulate throughout the food chain causing chronic diseases. We can find them in soil, air or water. Conventional detection methods (i.e. high performance liquid chromatography, HPLC) consist of bulky and expensive equipment, while the required sample handling processes are usually time consuming, limiting their use to specially designed laboratories. Thus, there is an urgent need for the development of portable devices for heavy ion detection in order to replace or complement the conventional detection methods. The solution can be provided by developing new detection systems based on the combination of microfluidic technolog and electrochemical sensing, such systems are lightweight, compact and portable, low cost and can be used in both laboratory and on-site measurements. To date, efforts towards this direction have been proposed, yet there is still room for new approaches which can facilitate the uptake of these novel approaches.
In this work, we propose a fast and easy way to implement a microfluidic device made of a mixing unit and detection unit incorporating an array of six Pt nanoparticle (PtNP) heavy metal ion sensors, on a low-cost polyimide (Kapton) flexible substrate using standard lithographic techniques. The mixing unit is necessary for the passive mixing of the sample (i.e. water) with a buffer solution prior to the detection of the heavy metal ions. The mixing unit takes the form of a square wave channel with two inputs: one for the sample and the second for the buffer solution. The design of the mixing unit accommodates an effective mixing index over a wide range of flow rates on a small footprint, while the detection unit encompassing six interdigitated electrode pairs (IDEs) is placed after the mixing unit. The device fabrication process consists of the following steps: First an array of six IDEs is deposited on a kapton substrate, consisting of an adhesive 10 nm thick Ti layer and 40 nm thick Au layer. The IDEs are patterned using photolithography having inter-finger spacing of 10μm. Then, a layer of a dry resist film is deposited on the kapton substrate using a laminator, followed by a lithography step to pattern the microchannels on the dry resist and unveil the IDE array. Afterwards, platinum nanoparticles (PtNPs), having a mean diameter of 4 nm, are deposited between the IDEs using a modified DC magnetron sputtering system that allows the control of the surface density covered by the PtNPs. The surface coverage of the PtNPs is close to 49%, which results in an interparticle distance of few nm. The resistance of the devices is of order the of a few hundreds of kOhms. To functionalize the sensors, the device is first treated in oxygen plasma to activate the channel followed by immersion in APTES solution. Applying this chemical functionalization procedure DNAzymes may be immobilized in between the PtNPs. The presence then of metal ions over the sensor area leads to the cleavage of the double-stranded DNAzymes which is then registered as a resistance increase enabling the detection of heavy metal ions. The device is finally ready to be used after sealing with a polyolefin film coated on one side with a silicone adhesive.
For the evaluation of the mixing channel a syringe pump was used, while the device was placed inside a pmma chip holder which enables the solutions to flow in and out of the flexible chip using silicone tubes. Yellow and blue food coloring solutions were used as starting solutions. These two solutions were inserted from the two inputs and were mixed before reaching the detection unit. The final solution at the channel output was green verifying the successful mixing of the two solutions. The same chip holder was then used to test the PtNPs sensors. As a proof of concept, the detection of 20 μM of Pb^{2+} ions using the prototype microfluidic device was achieved.

5:00 PM EL18.13.27
Highly Integrated Stretchable Electronics by Photo-patternable Elastic Polymer Electrolyte Jiyeon Ha[1], Wanho Cho[2], Hyukmin Kweon[1], Ukjin Jeong[1], Seokran Choi[1], Borina Ha[1], BongSoo Kim[2] and Do Hwan Kim[1]; [1]Hanyang university, Korea (the Republic of); [2]Ulsan National Institute of Science and Technology, Korea (the Republic of)

Recently, interest in ion-based materials has emerged, leading to the development of stretchable electronics such as healthcare monitoring, soft robotics, biosensors, wearable devices, and skin-like electronics. Stretchable polymer electrolyte is the best applied to organic electrochemical transistors (OECTs) for flexible neuromorphic circuits and various skin electronics due to ion-driven signal processing with low power consumption and its biocompatibility. To outstanding electronic devices functionality, the OECTs are required to have high integration capabilities through high-resolution patterning.

Nevertheless, this is challenging because of their intrinsic rubbery nature of the elastic polymer electrolyte, which is not accomplished simultaneously by microfabrication techniques.
In this work, we demonstrate an unprecedented photo-patternable elastic polymer network electrolyte (elastic-PNE), which thermoplastic polyurethane with ionic liquids (i-TPU) and azide ($-N_3$) photo-crosslinker with ethylene oxide (EO) could form the network structure by crosslinking through direct UV(254nm) exposure. The azide moieties in the crosslinker can be activated by UV exposure, which react with the alkyl chain of TPU to occur the C-H insertion reaction. With the increase of EO chains, the elastic-PNE retains their electrochemical properties even after the rinsing process as well as mechanical characteristics. These result from the EO structure of the crosslinker, which can supply superior ionic interaction and flexible chain segmental motion to electrochemical and mechanical properties. In addition, the elastic-PNE can achieve a high-resolution photo pattern with microscales size ($<$ 10µm) by direct microlithography process. Consequently, we believe that our approach will present new guidance for next-generation neuromorphic and skin electronics.

5:00 PM EL18.13.28
3D Printing of Conversion Cathodes for Enhanced Custom-Form Lithium Batteries Jorge A. Cardenas, John P. Bullivant, Bryan Wygant, Igor Kolesnichenko, Aliya Lapp, Devin J. Roach, Timothy Lambert, Eric Allcorn, A. A. Talin, Adam Cook and Katharine Harrison; Sandia National Laboratories, United States

Additive manufacturing techniques can enable the fabrication of batteries in nonconventional form factors, enabling higher practical energy densities due to improved power source packing efficiency. Furthermore, energy density can be improved by transitioning from conventional Li-ion materials to lithium metal anodes and conversion cathodes. Iron disulfide (FeS_2) and iron trifluoride (FeF_3) are two promising conversion cathodes of commercial and academic interest, but the 3D direct-ink-write (DIW) printing of inks made from these materials for custom-form battery applications has yet to be demonstrated. In this work, the deposition of FeS_2 and FeF_3 inks are investigated and optimized using DIW 3D printing to produce custom-form batteries. Two distinct custom form-factors, one on wave-shaped current collectors and the other on cylindrical current collectors, are demonstrated and shown to exhibit performance similar to coin cells when conventional Celgard separators are used. Additionally, FeF_3 cells are integrated with a DIW printed separator consisting of an electrolyte exchanged PVDF-HFP based ionogel [1], which resulted in 5-7 stable charge/discharge cycles before degradation occurred. Meanwhile, in FeS_2 inks, it was found that cathodes with a ridged surface, produced from the filamentary extrusion of highly concentrated inks (60-70% solids w/w%) exhibited optimal power, uniformity, and stability when cycled at higher rates (in excess of C/10) [2]. Overall, DIW printing of conversion cathodes is demonstrated to be a viable path toward the making of custom-form conversion lithium batteries. More broadly, surface ridging is found to optimize rate capability, a finding that may have broad impact beyond FeS_2, FeF_3 and DIW extrusion.

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5:00 PM EL18.13.29
Hybrid Elastomers with Variable Electromechanical Properties Guolin Yun[1], Tim Cole[2], Yuxin Zhang[2], Jiahao Zheng[2], Shuaishuai Sun[3], Yiming Ou-yang[3], Jian Shu[3], Hongda Lu[4], Qingtian Zhang[4], Yongjing Wang[2], Duc Truong Pham[2], Tawfique Hasan[1], Weihua Li[4], Shiwu Zhang[3] and Shi-Yang Tang[2]; [1]University of Cambridge, United Kingdom; [2]University of Birmingham, United Kingdom; [3]University of Science and Technology of China, China; [4]University of Wollongong, Australia

As two fundamental properties of any material system, mechanical stiffness and electrical conductivity typically remain unchanged. However, an increasing number of emerging applications in structural engineering, robotics, and intelligent electronics demand materials with programmable conductivity and stiffness. Such materials that can respond to environmental changes have attracted widespread attention. However, previous attempts show significant limitations as they usually require external control systems to change the electromechanical properties of materials. In addition, these materials fail to harness variable electrical and mechanical properties synergistically to achieve independence from external control. To address this drawback, we present an electro-mechano-responsive hybrid elastomer comprising hybrid fillers of Field's metal and spiked nickel microparticles. As a low melting point alloy, Field's metal can adjust the resistance and stiffness of the elastomer through phase transitions. The spiked nickel particles as secondary fillers further endow the composite with unconventional negative piezoresistivity and high strain sensitivity. Combining the elastomer's high strain sensitivity and variable resistance/stiffness, we demonstrate a self-triggered multi-axis compliant compensator for robotic manipulators. Our system can adjust its stiffness under deformation without external control, offering an order of magnitude better performance than the best commercial products. We also show a highly compact self-recovering resettable current-limiting fuse with a ten times faster response than the state-of-the-art. With such an extraordinary tunable electromechanical property, our new material is expected to revolutionize resilient robotic systems and intelligent electronics.

5:00 PM EL18.13.30
Conductive Electrospun PCL Fibers for use in Electrospun Photovoltaics Luke J. Suttey[1,1], Dennis J. Moritz[2], Ellie L. Ostermiller[1,1], John J. Borkowski[2], Jessica M. Andriolo[1,1] and Jack L. Skinner[1,1,1]; [1]Montana Technological University, United States; [2]Montana Statue University, United States

In recent years an interest in conductive electrospun (ES) microfibers has gained traction in the world of flexible electronics and hybrid perovskite photovoltaic applications. ES fibers are attractive for their large surface area to volume ratio and relative strength. Traditionally, conductivity in ES nanofibers has been accomplished using conductive or semiconducting polymers. Alternatively, conductivity in polymer thin films can be accomplished through addition of carbon nanotubes (CNTs) or graphene.

Previously, we have successfully formed hybrid perovskite crystals encased in ES fibers in situ, showing improved crystal stability. In other work, we demonstrated conductivity in melt ES graphene doped polymers. In current work, we will utilize the previously established method of multiwalled CNT (MWCNT) dispersion by combined use of a hydroxy-functionalized and unfunctionalized MWCNT blend in polycaprolactone (PCL) in preparation for electrospinning of a multi-layer solar cell structure.

Triaxial ES will be used to form the multi-layer solar cell structure described. In the design, a conductive PCL core will be coated with the previously established perovskite-polymer composite. Most exterior to the ES device will be a polymeric electron transport layer (ETL). Each layer of the device will be characterized. Here, conductivity of a PCL thin film doped with a mixture of functionalized and unfunctionalized MWCNTs will be characterized via a non-destructive four-point probe method. Conductivity characterization will be used to determine the percolation threshold and preferable ratios for the MWCNT-doped PCL composite used as the core of the functional fibers proposed. MWCNT dispersion in the composite as a function of sonication time will be characterized through crystallinity analysis via Raman spectroscopy and electron microscopy.

Presented work will include fabrication methods of a four-layer thin film system consisting of the conductive MWCNT-PCL composite, a polymer encapsulated hybrid perovskite layer, a polymeric ETL, and a transparent conductor. This work will provide the foundational preliminary data for future fabrication of an ES perovskite solar cell. The design will not include a hole transport layer as it has been previously established as non-consequential to perovskite solar cell performance. After proof of concept has been established the conductive ES nanofibers will be used as a central electrode in a triaxially ES photovoltaic cell. Fibers created during the final triaxial ES process will have a three-layer structure (from core to outer shell) consisting of: (1) a conductive PCL composite, (2) a hybrid perovskite active layer, and (3) a polymeric ETL.

5:00 PM EL18.13.31
Enhanced Dielectric Properties of Bio-materials Derived from Renewable Resources for Electrostatic Chuck (ESD) Baekjin Kim; Korea Institute of Industrial Technology, Korea (the Republic of)

Dielectric materials are being applied in a variety of industries and used as electrical insulators in capacitors such as semiconductor devices and electrostatic chuck (ESD). Flexible materials for electric capacitors are getting more attention due to their superior processability, flexibility, and chemical resistance compared to inorganic materials. In our study, biomass based derived monomers and flexible oligomer were used to synthesize urethane materials with high dielectric constant. Especially we have adapted step by step method which synthesized well defined molecules in the desired position to confirm the effect of the two materials used on the dielectric constant. Sequentially synthesized UV curable urethane were qualitatively analyzed step by step through FT-IR and quantitatively analyzed through ^{1}H-NMR. In order to synthesize photo curable materials, acrylate were terminated at the both end of urethane oligomer chains and printed out disc type output (OD: 30mm) using Digital Light Process (DLP) 3D printer. Dielectric constants were observed $\varepsilon>5$ for printed out disc type urethane materials. In addition, we investigated that curing kinetics, film properties and mechanical properties of UV curable urethane materials.

5:00 PM EL18.13.32
External Electric Field Treatment to Printed N-Type Conjugated Polymer Films Applied for the Active Layer of Organic Field-Effect Transistors and Organic Photovoltaics Yina Moon, Nara Han, Dongseong Yang and Dong-Yu Kim; Gwangju Institute of Science and Technology, Korea (the Republic of)

External electric field (EEF) treatment could be a promising simple non-contact method for controlling the morphology of conjugated polymers during organic electronics printing process. Because EEF treatment uses an electric field to induce dipole alignment in molecules and expansion and alignment of molecular crystals, it is possible to control the morphology in the desired direction by freely controlling the direction of the electric field according to the channel direction of the electrical device. So, with EEF treatment, the aligned polymer and the enlarged crystal of the polymer can show improvement in the charge carrier transport. In this study, an n-type conjugated polymer, P(NDI2OD-T2), which has high electron mobility, improved the electrical performance as the active material of organic field-effect transistors (OFETs) and organic photovoltaics (OPVs) by EEF treatment with the printing process.
First, in this study, it was confirmed that improved electron mobility of OFETs by applying an EEF treatment during solidifying of the P(NDI2OD-T2) film right after blade coating, so, the average electron mobility improvement was improved from 1.22 cm^2/Vs to 1.98 cm^2/Vs. This achievement can be caused by aligning the dipole, enhancing the planarity of this polymer backbone, and enlarging polymer crystal by EEF treatment right after printing process. Furthermore, organic solar cells were fabricated using P(NDI2OD-T2) as an acceptor with PTB7-Th as a donor in the active material, and the power conversion efficiency was increased by EEF treatment with adding a polar solvent. Because a polar solvent was introduced as a solvent additive to improve the contribution of EEF effect to thick bulk-hetero junction film. As a result, by contrast to without solvent additive, 42% of enhancement of PCE from printed solar cells was achieved from EEF treatment compared with polar solvent additive approach only. The correlation between EEF treatment and morphology of conjugated polymer was analyzed by using UV-vis absorption, AFM, 2D-GIWAXS measurements and electrical performance of OFETs and OPVs. Consequentially, the improvement of electron mobility and PCE of this study suggests an effective way to advance the electrical characteristics of the device by applying the external electric field treatment.

5:00 PM EL18.13.34
Thick Lattice Electrodes with Core-Sheath Structure for Supercapacitors Manufactured by Material Extrusion 3D Printing Yuqi Gao and Junjun Ding; New York State College of Ceramics at Alfred University, United States

Manufacturing thick electrodes is a promising strategy to enhance energy storage per unit area. However, the electrochemical performance is still limited by the low electrical conductivity due to either the properties of materials or geometrical thickness. Material extrusion 3D printing has received enormous attention to potentially overcome the limits by tailoring and designing thick electrodes.

In this work, we prepared a thick reduced graphene oxide:carbon nanotube-reduced graphene oxide:manganese oxide/carbon nanotubes: carbon nanotubes (rGC-rGMC) electrode with controlled lattice architectures, core-sheath structure, and hierarchical porosity by material extrusion 3D printing, freeze-drying, and thermal treatment. The volume ratios of core to sheath, including 100%-0%, 0%-100%, 20%-80%, 30%-70%, 40%-60%, 50%-50%, and 30%+70%, were designed to investigate the influences of core-sheath structure on thick electrodes. Specifically, 100%-0% electrode, only including rGO and CNT, had an excellent rate capability and low capacitance (80.8 mF cm^{-2} at 1 mV s^{-1}) contributed by double-layer electrical capacitance. While 0%-100% electrode (rGMC only) showed a high area specific capacitance (356.0 mF cm^{-2} at 1 mV s^{-1}) due to introducing MnO$_2$/CNT composites, but a significant capacitance decay from 1 mV s^{-1} to 100 mV s^{-1} was observed. Either the rGC or rGMC was not desirable for the practical applications of thick electrodes. The thick electrode with core-sheath structures improved electron transportation by the conductive rGC core, and the fast ion diffusions via the thinner rGMC sheath layer. As a result of the competition between material compositions and structures, 20%-80%, 30%-70%, 40%-60%, and 50%-50% electrodes exhibited the area specific capacitance of 310.3 mF cm^{-2}, 528.9 mF cm^{-2}, 410.0 mF cm^{-2}, and 390.2 mF cm^{-2} at the scan rate of 1 mV s^{-1}, respectively. All capacitance decays from these core-sheath electrodes were smaller than rGMC (0%-100%) electrodes, indicating the improved rate capability from the core-sheath structure. rGC core was found to be effective as a conductive channel, and thus the rGMC concentrated in the sheath region could be more efficiently utilized. Electrodes with a core-sheath volume ratio of 30%-70% were compared with electrodes made of homogenous 30% rGC and 70% rGMC mixture to show the influence of the core-sheath structure on the electrochemical performance. Lower capacitance (400.1 mF cm^{-2}at 1 mV s^{-1}) of 30%+70% mixture electrode without core-sheath structure suggested less efficiency to harvest electrons from the redox reactions. Electrochemical impedance spectroscopy (EIS) data further supported and explained the resistances of thick electrodes with different volume ratios.

5:00 PM EL18.13.35
Fully-printed Micro-OECT Patch for Real-time Sweat Multi-analytes Detection Mohammad Shafiqul Islam, Brince Kunnel, Md Farhad Hassan, Angsagan Abdigazy and Yasser Khan; University of Southern California, United States

Wearable devices have gathered substantial consideration in recent years owing to their great potential in personalized health care and fitness analysis.

Amongst these, advances in wearable technology have empowered the fabrication of sweat monitoring devices for in situ real-time and continuous analysis of proteins, ions, and metabolites. However, these sensing platforms should be disposable and scalable. In this regard, printing technologies show promise as a quick, high-throughput, and inexpensive alternative to the more time-consuming multi-step photolithography techniques. In this work, we present an epidermal wearable chemical sensing patch for sweat ions analysis fabricated using inkjet printing and direct 3D writing, which fully unleashes the advantages of using the OECT in wearable applications. Compared to conventional potentiometric sensors, OECTs offer signal amplification, improved miniaturization, and circumvent reference electrode requirements. We demonstrate for the first-time fabrication of the short channel micro-OECTs (~100 µm) by printing techniques for the detection of lithium (Li+) and sodium (Na+) ions from sweat. The concentration of Li+ in biological fluid plays an essential role in assessing bipolar disorders, while Na+ facilitates tracking the dehydration status of individuals. We hope this work will inspire further development of printed OECT-based biochemical sensors

5:00 PM EL18.13.37
A Novel Screen-Printed Platform for *In Situ* Soil pH Sensing Catherine Crichton, Elliot Strand, John-Baptist Kauzya, Anupam Gopalakrishnan, Madhur Atreya, Eloise Bihar and Gregory L. Whiting; University of Colorado Boulder, United States

Soil pH significantly affects agriculture by regulating available nutrients and water-soluble chemicals available to plants, thus driving the need for low-cost, durable soil pH sensors. A few potential solutions include expensive commercial pH sensors and printed sensors that only work in liquid media. Each of these solutions poses its own set of unique challenges perpetuating the affordable soil pH sensing dilemma. Here, we present a novel pH sensor platform based on an array of low-cost, durable, screen-printed electronics for in situ soil sensing. We show the stabilization of the pH-sensitive dye, alizarin, in the printed pH devices allowing for extended sensing periods in soil. We compare different alizarin dye immobilization techniques and have evaluated the effects of soil pH on sensor durability. This new affordable, stable printed pH system pioneers the development of printed electronics for new alternatives to assess soil pH.

5:00 PM EL18.13.38
Printed Potentiometric Sensors for Soil Nitrogen Monitoring Carol Baumbauer, Lucas Lahann, Payton Goodrich, Carolyn Schwendeman and Ana Arias; University of California, Berkeley, United States

Managing nitrogen is a central concern for precision agriculture and environmental science in order to maximize fertilizer use efficiency and minimize nitrate leaching and greenhouse gas emissions. However, measurement methods for in-soil nitrogen are limited. State-of-the-art soil nitrogen analysis requires taking soil or liquid samples to laboratories for chemical or spectrographic analysis. These methods are accurate, but costly, labor intensive, and cover limited geographic scope. Printed potentiometric nitrate and ammonium sensors are a promising alternative method for nitrogen monitoring because they are small, low power, involve no moving parts, and are mass-producible. Printing techniques are scalable and compatible with unconventional materials used for environmentally-benign sensors.

Potentiometric sensors are composed of two electrodes: an ion-selective electrode (ISE) and a reference electrode (RE). The signal output is the potential difference between the two electrodes at zero-current conditions. Potentiometric ion sensors have been widely studied for health monitoring applications, however, several unique challenges arise when developing potentiometric sensors for environmental applications. Sensors used for soil monitoring must 1) exhibit very low drift to enable functional lifetimes of several months, 2) be insensitive to other chemicals at concentrations commonly found in soils 3) be paired with stable printed references, and 4) be robust to biofouling and damage from microbial activity in soil.

Here we present work towards achieving these aims. Materials for the sensing electrode, ion-to-electron transducer layer, and ion selective membrane are compared and chosen for sensitivity, selectivity, and stability. The reference electrode transducer and membrane layers are likewise optimized for stability minimal drift. Encapsulation techniques are explored for robust production of sensitive electronics, enabling long lifetimes.

5:00 PM EL18.13.39
Enhancing Hydrophilicity of the Skin-interfaced Microfluidic Systems for Sweat Monitoring Fina Lu, Ji Hyun Yang and Ahyeon Koh; Binghamton University, United States

Sweat sensors are an emerging technology for real-time, non-invasive health monitoring and analysis at the skin-interface. This skin-interfaced wearable system allows for a detailed analysis of sweat, a biofluid that contains a wide range of essential biomarkers that possess a powerful potential in clinical diagnostics and commercialization. Polydimethylsiloxane (PDMS) is the most commonly used material in microfluidics due to its characteristics such as biocompatibility, low elastic modulus, and moldable structure at high resolutions. The most notable drawback is the intrinsic hydrophobicity of PDMS, inhibiting non-specific protein adsorption and wettability issues that affect how sweat is driven up the microfluidic device. Previous studies focused on the blending of PDMS and copolymer polyethylene glycol (PEG) to improve hydrophilicity. They have reported on the biofouling of these block copolymers, affecting the structure of the material. However, the distribution and behavior of these compounds in the PDMS still need to be fully understood.

In this study, we aim to improve the hydrophilicity of the PDMS and reduce the threshold pressure for sweat collection at the skin-interface. We explored engineering strategies to exploit the material's chemical and physical properties. The PEG block-co-polymer was used as an additive and contact angles were tested for the PDMS/PEG as a function of wt% PEG block-co-polymer. To test this, we conducted a set of experiments on four different surfaces over time. PDMS thin films were prepared using soft lithography by mixing a PDMS solution comprising of a PDMS base and a crosslinking agent in a ratio of 10:1. PDMS was set as the control for each experiment, coupled with PDMS/PEG wt% of 0.5 wt%, 1.0 wt%, and 3.0 wt%. Each experiment consisted of these four samples cured on four surfaces of polystyrene (PS), polyamide (PI), polycarbonate (PC), and polyethylene terephthalate (PET) films. The PDMS/PEG thin film specimens were approximately 1000 µm thick using a thin film applicator. All samples were cured for 24 hours at 60 °C, and contact angle measurements were carried out at 0 hours, 24 hours, 1 week, 2 weeks, 3 weeks, and 1-month marks. We observed the difference in the water contact angle for the PDMS/PEG interface and air and how it differs across different types of surfaces over time. The results from the initial contact angle measurements showed a difference between the air and polystyrene (PS) interface, for PDMS (air-102.9°, PS surface-99.2°) and 3.0 wt% PDMS/PEG (air-51.0°, PS surface-8.6°). The water contact angle is minuscule between the air and surface for 0 wt%, while 3.0 wt% shows a significant difference.

The initial material surface hydrophilicity is lower on every surface except for PDMS control, for PI (3.0 wt%, air-51.6°, PI surface-13.6°) and PC (3.0 wt%, air-29.3 °, PC surface-11.2°), meaning the type of surface does affect the contact angle and hydrophilicity of the PDMS material. Polycarbonate (PC) shows the least difference in contact angles between the air and interface. The percent recovery of the polystyrene surface at 1 month for PDMS (air-99.2°, 3.6% recovery; PS surface-93.6°, 5.6% recovery) and 3% PDMS/PEG (air-41.7°, 19.5% recovery; PS surface-32.5°, 26.5% recovery). The slow recovery of PDMS hydrophobicity is promising for commercialization. Continuous contact angle measurements are to be made in the subsequent months. Mechanical testing included bending, peeling, and shear stress using a Mark-10 tensiometer. The microfluidic flow threshold pressure will be quantified using Fluigent Flow EZ equipment for each material.

The polystyrene (PS) surface shows the most promising results for fabricating sweat sensors. Our research shows insight into the PDMS/PEG block copolymer system and offers engineering strategies to improve PDMS/PEG hydrophilicity for use in skin-interfaced microfluidic devices.

5:00 PM EL18.13.41

Stretchable and Conductive Polydimethylsiloxane/Liquid Metal Composites by Material Extrusion 3D Printing Chao Liu and Junjun Ding; New York State College of Ceramics at Alfred University, United States

Gallium-based liquid metal (LM) alloy is a promising material in applications such as flexible electronics and thermal management due to its outstanding electrical conductivity, thermal conductivity, and reconfigurable under harsh stretching conditions. Polymeric elastomers are extensively used as matrix materials to embed LM reinforcement to form composites for better electromechanical performance. Polydimethylsiloxane (PDMS) is a widely used elastomer due to its stretchability, biocompatibility, and moldability. Research has shown that PDMS/LM composites demonstrate excellent electrical conductivity and robust elasticity as flexible conductors and strain sensors. LM particles are homogeneously dispersed in the PDMS matrix, which demonstrates an isotropic performance of electrical conductivity. However, these composites usually require mechanical activation process to create electrically conductive channels in the composites. In addition, little research has focused on forming non-uniform structure for an anisotropic electrical property which is required in many electrical devices.

In this work, we fabricate an inhomogeneous PDMS/LM composite by material extrusion 3D printing method. LM particles sink down and deposit on the bottom of the composite due to a larger density compared to PDMS. A higher viscosity PDMS (SE 1700) and a lower viscosity PDMS (Sylgard 184) are used to study the influence of matrix viscosity on the sinking down process. The experimental results are compared to the simulation results for the understanding of the self-assembly process. The deposited LM layers demonstrate a larger local density of electrical pathways compared to structure with homogeneous dispersion. Therefore, the hierarchical PDMS/LM composite demonstrate a better electrical conductivity on the bottom surface, but nonconductivity between top and bottom surface. The material extrusion 3D printing method is used to fabricate the composites due to its advantages of building complex structures in line-by-line and layer-by-layer mechanisms. Rheological analysis, such as viscosity and storage/loss modulus, is studied before 3D printing process for a printable ink. Prepared ink is transferred into a syringe and extruded from the nozzle by a stepper motor. The influence of printing parameters, such as nozzle size, line width, and printing speed, on the conductivity of the composites will be further investigated.

5:00 PM EL18.13.42

Reliable Fabrication of Freely Scalable and Designable Porous-type Tactile Sensor Using Micro-Patterned Water-Soluble Sacrificial Layer Bon-Jae Koo and Min Ho Seo; Pusan National University, Korea (the Republic of)

Recently, polymer-based micro/nano-porous structured pressure sensor has gained significant interest in tactile sensor applications because of their high sensitivity and fast response & recovery time. Conventionally, the porous structured pressure sensors have been produced utilizing a solvent-soluble bulky porous template, such as a sugar cube. However, the bulky template makes the sensor inevitably voluminous, obstructing miniaturization essential for recent robotics, virtual reality (VR), augmented reality (AR), and biomedical Engineering. Moreover, the conventional methods unavoidably form randomly located porous structures, which constrains the reproducibility and reliability of the tactile sensor required for industrialization. Therefore, a reliable manufacturing method for high-performance miniaturized porous pressure sensors with high reproducibility and scalability is required.

Here, we report a simple and reliable method to fabricate a freely designable and scalable micro-porous type pressure sensor. The proposed fabrication method exploits a micro-machined and ultra-thin water-soluble sacrificial layer (Polyvinyl Alcohol, PVA) instead of the bulky template. By conventional screen-printing, a thin tri-layer of a conductive polymer-micro machined sacrificial layer-conductive polymer can be produced. Then, by removing the sacrificial layer, the designable porous structure inside the pressure sensor formed. Importantly, the shape, location, and dimension of the porous structure inside the pressure sensor are freely designable since the sacrificial layer is manufactured by UV-Laser machining. In addition, the thickness of the polymer also can be freely adjustable by controlling a stencil mask during the screen-printing method. Thus, the micro-porous inside the conductive layer can be easily scalable and designable, finally providing reproducibility at the sensor device level. To practically prove the proposed concept, we first screen-printed a 100 µm-thick conductive polymer, C-PDMS (Carbon Black-polydimethylsiloxane), layer on the electrode-formed substrate. Then, the pre-porous layer was formed by an 80 µm-thick micro-machined PVA, and 200 µm-thick C-PDMS for the upper layer was fabricated by screen-printing. Finally, after the PVA layer etching process in the water, we demonstrated the designed micro-porous embedded ultra-thin (380 µm) piezoresistive pressure sensor. The fabricated sensors showed a sensitivity of 0.08176 ($R \times kPa^{-1}$) which is 200 % higher than that of a non-porous sensor ($R \times kPa^{-1}=0.03725$), in the pressure range of 25 kPa to 100 kPa. More importantly, we practically confirmed the highly reproducible base resistance and sensitivity ($219.8612 \pm 8.3028\ \Omega$ and $0.1163 \pm 0.0048\ R \times kPa^{-1}$ in 0.5 kPa to 100 kPa, respectively) of the fabricated sensors (n=8) that were achieved by the designed porous structure. Based on the proposed concept, we further fabricated a tactile sensor array composed of 3x3 miniaturized micro-porous sensors. The fabricated sensor array not only successfully recognized the magnitude and location of the static pressure of various weights but also detected the dynamic pressure of tapping the finger in real time.

5:00 PM EL18.13.43

Self-Cooling Transformative Electronics with a Radiative Cooler for Reliable Stiffness Tuning in Outdoor Use JooHo Yun[1], Sang-Hyuk Byun[2], Seyeon Heo[1], Gil Ju Lee[3], Jae-Woong Jeong[2] and Young Min Song[1]; [1]Gwangju Institute of Science and Technology, Korea (the Republic of); [2]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [3]Pusan National University, Korea (the Republic of)

Traditionally, electronics are designed to have invariant mechanical properties to serve specific purposes. For example, rigid electronics provide convenient and robust handling, optimized for handheld or tabletop setup, and soft electronics are capable of deforming their shapes and geometries dynamically, enabling comfortable wearing on the body. Unfortunately, however, current electronics cannot provide advantageous features of both rigid and soft electronics due to inherent limitations in their form factors. To leverage key features of both rigid and soft electronics, we have developed a transformative electronics system (TES), which can change their shape and stiffness to realize both rigid handheld and soft wearable configurations as needed [1]. The TES integrates flexible, stretchable electronics onto a thermally responsive transformative platform which is composed of gallium (T_{melt} = 29.76 °C, where T_{melt} represents a melting point of gallium) to implement stiffness tuning by changing its phase between solid and liquid. However, the TES have difficulties converting into a rigid form outdoors because excessive heat is accumulated from themselves or the environments such as the sun. Integrating a flexible thermoelectric device with TES [2] can address this issue, but it requires a huge amount of power to maintain rigid operation mode outdoors.

Here, we present a design of transformative electronics with the integration of a radiative cooler (TER-RC), enabling reliable bidirectional stiffness tuning in both indoor and outdoor environments. Specifically, rigid-mode outdoor operation under the sunlight has been substantially improved by a radiative cooler. We fabricated a flexible and stretchable radiative cooler (FSRC) that achieves ~97% of reflectivity in the solar spectrum and ~90% of emissivity in an atmospheric window so that it can effectively block solar energy and radiate internal thermal energy [3]. The radiative cooler can maintain its temperature 3.9 °C below the melting temperature of gallium under 1000 W/m^2 of direct sunlight and an additional 4469 mW/m^2 of external heat input. Based on this, we have demonstrated a transformative optoelectronic device that can convert between rigid handheld and stretchable wearable forms. The integrated radiative cooler successfully reduces the temperature of electronics and enables stable rigid mode operation even in the hot outdoor environment, thus making transformative electronics highly reliable both in rigid handheld setup and soft wearable form.

In conclusion, the transformative electronics with radiative cooler (TER-RC) enables desired stiffness tuning between rigid and soft modes without dependence on ambient temperatures and environments. The integrated FSRC can effectively reflect solar energy and radiate thermal energy so that it cools down the TES to allow rigid mode under sunlight. Finally, we verified the design concept through the demonstration of an optoelectronic device that can convert between rigid handheld and stretchable wearable forms to overcome the limited applications of the existing TES.

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5:00 PM EL18.13.44
Optical Physically Unclonable Functions Device Using Random Fibrous Media Fabricated by Electrospinning MinSeok Kim, JooHo Yun, Dong Hyun Seo and Young Min Song; Gwangju Institute of Science Technology, Korea (the Republic of)

Recently, the demand for encryption to verify user identity and authenticated products for protection against counterfeit products and privacy/confidential information is increasing in daily life. The physically unclonable functions (PUFs), which is a non-algorithmic one-way functions composed of stochastic random factors, have been mentioned as new cryptographic physical devices. Because PUFs are generated in a random or probabilistic process, each manufactured PUFs devices exhibit unique characteristics. Since the initial introduction of the PUF concept, various types of PUFs using optical, magnetic, and electronic have been reported. Compared with other PUFs, the optical-based PUF has the advantages of high entropy, high output complexity, and high security against modeling and replication attacks.
Optical-based PUFs using a random laser is an attractive researched field, unlike conventional lasers. Random laser has no optical resonator and uses a feedback loop of scattering particles in a random material to randomly emit light. Random lasers are generated through a phenomenon of Anderson light localization generated in a random region when light is strongly scattered through a random medium. However, manufacturing large-area random media that causes random lasing at low cost remains a challenge. In this paper, we propose a method of extracting bits by fabricating an optical PUFs device with random lasing characteristics using electrospinning, which can implement a random structure in a large-area process, and apply it to security devices.
To implement optical PUF, a method of fabricating nano/microfibers using electrospinning is used. 2 g of polymethyl methacrylic acid (PMMA) was dissolved in 9 g of dimethylformamide (DMF) and acetone, respectively, to prepare a solution usable for electrospinning. To sufficiently dissolve the PMMA in the solvent, a heat stirrer was used at 60 °C for 8 hours. To have emission characteristics ranging from 560 nm to 640 nm, 4-(dicyanomethylene)-2-methyl-6-(4-dmethylaminostryl)-4H-pyran (DCM) was dissolved in 2 mM at a temperature of 60°C for 2 hours. The prepared solution was subjected to an electrospinning process through a high voltage of 14 kV at an extraction rate of 1 mL/hr using a 23 gauge nozzle. The micro random fibers produced by the electrospinning method have a similar diameter distribution and thickness. The fabricated samples have similar fiber diameters across the entire area, but have different random laser properties due to different fiber structures at different locations in the sample. To confirm the random lasing phenomenon, an optical pumping method was used to obtain random peaks representing random lasing. For optical pumping, a 3rd Harmonic ND:YAG laser with a wavelength of 355 nm was used at a repetition rate of 10 Hz. The 355 nm laser was focused on the fabricated sample with a plano-convex lens with a focal length of 50 mm. A 60x objective lens and a UV-visible spectrometer were used to acquire the generated wavelength data of a random laser. The wavelength data measured at four different points within the same sample shows a random peak from 580 nm to 620 nm at each location. In order to use the peak obtained with optical PUFs devices, the baseline of the spectrum was decomposed to remove the spontaneous emission component. The positions of the obtained peaks were digitized through binning. In order to improve the uniformity of the digitized data and final bit was extracted using the Von Neumann De-biasing method to improve the uniformity of the digitized data.

5:00 PM EL18.13.45
Statistical Analysis of Printed Graphene Coating using Optical Imaging Kh M Asif Raihan[1], Bepeh Amama[2] and Suprem R. Das[1]; [1]Kansas State University, United States; [2]Manhattan High School, United States

Materials for functional coating have significant technological implications in modern society starting from building smart building to aerospace applications. However, a single material is difficult to achieve to fulfil many of the requirements for a wide variety of applications. Despite challenges to address in a case-by-case basis, with the advent of nanomaterials and nanotechnology, multifunctional coating has emerged as a practical avenue often developed from laboratory benchtop experiments to emerging industries. Graphene, a material discovered in 2004, is presently representing a leading material to address many applications in the form of functional coating. However, the quality of coating is the first step to understand in order to further apply it in real applications. In our laboratory, we print graphene on flexible substrates with the intention to use in various flexible electronics. In this poster presentation, we study the quality of coated graphene, fabricated by printing and by capturing hundreds of optical images and subsequently performing its statistical data analysis. The analysis not only predicts the coating uniformity but high-resolution imaging guides further the need of future printing technology to further push the resolution of such coating technology.

5:00 PM EL18.13.46
Metallic Micro-Pattern Embedded Stretchable Conductive Dry Electrode for Long-term Reliable and Wearable ECG Monitoring Onyu An, Sang-Min Kim and Min Ho Seo; Pusan National University, Korea (the Republic of)

An active electrocardiogram (ECG) can record a continuous heartbeat and is therefore utilized to accurately monitor the presence of arrhythmias. Conventional biopotential electrodes for the ECG measurement in clinical-level are based on wet Ag/AgCl (conductive gel) electrodes, reducing skin-electrode contact impedance. However, as the conductive gel dries over time, there is a problem in that the contact resistance increases and signal degradation occurs, finally limiting the long-term reliable ECG measurement. To address the long-term reliability issue, a dry electrode, generally based on conductive-polydimethylsiloxane (C-PDMS), has been developed. The dry electrode is not only flexible, also stable without physical and chemical degradation, thus, it has shown the long-term reliable and continuous ECG measurement with wearable configuration. Nevertheless, interconnection of the polymer electrode with conventional instrumental systems still remains a challenge for the development of the polymer-based dry electrode to industrial grade and for the practical usage in widen applications.
Here, we introduce a novel design of dry C-PDMS electrode that includes an optimized micro-scale copper (Cu) pattern inside. The developed dry electrode exhibits electromechanically stable interconnection with commercial instrumentation systems because it includes the Cu micro-pattern compatible with conventional interconnection methods, such as soldering and mechanical connector. Importantly, since dimension of the Cu pattern is theoretically optimized, using finite element method (FEM), the developed dry electrode maintains its high flexibility and stretchability; quantitatively, we confirmed the effective stiffness of electrodes can be reduced and become similar to the stiffness without the Cu pattern when area of Cu pattern is 20% of the radius of the C-PDMS layer. To demonstrate the designed electrode, a simple microfabrication process using laser ablation and screen printing was developed. The fabricated dry electrode does not only show stable impedance characteristics (4kohms @1kHz) with high reproducibility (36.1 of resistance variance, n=95), but also show stable adhesion to human skin even with various movements. More importantly, the fabricated electrode shows successful electrical interconnection with a commercial wire through the conventional soldering and conductive magnet. We also tested the long-term reliability of the electrode. After exposing the fabricated dry electrode to a 40°C oven for 12, 24, and 36 hours, the developed dry electrode stably maintains its electrical properties (1.74 % resistance change), while the wet electrode showed crucial performance degradation (-67.5 % resistance change). Finally, we further

developed a wearable ECG hardware that can be connected to the developed electrode through the conventional soldering. Then, in the continuous ECG measurement for 24 hours, the developed dry electrode-based ECG module successfully measured a clear PQRST peak without significant signal degradation. More importantly, the developed sensor reliably detects ECG signals even while a person is walking.

5:00 PM EL18.13.48
Tailoring the Internal Structure of Porous Copper Film via Size-Controlled Copper Nanosheets for Electromagnetic Interference Shielding Ho Kwang Choi, Seungyeon Kim, Young-Seok Song and Tae-Wook Kim; Jeonbuk National University, Korea (the Republic of)

The advances of technologies, such as latest telecommunications, electric vehicle and electronic device has prompted demand for ultra-high performance and cost-effective shielding materials to protect against the potentially harmful effects of electromagnetic interference (EMI) on human health and electronic devices. Materials commonly used as shielding for EMI are metal-based thin films, foils, and meshes. Currently, several types of conductive filler materials, two-dimensional (2D) materials and polymer composite materials are being studied as core materials for EMI shielding because of their cost, performance, and weight. Among them, large-area 2D metal nanosheet enables more efficient film formation on a substrate compare to other conductive fillers such as nanoparticles or nanowires. The existing strategy for preventing EMI is to block electromagnetic waves using mechanisms such as reflection or absorption, which depend on impedance differences and skin depth. The multiple reflections caused by scattering inside the shield are considered to be a third shielding mechanism. Multiple reflections can be caused by various porous structures formed inside the shielding material. Therefore, 2D copper nanosheets (Cu NSs) have been introduced to enhance EMI shielding effectiveness (SE) by forming an internal layer by- layer stacked structure inside the films. In the case of 2D nanomaterials such as graphene, transition metal dichalcogenides, and MXene, it is difficult to control the spacing between each atomically thin layer when forming a thin film due to the strong van der Waals force. On the other hand, Cu NSs enable the formation of an internal porous structure in films with submicron or micron scaling gaps between the layers of stacked Cu NSs, and the size-controlled Cu NSs can realize various internal structures. In that context, it is important strategy to control the internal structures of such porous films for EMI shielding applications and the requires size-controlled Cu NSs. Metals have highly symmetrical lattices and their 2D morphology for a metallic crystal is not thermodynamically favored during bottom-up growth or synthesis. For this reason, the control of crystal growth is achieved by controlling the total free energy of the metal nanostructure and the rate at which metal ions are reduced to metal clusters. Because the surface energy could dominate in the total free energy of 2D nanostructures with a high surface-to volume ratio, this strategy often involves reducing the surface energy of 2D metals with capping agents. Here, we observed the use in EMI shielding of hierarchical porous Cu foils with various internal structure according to assembly of single-crystalline, nanometer-thick range, and micrometer-length range size-controlled copper nanosheets and characteristic changes according to various state of hierarchical porous Cu foils. Cu NSs were size controlled by adjusting the concentrations of the shape modifying agent (iodine), the stabilizer(hexadecylamine) and the reductant (glucose). Size-controlled Cu NSs were synthesized in various sizes from 3 to 30 μm. The layer-by-layer assembly of the synthesized Cu NSs enabled formation of a hierarchically-structured porous Cu NSs film with features such as multi-layer stacking. The hierarchical porous Cu foil exhibited superior EMI shielding performance compared to the same thickness of dense copper and other materials, resulting in EMI SE values of up to 100 dB depending on the thickness. In addition, the EMI SE of the hierarchical porous Cu NSs film exhibited various EMI SE values according to changes in the internal structure, and showed various characteristics according to oxidation through high-temperature heat treatment. These findings suggest that Cu NSs and their layer-by-layer assemblies are one of the promising EMI shielding technologies applicable to a variety of practical electronic applications.

5:00 PM EL18.13.49
Understanding the Effects of Polar and Non-Polar Surfactants on the Oxidation Performance of Copper Nanoparticles LaRico J. Treadwell; Sandia National Laboratory, United States

Copper nanoparticles (Cu-NPs) have garnered attention due to their high electrical and thermal conductivity, high melting point, and relatively low cost compared to other metals (i.e., gold and silver). The wide spread usage of Cu-NPs is hindered due to their susceptibility to oxidize and corrode, as well as the difficulty to achieve an synthetic route that easily scalable with controlled morphology and does not encompasses parasitic conditions (i.e., harsh reactants, high temperature). Many of the published routes involve harmful/toxic compounds and reducing agents, as well as very high temperatures/long reaction times, and despite the harsh synthetic conditions the nanoparticles are extremely susceptible to oxidation. Therefore, developing a cost effective and green synthesis that can produce Cu-NPs that is resilient/controllable to oxidation and corrosion environments is critical for Cu-NPs to be usable in industrial and commercial usage. In this work, a novel microwave-assisted synthetic route is demonstrated using an organometallic precursor (Copper (I)-Mesityl) and a variety of green solvents (glycols) and surfactants (hexadecylamine [HDA]). Numerous synthetic parameters (i.e., solvent/surfactant combinations) were systematically investigated to evaluate their effect on the particle size and morphology as well as how the solvent/surfactant prevent oxidation/corrosion in atmospheric corrosion environments. The various surfactant/solvent coated nanoparticles were subjected to a variety of environments such as 100% relative humidity (RH) and 10 ppm H_2S/50% RH. The nanoparticles were characterized pre- and post-exposure to understand the role of the solvent and surfactant species effect on hindering oxidation. Particles were characterized via powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and Fourier transform-infrared (FT-IR) spectroscopy. Results show the combination of glycols/HDA yielded a synergistic effect that lead to a reduction in the oxidation kinetics upon exposure to atmospheric corrosive environments, yielding oxidative resistant nanoparticle (> 14 days).
Details on the synthesis route, characterization, and oxidation stability are presented.

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5:00 PM EL18.13.51
Functional Paper for Magnetically Controlled Soft Actuators and Deformable Sensors Jeong Woo Chae[1], Gooyoon Chung[2], Wooseok Kim[1], Yoonseok Park[2] and Sang Min Won[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Kyung Hee University, Korea (the Republic of)

Since its invention from more than 2200 years ago, paper has been indispensable in many parts of our everyday life such as writing, printing, cleaning, and packaging. In recent years, growing interest in the creation of functionalized paper has expanded the application scope of paper for batteries, energy harvesters, actuators, sensors, conductors, semiconductors, and biomedical uses, which exploit the inherent characteristics of paper, namely flexibility, foldability, bendability, recyclability, and lightness in weight. In this study, reprogrammable, magnetically controlled actuators, and highly deformable electrodes and sensors are fabricated by a simple and low-cost process. For the fabrication, commercially available water-soluble cellulose paper, consisting of wooden pulp and sodium carboxymethyl cellulose (Na-CMC) is used, and either Neodymium-Ferro-Boron (NdFeB) microparticles or ethanol-treated carbon black (CB) nanoparticles are uniformly dispersed in an aqueous solution of cellulose paper by sonication. The compound is heated for solvent evaporation where the coating of wooden pulp by CMC and filler particles composite takes place. The CMC-containing paper allows the final product to be glued together or recycled in the easiest way that needs no shredding or chemicals owing to its water-solubility at any temperature. Therefore, conductive paper strips can be joined to form an extended wiring, and recycling can be achieved by dissolving the paper in water and drying the solution to produce a new sheet of paper.

Magnetic cellulose paper for shape-morphing soft actuators is designed to perform dynamic locomotion such as crawling, rolling, sliding, and folding in magnetic fields. To form magnetization profiles on the paper that initially has random domain orientation, magnetic torque is applied to the paper under a programming magnetic field and reorient the NdFeB particles to align the local magnetization, either in-plane or out-of-plane, which determines the locomotion mode. The paper is then folded in origami or selectively integrated onto pristine paper for desired actuation that is driven by an electromagnet with 2-axis Helmholtz coils at a very low magnetic field down to 0.3 mT. Increasing the magnetic field to 2 mT leads to a large-degree deformations up to ±90°. The magnetization profile can be reprogrammed by repeating the same procedure above, but with different alignment under a programming magnetic field. In such manner, the initially torque-driven magnetization changes its orientation and thus the modes of locomotion straightforwardly.
Electrically favorable properties and durability of conductive cellulose paper are illustrated through mechanical deformation tests and sensor demonstrations. The electrical conductivity of the paper is saturated to 118 S/m when the mass ratio of CB to pristine cellulose paper is over 0.4 as the binding sites for CMC/CB in wooden pulp are restricted in amount. Bending up to a bending radius of 60 µm or repeated 180° folding cause no mechanical or electrical damage to the paper-based electrodes (resistance change below 0.1 % and 0.3 %, respectively). While the electrode dissolves completely in DI water, its partial dissolution can be recovered merely by drying the dissolved area without damaging the electrical characteristics. A paper-based parallel plate capacitor manifested negligible difference between the experimental and modeling data, and a capacitive touch sensor with paper electrodes evinces stable capacitance values during repetitive touching. The results unlock the implementation limit of the conductive paper for a variety of conditions that require bending, folding, instant dissolution, recovery after dissolution, lightweight capacitor, etc. Furthermore, the combination of the two types of functional paper provides magnetically controllable electric circuits whose wire connection can be steered and recuperated by maneuverable locomotion under magnetic fields.

5:00 PM EL18.13.52
Laser-Induced Graphene-Based Structures Derived from Cellulosic Materials for Flexible and Green Electronics Applications Sara Silvestre, Tomás Pinheiro, Ana Carolina Marques, Rodrigo Martins, Luís Pereira and Joao Coelho; CENIMAT|i3N - NOVA School of Science and Technology, Portugal

In recent years, with the evolution of modern societies, new and emerging technologies, such as flexible and wearable electronics, have improved overall well-being and human quality of life. Toward what can be introduced in the future, from the evolution of current technology to the development of new smart devices, researchers around the world are pushing technology barriers further, exploiting the full potential of such systems. In this context, flexible electronics have been increasingly growing, integrating sensors, capacitors, antennas, and so on, offering a novel range of applications, such as biological and environmental monitoring, energy harvesting and storage, intelligent robotics, smart clothing, flexible displays, healthcare sensors, and much more. These technological trends also require exploring novel materials, being carbon substrates some of the most promising options over the past decade. For instance, graphene presents amazing properties, such as remarkable conductivity, flexibility, high strength, and thermal and chemical stability. Although graphene-based materials stand out for their great features, the conventional fabrication processes are complex, expensive, and not industrially scalable, highlighting the need to find sustainable alternatives. Therefore, exploring renewable materials and environmentally friendly methodologies is necessary to develop high-efficiency, lightweight, flexible, durable, and low-power consumption devices[1–4].
This work reports an eco-friendly approach for the production of green, flexible, and discrete structures based on a single-step direct laser writing (DLW) approach. Using this process, it is possible to convert cellulosic derivatives, such as agglomerated cork and paper substrates, into three-dimensional porous laser-induced graphene (LIG). By using different wavelength lasers (CO_2 and fiber), applying different substrate pre-treatments, varying the laser parameters, and studying the interaction mechanism of the laser and materials, LIG structure properties were easily tuned. The obtained "Green LIG" exhibits the typical Raman spectra along with high electrical conductivity, presenting exceptionally low sheet resistance between 5-10 ohm sq^{-1}. The friendliness of the used production method makes it an interesting tool for future technological applications. To show its applicability, the production of sensitive pressure resistive sensors and micro-supercapacitors was demonstrated, which paves the way for its integration into self-sustaining technological platforms and smart wearable systems.

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5:00 PM EL18.13.53
Photosynaptic Transistor Memories Based on Solution-Processing Semiconductors and Donor-Acceptor Electret Polymer Dots Waner He and Tsuyoshi Michinobu; Department of Materials Science and Engineering, Tokyo Institute of Technology, Japan

Organic field-effect transistor (OFET) memories have attracted considerable attention due to their variety of applications in organic electronics. In contrast to conventional electrical memories, OFET memories have the advantages of structural flexibility, low-cost fabrication, and integration with CMOS technology. Recently, a light energy source was employed to erase recorded memory information. This data deletion/recovery process is considered as a green technology because light replaces electrical stress. Therefore, using an electronic device with the photo communication capability must become the mainstream technology in the future. To enhance the photo-responsive OFET memory characteristics, further improvement of polymer electrets is required. It was expected that polymer electrets with nonplanar conjugated structures show efficient photoelectric and charge-trapping properties. In this work, nonplanar donor-acceptor units were introduced, which can be readily constructed in quantitative yields by [2+2] cycloaddition-retroelectrocyclization (CA-RE) of electron-rich alkynes and electron-deficient olefins under mild conditions. The charge-trapping polymer electret dots of the OFET memory architecture was thus fabricated by the [2+2] CA−RE reaction between the dialkylaniline-substituted alkyne polymer P1 and 7,7,8,8-tetracyanoquinodimethane (TCNQ) polyester P2. Due to the crosslinked polymer electret, semiconducting layers (PBTTT-C14 and N2200) could be fabricated by wet process. Finally, OFET memory characteristics were systematically investigated in both electrical and optical operation modes. In addition, phototransistors are also applicable in the artificial synapse to fulfill short/long-term memory or plasticity and multilevel information recording.

5:00 PM EL18.13.55
Comparing Electronic Properties of Spin-Cast and Inkjet-Printed Indium Oxide Thin Films Andrew K. Lambert[1], Jacob Manzi[1], Harish Subbaraman[1], Tom Weller[1] and John Labram[2]; [1]Oregon State University, United States; [2]University College London, United Kingdom

Additive manufacturing is an emerging technology which enables relatively low-cost, high-volume device fabrication, with modest capital equipment requirements. Printable electronics refers to devices fabricated using different additive manufacturing processes such as inkjet printing, dispensing, and aerosol printing. The more traditional deposition techniques such as solution processing, vacuum deposition, sputtering, and evaporation currently offer higher quality, but at a higher cost due to material use and infrastructure investment. One of the challenges that printable electronics face is device quality optimization. While recent advances in solution-processed metal oxide thin film transistors (TFTs) have been impressive, most high-performance devices have been reported using spin-coating rather than additive manufacturing. Spin-coating is a useful technique for laboratory testing but is not industrially scalable. Ultimately, comparable performance needs to be achieved using techniques such as additive manufacturing for solution processed metal oxides to be commercially viable.

In this study, we compare device performance between inkjet printed and spin-coated metal oxide TFTs. The device under consideration is the indium oxide TFT, a material known to exhibit a high electron mobility in spin-cast TFTs. We study how conversion temperature, a critical parameter for compatibility with mechanically flexible substrates, affects performance in both sets of devices. We observe non-negligible differences in mobility and threshold voltage between the two deposition methods. For spin-coated devices, the mobility ranged from 5 cm^2/Vs to 9 cm^2/Vs going from thinner to thicker indium oxide layers. The thinner devices were more subject to defects which increased resistance against the carriers. The threshold voltage for solution processing ranged from -75 V to 10 V where the thickest layers have the lower voltages. This is likely due to trap states. This information will be critical for future efforts to optimize additive manufacturing processes for mechanically flexible electronics.

5:00 PM EL18.13.56
Facile Method for Crystallinity and Alignment Tuned Organic Semiconductor Layer through Solution Shearing Process Kibeom Nam, Dong Yun Lee and Kwang Woo Jeon; Kyungpook National University, Korea (the Republic of)

In this study, we introduce the patterning method for the thin film transistor with organic conducting materials. We exploited the flow coating method to control the physical and electronic properties of the conducting layer. Here, we demonstrate a high-performance Poly(3-hexylthiophene-2,5-diyl) regioregular (p3ht), and 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-PEN) as conducting film. It is because that both materials have a fine holes transfer property that it becomes a common material for various application such as organic field-effect transistors (OFETs) or organic photovoltaics (OPV). However, it is difficult to make them into a superb positive charge transfer layer. Because or that they need to form aromatic π- π stacking structures which allow holes hop to the adjacent polymer. To solve such problems, the flow coating system was adopted as a patterning method. The flow coating system is the solution shearing method that gives mechanical shear to solutions on a substrate. As solutions evaporat, the solutes moved toward the contact line to replenish the evaporated solvent and maintain the contact line due to the pinning force of the liquid on the substrate. With the movement of the blade, the solution also moved along the direction of the blade, leaving behind a tail of the meniscus. Such a process could control the stick-slip motion and the deposition volume of the solute. Therefore, various width of organic conducting patterns were fabricated within a minute. Furthermore, flow coating gave shear stress on the solution into a certain direction and it induced alignments of linear polymer chains. The aligned such as p3th showed an excellent electric property and its structures were measured x-ray diffraction. Clear (100) and (001) peaks mean regularly stacked parallel p3ht layers. To develop high-efficiency, cost-effective electronic devices, the technology that can print each element of the functional materials of the device without lithography is required. The solution shearing coating could be a powerful method to control the crystallinity of the organic semiconductor material and to improve the pattern and device efficiency below micrometer. The identification of the crystallization mechanism of organic materials that depends on the correlation between the coating speed, concentration, and gap size would be a core technology for next-generation organic semiconductors.

5:00 PM EL18.13.58
Targeted Nanomaterial Delivery via Self-Limiting Electrospray Deposition for Device Fabrication Michael Grzenda[1], Kelly Hughes[1], Maria Atzampou[1], Rachel Vladimirsky[1], Christopher E. Shuck[2], Yury Gogotsi[2], Jeffrey Zahn[1] and Jonathan P. Singer[1]; [1]Rutgers, the State University of New Jersey, United States; [2]Drexel University, United States

Electrospray deposition (ESD) uses strong electric fields to produce generations of monodisperse droplets from solutions/dispersions that are driven towards grounded targets. Self-limiting electrospray deposition (SLED) is a phenomenon recently discovered by our group in which targeted, 3D coatings can be achieved by spraying insulating polymers below their glass transition temperatures, which trap charge and repel incoming spray droplets. However, when conductive particles are added to SLED sprays to add functionalization, the buildup of charge required to repel incoming material becomes disrupted as particle loading increases. On the other hand, recent work from our group has shown that methylcellulose (MC) exhibits self-limiting behavior when sprayed from water/ethanol solutions and is capable of forming nanowire morphologies due to its fibril gelling behavior. By employing this unique material as a composite binder, we are able to separate conductive particles and prevent percolation with relatively low binder concentrations. We are also able to show that the morphology of these composites depends on the particle shape, size, and concentration, creating a high level of control over our deposited films. After spray, the MC can be removed which collapses the particles slightly into a connected network. Through this highly controlled spray regime, we are able to selectively target conductive and charge mobile substrates including metals and laser induced graphene, as well as nylon, high-humidity glass, and even plant material. Tested deposition materials include 2D MXene ($Ti_2C_3T_X$), ITO, and silver nanoparticles. All told, we demonstrate a novel and unique platform for upgrading flexible patterned substrates with high efficiency and low cost. As one example, we show that we can easily upgrade interdigitated electrodes patterned on flexible polyimide backings with MXene particles to vastly improve capacitance.

5:00 PM EL18.13.59
Aerosol Jet Printing of 3D Pillar Arrays from Photopolymer Ink Vitor Vlnieska[1], Evgeniia Gilshtein[1], Danays Kunka[2], Jakob Heier[1] and Yaroslav Romanyuk[1]; [1]EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [2]Karlsruhe Institute of Technology (KIT), Germany

An aerosol jet printing (AJP) printing head built on top of precise motion systems can provide positioning deviation down to 3 µm, printing volume as large as 20 cm x 20 cm x 30 cm, and five-axis freedom of movement. Typical uses of AJP are 2D printing on complex or flexible substrates, primarily for applications in printed electronics. Nearly all commercially available AJP inks for 2D printing are designed and optimized to reach desired electronic properties. In this work, we explore AJP for the 3D printing of free standing pillar arrays. We utilize aryl epoxy photopolymer as ink coupled with a cross-linking 'on the fly' technique. Pillar structures of 550 µm in height and with a diameter of 50 µm were printed. Pillar structures were characterized via scanning electron microscopy, where the morphology, number of printed layers and side effects of the AJP technique were investigated. Satellite droplets and over-spray seem to be unavoidable for structures smaller than 70 µm diameter. Nevertheless, reactive ion etching (RIE) was investigated as a post-processing step, and it can mitigate AJP side effects. AJP-RIE together with photopolymer-based ink can be promising for microstructure 3D printing, offering fast and maskless manufacturing process without wet chemistry development and heat treatment post-processing steps.

5:00 PM EL18.13.60
Higher Molecular Weight Polymer Yields Higher Performing Organic Electrochemical Transistors Lucas Flagg[1], Jonathan W. Onorato[2], Christine Luscombe[3,2] and Lee Richter[1]; [1]NIST, United States; [2]University of Washington, United States; [3]Okinawa Institute of Science and Technology, Japan

Organic Electrochemical Transistors (OECTs) are an important platform for benchmarking emerging applications in polymeric mixed ionic/electronic conductors. In such applications, the polymer semiconductor is swollen by the electrolyte, which leads to drastic changes in design rules compared to the more well understood alkyl-side chain polymers that have been studied for flexible electronic applications for the past few decades. Here we study the model mixed conductor poly(3-(methoxyethoxyethoxymethyl)thiophene) (P3MEEMT) as a function of molecular weight, thermal annealing, and regioregularity. We first show that OECT performance increases with increasing molecular weight. We next show that low molecular weights are unable to withstand even moderate thermal treatments. We hypothesize this is due to less inter-crystal connections in the lower Mn polymers and that this detrimental effect is enhanced in OECTs, compared to conventional Organic Field Effect Transistors (OTFTs), due swelling. Finally, we investigate the role of regioregularity on the OECT performance. Surprisingly, we find reduced regioregularity increases the volumetric capacitance of these films at the expense of carrier mobility. However, these competing effects tend to offset resulting in device performance that is largely independent of regioregularity. These findings will help establish design rules for novel polymeric mixed conductors going forward.

SESSION EL18.14: Flexible, Stretchable and Printed Energy Devices
Session Chairs: Sihong Wang and Yilei Wu
Friday Morning, April 14, 2023
Moscone West, Level 3, Room 3018

8:00 AM EL18.14.01
Process Development of Flexible Thermoelectric Modules Based on Printing and Sintering Technology Lu-Cheng Hou, Shih-Yao Chien and Chien-Neng Liao; National Tsing Hua University | Taiwan (ROC), Taiwan

Thermoelectric generators (TEGs) that can convert environmental thermal energy into electricity are regarded as a potential solution to support the intermittent energy consumption of wearable devices and remote wireless sensors. Flexible TEGs (*f*-TEGs) based on printing technology have gained growing interests due to their design flexibility, ease of fabrication, and low cost. In this report, we have demonstrated a planar *f*-TEG with 8 pairs of Bi-Te based thermoelements prepared by dispenser printing and pressured sintering processes. The *f*-TEG can deliver a power of 68 μW under a temperature difference of 33 K. A modular assembly of 7 planar *f*-TEGs is sufficient to power a light-emitting diode and charge a 1.2 V NiMH battery. In addition to planar TEG configuration, a *f*-TEG with vertical thermoelement arrangement is also under development. The major issue associated with the vertical TEG fabrication is the poor electrical and mechanical contacts between Cu electrodes and thermoelements caused by gross interfacial reaction during the pressured sintering process. We have introduced a Pd/Ni composite barrier metallization in between the Cu electrode and the printed thermoelements by a selective chemical deposition method to resolve the contact issue. The influence of pressured sintering conditions on the microstructure and contact property of the Cu/thermoelements is investigated.

8:15 AM EL18.14.02
Thermocleavable Sidechains Prevent Phase Separation of Polymer Photovoltaic Blends in Extreme Desert Temperatures Nathaniel L. Prine[1], Haoyu Zhao[1], Andrew Bates[1], Guorong Ma[1], Stephanie Samson[2], Jordan Shanahan[2], Wei You[2] and Xiaodan Gu[1]; [1]The University of Southern Mississippi, United States; [2]University of North Carolina at Chapel Hill, United States

The morphology of organic photovoltaic (OPV) polymer blends remains unstable if exposed to temperatures above the combined glass transition temperature (T_g) of the OPV blend. Incorporating thermocleavable sidechains onto the backbone of polymer donors enables the solution processability of the blend while reserving the option to cleave those sidechains from the backbone thermally. Cleaving the sidechains drastically slows chain dynamics by raising the polymer backbone's Tg and preventing the morphology from shifting toward equilibrium. In this work, a polythiophene polymer donor featuring cleavable sidechains (P3ET) is blended with a PCBM small molecule acceptor and examined to determine the effect of cleavage on morphology. The blend is examined pre- and post-cleavage using atomic force microscopy paired with infrared spectroscopy (AFM-IR) to determine the nanoscale composition of the topography. First, we studied the effect of cleavage temperature on BHJ morphology. We observed that thermal cleavage at 140 ^{0}C, near the donor's crystallization temperature, induces undesired crystallization of the donor and drives large phase separation. In contrast, the blend annealed at 200 ^{0}C allowed efficient cleavage and exhibited similar morphology to the as-cast film, albeit some dewetting occurs. For long-term stability measurements, the sidechains were cleaved entirely from the backbone by heating the blend at 200 ^{o}C for two hours. We demonstrated that after cleavage, the sample was stable over a long period of thermal stress (e.g. 100 ^{o}C over multiple days) without significant changes in morphology. Overall, incorporating thermally-cleavable sidechains onto a polymer electron donor is a suitable strategy for preventing significant morphology shifts in OPV blends exposed to temperatures up to 100 ^{o}C.

8:30 AM EL18.14.03
High-Performance, Stretchable Thermoelectric Generators with Reduced Internal Resistance for Fully Untethered Wearables Dongju Jang[1], Hyeon Cho[1], Jinsu Yoon[1], Byeongmoon Lee[2], Seungjun Chung[2] and Yongtaek Hong[1]; [1]Seoul National University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)

Emerging sustainable energy sources are keys to realizing the concept of Internet of Things (IoT), precluding the necessity of human interference and extending the potential of electronics towards self-powered and fully-automated systems. Among various candidates, thermoelectric energy generators (TEGs) represent a promising technology for implementing such systems due to their ability to convert waste heat into electricity.

Stretchable TEGs have recently been developed for efficient energy harvesting from shape-changing, arbitrary-shaped heat sources such as the human body. Moreover, integrated platforms with high-performance conventional thermoelectric (TE) materials and soft electrodes have been widely explored with the rising demand for high-performance soft and stretchable TEGs for practical applications. However, previously reported TEGs of such forms have displayed low power generation capacity due to poor interfacial properties between rigid-soft materials and unsatisfactory electrical and thermal performance of soft components.

In this presentation, we will report facile and effective strategies to improve the TE performance of stretchable TEGs for low power, wireless and wearable applications. First, functional interlayers that bridge discrete electromechanical properties at the rigid-soft interface are introduced into the platform using a scalable approach. Second, a solution-based welding method [1] is applied to generate a highly conductive stretchable electrode based on a volumetrically connected network of one-dimensional metal nanowires. Third, intrinsically soft thermal conductors are incorporated into the soft substrate to match the thermal impedance between the TEG and heat source [2]. Such techniques effectively resolve the issues in previously reported high-performance stretchable TEGs and enhance the power generation capacity by 540 % of the original value of a reference TEG. This corresponds to the highest normalized power density of ~1.48 μW cm^{-2} K^{-2} when excluding the applied temperature and device dimensions for accurate comparison. These results highlight the viability of our strategies to realize high-performance stretchable TEGs for self-powered wearable applications. The detailed methods and results will be discussed at the conference.

Acknowledgment
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8:45 AM EL18.14.04
Tunable Thermoelectric Performance of Thin-Film Multilayered PEDOT:PSS for Flexible Devices Tzu-Yi T. Yu, Bokai Zhang, Hasan Emre Baysal and Francisco Molina-Lopez; KU Leuven, Belgium

Power supply is a main challenge for wearable electronics and thermoelectric generators (TEGs), which directly convert a temperature difference into electrical power, are a promising solution. Owing to their great mechanical flexibility, material abundance, printability, and low toxicity, TEGs based on organic materials (OTE) show greater potential than their inorganic counterpart to power wearable devices. Among the OTE materials, PEDOT:PSS exhibits one of the best thermoelectric performance. The performance of thermoelectric materials/devices is usually evaluated by the power factor, which is the product of electrical conductivity to the square of the Seebeck coefficient. Many strategies – such as using secondary dopants, post-treatments, and morphological alignment – have been reported to boost the power factor of PEDOT:PSS via increasing the electrical conductivity. However, thus far, the only method to increase the Seebeck coefficient of PEDOT:PSS is de-doping it by the addition of reductive agents. However, de-doping strongly harms the electrical conductivity, which limits the strategies for TEGs design. Herein, we demonstrate a new structure-based approach to improve the Seebeck coefficient of PEDOT:PSS without strongly degrading its electrical conductivity. Inspired by the energy filtering effect used in inorganic TEs, our approach consists of the fabrication of a thin-film multilayer stack that promotes the interfacial scattering of the low-energy carriers detrimental to the Seebeck effect. Optical spectroscopy and X-ray scattering techniques will be used to study the oxidation level and morphology of the produced stack, shedding light on the structure-performance relationship in the material and paving the way to the optimization of the thermoelectric performance. To demonstrate the suitability of our approach for wearable devices, a flexible version of the multilayered material will be produced.

9:00 AM *EL18.14.05
A soft future - From Electronic Skins and Triboelectric Nanogenerators to Autonomous Wearables and Soft Robots Ying-Chih Lai; National Chung Hsing University, Taiwan

Deformable and wearable soft devices (including sensors, electronics, and machines) have attracted huge interest because they cannot only extend the scope of smart systems but also provide compliant and safer user experience. Operating those devices inevitably need power sources. However, traditional batteries suffer from heavy weight, bulky volume, and limited capacity and lifetime, hindering the practical uses of those emerging devices. Toward the soft future, it is necessary to explore new energy and electronics technology. In this talk, deformable and mechanically-durable energy-harvesting nanogenerators will be demonstrated for not only serving as new energy providers but also self-powered e-skin uses. First, super-stretchable triboelectric nanogenerators will be presented for generating electricity by contacting with other materials regardless of various extreme deformation required from uses, such as extreme stretching, multiple twists and folds. Surprising, even experiencing severe tearing damages, the device can retain its functionality. Such technology can be introduced into fabrics for wearable energy and sensing uses. Then, we will discuss the use in self-powered and deformable electronic skins that can actively sense proximity, contact, and pressure to external stimuli via self-generating electricity. The perfect integration of the tribo-skins and soft actuators enables soft robots to perform various actively sensing and interactive tasks including actively perceiving their muscle motions and working states, checking baby diaper conditions, and even detecting subtle human physiological signals. The self-generating signals enable visual communication and can be processed for diverse sophisticated uses. Then, let’s imagine a self-healing robotics in science fiction turning into reality. We will show you a self-healing, highly-transparent, and super-stretchable device with energy-extracting and activity-sensing abilities. Finally, a new energy harvesting technology that can convert ambient electromagnetic energy into available electricity for soft devices will be presented. These works will inspire you lots of great ideas and show tremendous potentials of wearable/stretchable/deformable electronics, artificial e-skins, smart interfaces, and soft robots.

9:30 AM EL18.14.07
All-Solid-State Printed Graphene Aerosol Gel - Polymer Energy Storage Devices for Flexible and Twistable Electronics Suprem R. Das, Kh M Asif Raihan and Surjit Sahoo; Kansas State University, United States

The continual evolution and rapid implementation of smart electronic appliances and many microelectromechanical systems have led to growing interest in developing micro or nanoscale power sources [1]. With exceptional electrochemical performances such as rapid charge-discharge rate, prolonged cycle life, and ultrahigh power density, supercapacitors (SCs) possess substantial potential as an effective energy storage device, as an alternate storage framework, besides batteries. However, conventional SCs are too bulky to combine with micro-scale electronic devices. Therefore, the design and manufacture of high-end micro-scale SCs, known as micro-supercapacitors (MSCs), with desired device dimensions (of the order of few centimeters/millimeters) and high-performance metrics are needed [2]. During last few years, considerable efforts have been dedicated to fabricating 2D planar interdigitated configuration patterns for MSCs using inkjet printing techniques due to their geometric flexibility and wearable applications [3]. Herein we designed the inkjet-printed graphene aerosol interdigitated electrodes based on flexible all-solid-state MSCs with highly stable and reliable energy storage performance. The fabricated graphene aerosol-based solid-state MSC obtained a high volumetric specific capacitance of 376.63 mF cm^{-3} (areal specific capacitance of 76.23 μF cm^{-2}) at the applied current of 0.25 μA with excellent cyclic stability (~99 % of capacitance retention over 10000 cycles). Further, MSCs with modular connections in series and parallel were made to achieve tunable operating voltage and capacitance output. To elucidate the mechanical flexibility of the as-fabricated MSC, the electrochemical performances of the graphene aerosol-based solid-state MSC under different bending and twisting states and results in outstanding mechanical flexibility. The electrochemical performance of as-fabricated graphene aerosol-based all-solid-state MSC creates a promising way to develop highly scalable and reliable future miniaturized energy storage devices for integrated wearable electronics.
Keywords: Graphene aerosol, Micro-supercapacitors, Volumetric specific capacitance, Wearable devices.
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9:45 AM BREAK

SESSION EL18.15: Flexible and Stretchable Devices II
Session Chairs: Ying-Chih Lai and Wentao Xu
Friday Morning, April 14, 2023
Moscone West, Level 3, Room 3018

10:30 AM *EL18.15.02
A Smart Wound Dressing with Self-Powered Electrical Stimulation and Monitoring Capabilities Zong-Hong Lin[1,2]; [1]National Taiwan University, Taiwan; [2]National Tsing Hua University, Taiwan

Electrical stimulation based therapy are known to accelerate the healing of the chronic wounds. However, its usage is limited by requirement bulky power-consuming sources that definitely requires patient hospitalization. To resolve these constraints, we have developed a self-powered multi-functional wound dressing which can be activated by both triboelectric and thermoelectric effect. The integrated electrodes are connected to wearable nanogenerators to provide electrical stimulation for accelerated wound closure. The dressing is coated with thermocatalysts to kill the bacteria in the wound owing to the formation of reactive oxygen species. In addition, a wireless measurement module was incorporated into the system to realize remote wireless monitoring of wound recovery in a non-invasive way. The reported self-powered dressing holds great potential in facilitating personalized and user-friendly wound care with significantly improved healing and monitoring outcomes.

11:00 AM EL18.15.03
Autonomous Self-Healing Strategy for Deformable Electronics Based on Ionic Copolymer-Mediated Ion Clusters Yong Min Kim and Hong Chul Moon; University of Seoul, Korea (the Republic of)

Implementing self-healing capability on a deformable platform is one of the critical challenges for achieving future wearable electronics with high durability and reliability. Moreover, self-healing materials are expected to maximize the utility of electronic equipment in extreme conditions not easily accessible to humans, such as the space and deep-sea. Nonetheless, most systems required external energy (e.g., heat or UV) to promote polymeric chain mobility and to be quickly and completely healed, irrespective of the utilization of covalent and non-covalent bonds. In this work, we propose an innovative self-healing process driven by the rapid dynamic formation/dissociation of ion clusters (ICs). The novel aspect of this work lies in (1) achieving record-high self-healing performance (efficiency > 90% even in 1 min at 25 °C), with no energy injection, (2) overcoming the conventional trade-off between mechanical robustness and healing performance present in previously reported systems, (3) unveiling underlying fundamental science related to IC-driven mechanism that does not require significant movement of polymeric chains for self-healing, and (4) successful demonstration of a new future electronics platform, “reconfigurable electronics”, which can change shape according to the users’ demands through a cutting/healing protocol. Overall, the present results highlight the high potential impact of self-healable ionoconductor and provide insights into future electronics platforms.

11:15 AM EL18.15.04
Tailoring Auxetic Mechanical Metamaterials of Strain-Engineered Transparent Elastomeric Substrates for Distortion-Free Stretchable Display Jun-Chan Choi[1], Jae-Hong Sun[1], Seunghyun Lee[2] and Seungjun Chung[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Seoul National University of Science and Technology, Korea (the Republic of)

Form factor innovation is essential for the future of display technology. Representatively, flexible, foldable, and rollable displays shed light on various electronic devices such as monitors, smartphones, and smartwatches by allowing a high degree of design freedom. Recently, stretchable displays, evaluated as the end point of shape-deformable display technology, are attracting attention as the next-generation display technology. Due to their free-form deformability, stretchable displays can be combined with various future electronic applications such as wearable electronics, biosensors, and robots to expand the application fields of display technology. From an actual application perspective, it is desirable to exhibit a stable tensile/recovery deformation in the range of about 30% and use transparent elastomeric polymers having a relatively low Young's modulus as substrate materials. However, elastomeric materials inherently have a Poisson's ratio of ~0.5, which is defined as the ratio of transverse strain to longitudinal strain resulting in compressive strain in the direction perpendicular to the tensile direction. When the substrate deformation by the Poisson’s effect occurs in stretchable displays, undesirable image distortion, so it has to be addressed to provide accurate information. Here, we propose a strain-engineered transparent elastomer composite as a substrate of stretchable displays. To control the Poisson's ratio of the stretchable substrate, a relatively rigid mechanical metamaterial frame was embedded into the elastomeric matrix material. Among various mechanical metamaterial structures, a ribbon-shaped auxetic structure was employed with the consideration of both display pixel movement and bidirectional independent deformation control under stretching conditions. According to the tensile direction of the stretchable substrate, both intrinsic tensile deformation of the elastomer and the structure-dependent deformation occurred simultaneously in a complex manner, and it was possible to realize the biaxially zero Poisson's ratio by overcoming the deformation limit of the existing mechanical metamaterial. As a result of quantitatively evaluating the tensile axis-dependent Poisson's ratio according to the Young's modulus ratio of the frame and the matrix materials, when Young's modulus deviation was about 20 times, the Poisson's ratio (< 0.1 irrespective of the tensile axis) was significantly reduced compared to that of the pristine elastomer substrates. In addition, by matching the refractive indices between the heterogeneous elastomer materials used for the frame and the matrix, the scattering effect caused by the refraction of the light incident on the substrate was suppressed, thereby showing excellent light transmittance (~87% in the visible range) and visibility. Our work will provide a key pathway to demonstrate the programmable deformation of stretchable platforms overcoming the Poisson’s effects of conventional elastomeric substrates, which is necessary to realize further reliable stretchable display applications.

SESSION EL18.16: Flexible and Stretchable Devices III
Session Chairs: Erin Askounis and Wentao Xu
Friday Afternoon, April 14, 2023
Moscone West, Level 3, Room 3018

1:30 PM *EL18.16.01
A Processable, High-Performance Dielectric Elastomer and Multilayering Process Erin Askounis[1], Ye Shi[1], Roshan Plamthottam[1], Tom Libby[2], Zihang Peng[1], Kareem Youssef[1], Junhong Pu[1], Ron Pelrine[2] and Qibing Pei[1]; [1]University of California, Los Angeles, United States; [2]SRI International,

United States

Dielectric elastomers (DEs) can act as deformable capacitors that generate mechanical work in response to an electric field. DEs are often based on commercial acrylic and silicone elastomers. Acrylics require prestretching to achieve high actuation strains and lack processing flexibility. Silicones allow for processability and rapid response but produce much lower strains. In this work, a processable, high-performance dielectric elastomer (PHDE) with a bimodal network structure is synthesized, and its electromechanical properties are tailored by adjusting cross-linkers and hydrogen bonding within the elastomer network. The PHDE exhibits a maximum areal strain of 190% and maintains strains higher than 110% at 2 hertz without prestretching. A dry stacking process with high efficiency, scalability, and yield enables multilayer actuators that maintain the high actuation performance of single-layer films.

2:00 PM EL18.16.02
A Nanomesh Skin-Sensor that Rapidly Learns Hand-Based Tasks with Limited Trials Kyun Kyu Kim and Zhenan Bao; Stanford University, United States

With the help of machine learning, electronic devices — including gloves and electronic skins — can track the movement of human hands and perform tasks such as object and gesture recognition. However, such devices can be bulky and lack an ability to adapt to the curvature of the body. Furthermore, the existing models for signal processing require massive amounts of labelled data for individual tasks and users.
Here, we report a nanomesh receptor that is integrated with an unsupervised meta-learning scheme and can be used for data-efficient user-independent recognition of different hand tasks. The nanomesh is based on biocompatible materials and can be directly printed onto the skin without the need for an external substrate, which improves user-comfort and avoids potential substrate mechanical constraints. The system can translate skin stretches into proprioception information, analogous to the way cutaneous receptors provide feedback for hand. With the approach, complex proprioceptive signals can be decoded using a single sensor along the index finger, without the need for a multi-sensing array. Highly informative multi-joint proprioceptive information can thus be produced in low-dimensional data, reducing computational processing time of our learning network. Our learning framework does not require large amounts of data to be collected for each individual user. We develop a time-dependent contrastive learning algorithm to provide an awareness of temporal continuity and to generate a motion feature space. Our system pretrains unlabelled signals collected from three different users to distinguish user independent, task specific sensor signal patterns from random hand motion. We show that the pretrained model can quickly adapt to different daily tasks —motion command, keypad typing, two-handed keyboard typing, and object recognition — using only a few personal hand signals. [1]
Reference:
1. K.K.Kim, Z.Bao*, Nature Electronics, in press

2:15 PM EL18.16.03
Towards More Sustainable Organic Electronics Julianna Panidi, Martina Rimmele, Nicola Gasparini and Martin Heeney; Imperial College London, United Kingdom

Organic semiconductors are an emerging class of materials with various optoelectronic applications. The high commercialization potential of this technology is evidence by few companies that have already launched their products into the market or working towards this goal. More specific, organic solar cells have recently attracted immense attention due to the development of a new family of semiconductors which allows highly efficient light harvesting in both indoor and outdoor conditions. In addition, solution processed organic photovoltaics in conformable substrates have been recently demonstrated, which broadens the applications range. Solar cells can now be part of the Internet of Things ecosystem by light harvesting and delivering enough output power to drive microelectronics. One currently limitation, though, is the use of not eco-friendly solvents and materials during the device development stages. Most of the organic electronic devices require halogenated and non-halogenated aromatic solvents during their fabrication. For large scale production and further commercialisation, this is a key limitation. This arise from the fact that organic semiconductors are highly soluble in this category of solvents, which are often carcinogenic or toxic to the human reproductive systems, as well as inducing negative impact on the environment.

Here we will show high performing organic solar cells developed from novel more sustainable organic semiconductors (in terms of less waste during synthesis and less energy consumption) as well as eco-friendly solvents. In particular, solvents derived from biomass have been explored for their application in delivering high performing organic photovoltaics. Eco-friendly flexible organic solar cells have also been developed on natural transparent materials. Electrical device characterisation and morphological studies were conducted in order to evaluate their performance. Overall, this work highlights the importance of replacing harmful chemicals and materials in the organic electronics fabrication stages, which it will result in faster and wider commercialisation and create new market opportunities.

2:30 PM EL18.16.04
Stretchable Light-Emitting Electrochemical Cell Fabricated by Spray Coating Sandra Gellner[1,2], Etienne Auroux[2], Ekaterina Nannen[1] and Ludvig Edman[2]; [1]University of Applied Sciences Niederrhein, Germany; [2]Umeå University, Sweden

The prospect of a stretchable light-emitting device is attractive since it enables a wide variety of applications that require adaptability to a dynamic environment. The light-emitting electrochemical cell (LEC) is a promising technology in this regard, due to its simple three-layer device architecture and its inherent tolerance to local active-material thickness variations. The latter advantages also render the LEC suitable for a scalable and low-cost solution-based fabrication. A number of reports on stretchable LECs have been reported,[1–3] but they either employ a poorly scalable spin-coating fabrication of the active material or a lamination of the top electrode on top of the active material. This renders the fabrication wasteful with materials and expensive and results in a poor long-term stability because of delamination issues. Here, we report on a material-efficient and lamination-free fabrication of the entire stretchable LEC structure, including both electrodes, using scalable spray coating under ambient air.

Literature
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(2) Liang, J.; Li, L.; Niu, X.; Yu, Z.; Pei, Q. Elastomeric Polymer Light-Emitting Devices and Displays. *Nat. Photonics* 2013, *7* (10), 817–824.
(3) Liu, J.; Wang, J.; Zhang, Z.; Molina-Lopez, F.; Wang, G.-J. N.; Schroeder, B. C.; Yan, X.; Zeng, Y.; Zhao, O.; Tran, H.; Lei, T.; Lu, Y.; Wang, Y.-X.; Tok, J. B.-H.; Dauskardt, R.; Chung, J. W.; Yun, Y.; Bao, Z. Fully Stretchable Active-Matrix Organic Light-Emitting Electrochemical Cell Array. *Nat. Commun.* 2020, *11* (1), 3362.

2:45 PM EL18.16.05
Cadmium-Free and Air-Stable Quantum Dot Light-Emitting Diodes Felix Hermerschmidt[1], Paul Hänsch[1], Selen Solak[1], Hyung Seok Choi[2], Yohan Kim[2], Manuel Gensler[2], Jiyong Kim[2], Christine Boeffel[2] and Emil J. List-Kratochvil[1,3]; [1]Humboldt-Universität zu Berlin, Germany; [2]Fraunhofer Institute

for Applied Polymer Research, Germany; [3]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany

The global market for printed, flexible and organic electronics is dominated by the display industry. Innovation is needed to increase screen resolution and displayable colour space in solution-processed displays. This requires the development of new printing methods and light-emitting material systems. The compatibility of solution-based materials with such scalable fabrication techniques has driven research towards new devices within the field of organic and hybrid optoelectronics.

The European Union's Horizon 2020 funded project *Hi-Accuracy* aims at developing high-resolution printing technologies to target a fully printed electroluminescent display incorporating quantum dots (QDs) as the light-emissive material [1]. This includes both the so-called front plane, which incorporates the luminescent components, as well as the so-called back plane, which incorporates the tiny electrical logic elements under each pixel.

QDs have found increasing use in display applications because of their high colour purity and fluorescence quantum yield, enabling devices with higher brightness and efficiency. But in order to access large-area printing and coating methods in ambient conditions, it is necessary to, firstly, move away from toxic cadmium [2], and secondly, to target materials that are air-stable. We have synthesised a new zinc selenide-based blue QD material which can be used in fully air-processed light-emitting diodes (LEDs) [3].

Multi-shell-structured ZnSeTe/ZnSe/ZnS (core-shell-shell) QDs show pure deep blue / purple fluorescence emission with a high photoluminescence quantum yield of 98%. Using these materials, LED devices are fabricated in ambient air conditions in a conventional structure with bottom light emission. The analysis of electron-only and hole-only devices using the same materials confirm the underlying transport mechanisms.

The QD-LED devices show maximum luminance of 3000 cd m^{-2} at 7 V with a turn-on voltage of 3 V and current efficacy of 0.6 cd A^{-1}. These results show for the first time air-processed and Cd-free QD-LEDs and pave the way for scaling display applications in order to move towards high-performance electronics [3].

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 862410 (HI-ACCURACY).

References

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[3] P. Hänsch et al., manuscript in preparation.

3:00 PM BREAK

3:30 PM EL18.16.06
Omni-directional Deformable Shear Sensor with Shear-Pressure Decoupling by Analyzing Frequency-Dependent Ion Dynamics Wonjeong Suh, Jaehyun Kim, Yebin Park, Dongbeom Kim and Unyong Jeong; Pohang University of Science and Technology, Korea (the Republic of)

Artificial tactile sensor realizes touch by mimicking human skin and receptors. They have been used for healthcare monitoring devices, human-machine interfaces, and artificial skin for robots. Especially, this sensor is attached to the robot's skin and recognizes the stimuli, as if it was felt by a human. When human grabs an object, they feel applied normal and shear force and control the pressure to prevent the object from breaking or falling. To realize this delicate grasping motion in the robot, a shear force sensor is essential. However, the shear force sensor is structurally complicated because the electrode must be configured in a three-dimensional structure to recognize the force applied horizontally. Moreover, during the grasping motion, also minimal pressure is applied so that both pressure and shear force need to be recognized.

Herein, we fabricated an ionic conductor-based soft sensor that can detect pressure and shear force separately. In an ionic conductor, various information can be obtained because the behavior of ions varies depending on the frequency. To use these advantages, the ion gel is placed between a hemispherical upper electrode and a flat lower electrode. The pressure is measured in low frequency to detect the electrical double layer(EDL) capacitance between the ion gel and the dome-shaped upper electrode, and the shear force is perceived in high frequency to detect bulk resistance of the ion gel. Therefore, with only ion gel, the sensor can perceive and differentiate pressure and shear force in different frequencies. Furthermore, the sensor can recognize shear force in any direction with 1 x 4 electrodes. Finally, the sensor can perceive various grasping in any direction and even delicate gestures such as opening a bottle cap.

3:45 PM EL18.16.07
Two-Dimensional Graphene and MXene Electrodes for Flexible and Stretchable Optoelectronics Huanyu Zhou[1], Shin Jung Han[1], Yury Gogotsi[2] and Tae-Woo Lee[1]; [1]Seoul National University, Korea (the Republic of); [2]Drexel University, United States

Two-dimensional (2D) materials such as graphene and MXenes have great potential applications in a variety of flexible and wearable optoelectronic devices as a replacement for conventional brittle indium tin oxide electrodes. However, the practical applications of such materials have been limited due to the high charge injection barrier at the electrode and organic interfaces. Here an environmentally stable MXene conductive electrode with high conductivity and work function (*WF*) = 5.84 eV was demonstrated; this provides the solution to the poor environmental stability of MXene thin films without sacrificing electrical properties. Besides, to tackle the charge injection problem occurred at the one-dimensional metallic nanowire/organic interfaces, a graphene layer was introduced on top of silver nanowire percolation networks to form a complete two-dimensional contact stretchable electrode (TCSE). The graphene layer significantly modifies the work function, promotes charge spreading, and impedes the inward diffusion of oxygen and moisture. Unprecedently, the low *WF* of 3.57 eV is achieved by forming a strong interfacial dipole after deposition of a newly-designed conjugated polyelectrolyte on the TCSE, which significantly facilitate the electron injection property. We have demonstrated intrinsically stretchable organic light-emitting diodes (ISOLEDs) with a record efficiency of 20.3 cd/A. These works lay a solid platform and provide a general guideline for designing highly-efficient flexible and stretchable optoelectronic devices.

Reference

Adv. Mater. 2022, 34, 2203040.
Adv. Mater. 2022, 34, 2206377

4:00 PM EL18.16.08
Fermi-Level Pinning in Organic Thin-Film Transistors Tobias Wollandt, Kathrin Küster, Sabrina Steffens and Hagen Klauk; Max Planck Institute for Solid State Research, Germany

Organic thin-film transistors (TFTs) are of interest for flexible electronics applications, such as flat-panel displays and sensors. An important performance parameter is the transit frequency, which is the highest frequency at which the TFTs are able to amplify electrical signals. The transit frequency is determined by several parameters, including the intrinsic channel mobility, the channel length, the gate-to-contact overlaps, and the contact resistance. It can be shown that in organic TFTs that have an intrinsic channel mobility of at least 5 cm^2/Vs and critical dimensions of a few microns, the transit frequency is limited almost entirely by the contact resistance. This implies a significant incentive for reducing the contact resistance to improve the dynamic TFT performance.

The contact resistance is determined mainly by the energy-level alignment at the interface between the semiconductor and the source/drain contacts, and (in the case of TFTs fabricated in the inverted coplanar device architecture) by the thin-film morphology of the semiconductor on the contact surfaces [Adv. Mater. **32**, 2104075, 2022]. Functionalizing the contact surfaces with a chemisorbed monolayer (e.g., a thiol) prior to the organic-semiconductor deposition can be helpful in improving the semiconductor morphology and in adjusting the Fermi level of the contacts by introducing an interface dipole. In principle, this dipole lowers the Schottky barrier between the Fermi level of the contact and the transport level of the semiconductor, thereby reducing the contact resistance. For TFTs fabricated on flexible polyethylene naphthalate (PEN) substrates using the small-molecule semiconductor diphenyl-dinaphthothienothiophene (DPh-DNTT) and gold source/drain contacts functionalized with a monolayer of pentafluorobenzenethiol (PFBT), we have measured an average contact resistance of less than 100 Ωcm (and an intrinsic channel mobility of 9 cm^2/Vs, a subthreshold swing of 65 mV/dec, a threshold voltage of -1 V, and an on-off current ratio above 10^8).

Perfect energy alignment at the interface between metal contacts and an organic semiconductor is, however, often prevented by a pinning of the Fermi level to the energy of localized electronic states in the semiconductor. Measurements have shown that any work-function changes induced by functionalizing the contacts with a thiol are eliminated once the organic semiconductor is deposited. Further significant reductions of the contact resistance will thus require that the Fermi level is depinned to allow energy-level alignment.
A promising approach to depinning the Fermi level is to introduce an interlayer between the metal and the semiconductor in order to decouple the metal from the localized states in the semiconductor. To investigate the effectiveness of this approach in organic TFTs, we fabricated DPh-DNTT TFTs using a wide range of interlayer materials. The interlayers and the organic semiconductor were deposited by thermal sublimation in vacuum. The interlayer thickness was limited to a few nanometers to balance the beneficial effect of charge decoupling and the detrimental effect of the tunneling barrier.

In the literature, it has been suggested that in the case of p-channel TFTs, the interlayer needs to have a large ionization energy [Adv. Electron. Mater. **6**, 1901352, 2020]. However, we have found that a high ionization energy alone is insufficient and that other factors, including the semiconductor morphology, the interlayer thickness and possibly electronic interactions such as doping must be considered. For some interlayer materials, we have observed a substantial reduction in contact resistance compared to TFTs without any interlayer (contact resistance as small as 15 Ωcm in TFTs fabricated using a 2-nm-thick tetratetracontane interlayer), but a clear correlation to the ionization energy of the interlayer remains elusive.

4:15 PM EL18.16.09
UV-light Monitor Based on Poly (vinyl alcohol)/Titanium Oxide Hybrids Abdulaziz Aldubayan and Natalie Stingelin; Georgia Institute of Technology, United States

Exposure to ultraviolet (UV) radiation can have a profound impact on human health, as about 90 precent of nonmelanoma skin cancers are associated with exposure to UV radiation, and more than 9,500 people are diagnosed with skin cancer every day in the United States. The excessive UV rays damage DNA in skin cells, and produce genetic mutations that subsequently lead to skin cancer and premature ageing. Yet, controlled quantities of UV rays offer several benefits, such as the production of vitamin D and treatment of various inflammatory skin diseases including eczema, psoriasis, and atopic dermatitis. We present, here, a highly versatile, eco-friendly and mechanically flexible UV sensor able to detect and measure harmful UVB rays. The sensor utilizes the dielectric constant change due to the formation of Ti^{+3} (from Ti^{+4} to Ti^{+3}) in poly (vinyl alcohol)/titanium oxide hydrates organic:inorganic hybrid materials upon irradiation, to provide instantaneous and cumulative analysis of property change upon UV light exposure. Thus, our work not only demonstrates a sustainable system to UV detection but also opens a new versatile and mechanically robust materials class towards an inexpensive reusable wearable device to help monitor personal recommended UV doses.

4:30 PM EL18.16.10
2D/3D Printed Metal Oxide Transistors Gabriel Cadilha Marques, Pooja Arya, Ben Breitung, Jasmin Aghassi-Hagmann and Hongrong Hu; Karlsruhe Institute of Technology, Germany

Metal oxide based nanoparticle inks allow to print electronic devices such as thin film transistors processed at low temperatures (around 100 °C). In addition, 3D printed assist structures can help to define key dimensions such as the width of inkjet printed transistors. The combination of 2d inkjet printing and laser printing of 3D structures based on two photon polymerization can yield novel device architectures that allow to reduce the variability in particular of important parameters such as the threshold voltage and enable small channel length smaller than 10 um. In addition to novel device architectures p-type oxides are explored with a matching performance to their n-type counterparts. This would improve the performance and power efficiency of CMOS type oxide circuits.
Along these lines transistors with In_2O_3-semiconducting nanoparticles printed into a 3D laser written polymer reservoir with 10 um height are presented. Electrical characteristics are discussed including transfer and output curves as well as FIB cuts and cross-sectional SEM images. Our devices show high Ion currents in the range of several hundreds of µA for typical widths of few hundreds of micrometers.
Furthermore, the performance of p-type based oxide semiconductors is improved by element doping. Thereby, copper oxide is doped with magnesium to improve the electronic band structure of pristine copper oxide. The magnesium improves the bonding between anions in the conduction band maximum, lowering the effective mass of holes and hence increasing the mobility of p-type oxide materials. The doped copper oxide compounds are based on nanopowders that are formulated into nanoparticle inks. This will enable to print high performance p-type oxide semiconductors at low temperatures.
In summary, the presented work will pave the way for high performance printed oxide based transistors with stable threshold voltages that can be used for reliable complementary circuits in printed electronics.

SESSION EL18.17: Virtual Session I
Session Chairs: Ho-Hsiu Chou and Francisco Molina-Lopez
Tuesday Morning, April 25, 2023
EL18-virtual

8:00 AM EL18.17.01

Efficient and Stable Organic Solar Cells with PM6:Y6-Based Photoactive Layer Enabled by p-Type Doping Nara Han, Yina Moon, Dongseong Yang and Dong-Yu Kim; Gwangju Institute of Science and Technology, Korea (the Republic of)

The introduction of molecular doping process is necessary to enhance the optic and electronic properties of organic semiconductors for facilitating charge transport. In particular, since the doping process has a positive influence on the charge transfer interaction between the host semiconductor and dopant, improved mobility has been efficiently achieved via these doping methods using p- or n-type dopants. Despite its advantages, doping technologies in organic solar cells (OSCs), which are generally known to have better hole mobility, are restricted to the development of n-type dopants used for balancing the electron and hole as increasing the electron mobility. In addition, since the bulk-heterojunction (BHJ) microstructure in OSCs has randomly blended phases of the donor and acceptor, it is important to optimize charge extraction without loss by controlling the morphology. In this study, we report OSCs by p-type doping with formic acid into a BHJ photoactive layer comprised of PM6 and Y6. The resulting champion device yields a significantly improved power conversion efficiency from 14.3% to 15.3% with a high fill factor of 71.7%. It is found that the p-doped photoactive layer exhibits enhanced conductivity, carrier mobilities, and suppressed charge recombination. The p-type dopant, formic acid, also acts as a film morphology modifier of the photoactive layer with enhanced phase separation to transport the charge efficiently. This work demonstrates that controlling the charge transport via introducing a small amount of dopant into the devices with not-only small-area but also printed large-area photoactive layers is a promising strategy for further improvement of device efficiency and stability in OSCs.

8:15 AM EL18.17.02
Flexible Capacitive Pressure Sensor based on Dielectric Nanocomposite of Porous Polydimethylsiloxane and Zinc Oxide Nanowire Liang-Cheng Shih, Chih-Chun Hsiao and Gen-Wen Hsieh; National Yang Ming Chiao Tung University, Taiwan

Elastomeric polymer films, owing to their flexibility, chemical resistance, biocompatibility and low cost with ease of fabrication, have became a popular choice of stress-sensitive dielectric layers for flexible and wearable pressure sensors. However, the pressure response of these flat polymer films is rather poor to tiny pressure change, and also insensitive to large applied pressure. Finding a flexible dielectric film that can be operated in a wider pressure range (e.g., from a few Pa to tens or hundreds KPa) remains a crucial challenge.

Toward this task, we propose the polymer-based dielectric nanocomposite based in porous polydimethylsiloxane and zinc oxide nanowire for capacitive pressure sensing. We anticipate that the porous matrix can improve the compressibility of the nano composite film, meanwhile, the incorporated nanowire can increase the dielectric permittivity. Primary results shows that the zinc oxide nanowire-porous polydimethylsiloxane capacitive pressure sensor exhibits an enhanced sensitivity of 21-100 times (in different pressure range) compared with that of flat, pristine polydimethylsiloxane device. Moreover, an ultra-low detection limit of 1 Pa, and remarkable pressure response behavior during 4000 pressing cycles can be archived. To sum up, this proposed strategy may provide broad application prospects in wearable electronics, health monitoring, and intelligent artificial robots/prosthetics.

8:30 AM EL18.17.03
Effects of Substituted Alkyl-Chain Length and Substitution Position in High Performance Organic Semiconductors—Case of *mono*-Alkylated-BTNTs. Satoru Inoue[1], Toshiki Higashino[2], Mutsuo Tanaka[3], Ryo Miyata[1], Shunto Arai[1], Hiroyuki Matsui[4], Sachio Horiuchi[2], Reiji Kumai[5], Seiji Tsuzuki[1] and Tatsuo Hasegawa[1]; [1]The University of Tokyo, Japan; [2]National Institute of Advanced Industrial Science and Technology (AIST), Japan; [3]Saitama Institute of Technology, Japan; [4]Yamagata University, Japan; [5]Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Japan

Solution-processable organic semiconductors (OSCs) are mostly composed of π-electron cores bonded with functional substituents. It was recently shown that normal alkyl-chain substitutions of rod-like π-cores are useful for obtaining high-performance OSCs as used in printed organic thin-film transistors (TFTs). It was demonstrated that self-organized alkyl-chain layers play essential roles in enhancing the layered crystallinity, which contributes to the formation of perfectly aligned semiconductor-insulator interfaces in the TFT device structure. In particular, one-sided unsymmetric substitution of semiconductive π-core, such as benzothieno[3,2-*b*][1]benzothiophene (BTBT), with an alkyl chain allows the formation of a *bilayer-type* layered herringbone packing (*b*-LHB), eventually enhancing the layered crystallinity. We suggest that such alkyl-chain substitutions should be effective for many other extended π-cores, though the application of this strategy has been limited so far.
In this study, we investigated the effect of substituted alkyl chain length and substituting positions on the structure-property relationships of high-performance and solution-processable OSCs of *mono*-alkylated-benzothieno[3,2-*b*]naphtho[2,3-*b*]thiophene (*mono*-C$_n$-BTNT). As the extended π-electron core of BTNT does not have inversion and mirror symmetry, we could select four unique (or independent) substituting positions at the peripheral positions of the rod-like π-core for the alkyl-chain substitutions, with roughly keeping the rod-like molecular shape over the whole molecule.
As a result, we found that the four kinds of regioisomers of *mono*-C$_n$-BTNT afford isomorphous *b*-LHB-type crystal packings. The intralayer herringbone arrangement of the BTNT cores are almost the same for all the regioisomers, while the all-trans chain planes of the substituent form two kinds of interchain ordering. Such difference affects the crystal stability correlated with the solubility, thermal property, and TFT device performance. Among them, the *mono*-C$_n$-BTNT substituted at the most peripheral position form the most stable crystal packing, and the stability is more enhanced with increasing the alkyl chain lengths. In particular, we found that a TFT device based on the *mono*-C$_n$-BTNT shows much higher intrinsic field-effect mobility that reaches as high as 14 cm^2/Vs. We will discuss the structure-property relationship in various *mono*-C$_n$-BTNTs based on the variation of crystal packings as revealed by full crystal structure analyses of all the compounds.
[1] S. Inoue, *et al*. *Chem. Mater. 27*, 3809 (2015). [2] H. Minemawari, *et al*. *Chem. Mater*. *29*, 1245 (2017). [3] T. Higashino, *et al*. *Chem. Mater. 33*, 7379 (2021). [4] S. Inoue, *et al. Chem. Mater. 30*, 5050 (2018). [5] S. Inoue, *et al. Chem. Sci. 11*, 12493 (2020). [6] S. Inoue, *et al. Chem. Mater. 34*, 72 (2022).

8:35 AM *EL18.17.04
A Neuron-readable Artificial Photoreceptor Composed of Photodeformable Liquid Crystal Polymers and Piezoelectric Materials Yanlei Yu, Bo Peng, Jia Wei, Guodong Zhu and Lang Qin; Fudan University, China

Artificial photoreceptors have been extensively developed to help the patients with serious eye diseases by conversion from light into electric signals. The researchers focus on the development of intelligent materials and novel mechanism in the new-generation photoreceptors to simplify the camera visual systems like Argus II. Photovoltaic materials such as cadmium sulfide nanorods, single-crystalline silicon photodiodes output photoelectric signals by the generation and migration of the photocarrier, but the reactive oxygen generated in photoelectrical conversion process is concerned in cytotoxicity and limits the organism application. Pyroelectric materials such as ZnO, poly(vinylidene fluoride-co-hexafluropropylene) are used for electric power output under NIR by the spontaneous polarization change with temperature; however, the photothermal effect of NIR limits the miniaturization of devices.
The conversion of light-stress-electric signals can be realized by the combination of photodeformable materials and piezoelectric materials, which provides an opportunity for the construction of novel artificial photoreceptors without above-mentioned disadvantages. Azobenzene moieties are usually used as a trigger to generate photo-induced stress in the polymers by trans-cis isomerization upon exposure to light irradiation. Combined with azobenzene polymers, the piezoelectric polymers convert the stress into electric signals due to the density change of dipoles. However, the existing systems still suffer from poor output signals, restricting signal transduction to cells.

Azobenzene-containing liquid crystal polymers (LCPs) provide a feasible solution to improve the photo-induced stress and output large electric signals, because the microscopic geometry variation of azobenzene moieties can be amplified into a macroscopic large deformation of the entire LCP materials owing to the alignment change of LC mesogens. Much effort has been made to develop photoresponsive soft actuators with the azobenzene-containing LCPs by ultilizing their quick and various deformation, including contraction/expansion, bending, twisting, oscillating, etc. Due to the cooperative effect of the LC mesogens, as long as 1 mol% of azobenzene moieties reach the photostationary state upon illumination, the generated alignment change can lead to the deformation of the whole LCP systems; therefore, photodeformable LCPs are an excellent candidate for the construction of the photoreceptor featuring a large photo-induced stress.
Here, a neuron-readable artificial photoreceptor with significant voltage output is constructed by using LCPs and polyvinylidene fluoride trifluoroethylene (P(VDF-TrFE)). The significant voltage output originates from light-stress-electricity conversion, where the photo-induced stress is attributed to the change of mesogens alignment in the photodeformable LCPs and subsequently converted into strong electric signals by the P(VDF-TrFE) layer. The photo-induced open-circuit voltage reaches up 0.79 ± 0.02 V, which is, to our knowledge, 19 times higher than the maximum voltage (0.04 V) that has been reported to date. Hence, such artificial photoreceptor successfully transduces photo-induced electric signals to cells and tissues, communicates with the neurons and triggers spiking activities in blind retinas. Besides, visual image recognition is demonstrated in a pixelated matrix by analyzing electric signals of each unit. This artificial photoreceptor opens new opportunities for the combination of the photodeformability and piezoelectricity, providing an avenue to develop neuron-readable artificial retinas and implantable sensors.

9:05 AM EL18.17.05
Self-Healable Printed Magnetic Field Sensors Using Alternating Magnetic Fields Rui Xu[1], Gilbert Santiago Cañón Bermúdez[1], Oleksandr V. Pylypovskyi[1], Oleksii M. Volkov[1], Eduardo Sergio Oliveros Mata[1], Yevhen Zabila[1], Rico Illing[1], Pavel Milkin[2], Leonid Ionov[2], Jürgen Fassbender[1] and Denys Makarov[1]; [1]Helmholtz-Zentrum Dresden-Rossendorf (HZ, Germany; [2]University of Bayreuth, Germany

Percolation network of fillers plays a critical role in rendering printable electronics functionality and durability. We employ alternating magnetic fields (AMF) to drive magnetic fillers actively and guide the formation and self-healing of percolation networks.[1] Relying on AMF, we fabricate printable magnetoresistive sensors revealing an enhancement in sensitivity and figure of merit of more than one and two orders of magnitude relative to previous reports. These sensors display low noise, high resolution, and are readily processable using various printing techniques that can be applied to different substrates. The AMF-mediated self-healing has six characteristics: 100% performance recovery; repeatable healing over multiple cycles; room-temperature operation; healing in seconds; no need for manual reassembly; humidity insensitivity. It is found that the above advantages arise from the AMF-induced attraction of magnetic microparticles and the determinative oscillation that work synergistically to improve the quantity and quality of filler contacts. By virtue of these advantages, the AMF-mediated sensors are used in safety application, medical therapy, and human-machine interfaces for augmented reality.

Reference:
1 Rui Xu et al., Nature Communications (2022), in press

9:20 AM EL18.17.06
Additive Manufacturing of IoT Housings with Integrated Electronics Thomas Schmiedinger, Markus Ehrlenbach, Martin Schafferer, Michael Petke, Bernhard Rittenschober and Christian Schmid; University of Applied Sciences Kufstein Tirol, Austria

Additive manufacturing (AM) is an established fabrication method for diverse applications. Due to the versatile manufacturing possibilities, AM provides totally new approaches in designing objects. An emphasis in the field of research was set to the development of unique materials for AM. Among them, conductive filaments were examined for applications in printed electronics. The combination of new materials and the innovative design approach offered by AM generates a comprehensive field of applications. Promising applications can be found on the “Internet of Things (IoT)” sector. The development of connected products includes physical and electronic components. Traditionally, the fabrication process of these products is linear, thus, the design and the fabrication of the physical components is separated from the electronic part. To overcome this separation, an AM approach can be applied in the fabrication of IoT devices. This hybrid fabrication approach enables the fabrication of mechanical and electric components in one fabrication process.
To prove this hybrid fabrication approach, we designed housings of IoT devices with integrated electronics such as an antenna for signal transmission. The housings were fabricated by material extrusion combining non-conductive and conductive filaments. Different antennas were designs focusing on two specific frequencies ranges: 2.4 GHz (Wi-Fi, Bluetooth), and 868 MHz (LoRa). To compare the AM antenna, reference antennas have been fabricated by milling and 2D-printing. Antenna behaviors were characterized by assessing quality parameters by a vector network analyzer. The hybrid IoT housings were tested in a real-world scenario for sensing temperature and humidity remotely.
Integrated fabrication of electronics by material extrusion is a feasible approach for IoT housings. The characteristics of AM based antennas in comparison to milled patch antennas are limited which is attributed to the lower conductivity of the applied filaments. Nevertheless, the hybrid fabrication process enables an integrated production approach which led to functional devices. In this sense, electronics and physical components are merged into a truly smart product.
Based on the findings, further applications of the hybrid approach will be investigated e.g., signal traces, passive electrical components to further strengthen the extensive application possibilities of additive manufacturing.

9:35 AM EL18.17.07
Effect of Sintering Atmosphere for the Fabrication and Characterization of Flexible RFID Antenna Tags Using Printed Copper Nanoparticulate Patterns Rajib Chowdhury[1], Karl Young[1], August Gallo[1], Rafael Cueto[2] and Seonhee Jang[1]; [1]University of Louisiana at Lafayette, United States; [2]Louisiana State University, United States

RFID is playing an essential role in the Internet of Things (IoT) technology by enabling contactless communication and information transfer between digital and physical entities. Different research procedures are being developed aiming for the highly precise pattern for metal conductivity, low electrical resistivity, low cost of material, and flexibility of the substrate. Among the electronics materials, copper (Cu) nanoparticle (NP) inks can be the main material for flexible printed electronics because it possesses high electrical conductivity, stability, and low price in addition to anti-ionic migration capability.

Cu NP ink (CP-008, NovaCentrix) was selected for printing and characterizing the conductive patterns. The ink had the following compositional properties: solids content of 88 wt%, a viscosity of 20-40 Pa.S at 50 s^{-1}, and a density of 3.9 g/ml. Kapton polyimide (PI) sheets with a thickness of 0.102 mm were used as the flexible substrate. Metallic ink comprises metal NPs, capping molecules, additive organic materials, and solvents. Terpineol was included as a solvent in ink, according to the ink specification, but the rest of the composition in ink was not revealed. Removal of organic substances is required to have electrical conductance along with the diffusion of particles resulting in neck growth and grain boundary to obtain electric conductance of the Cu NP patterns. Air, N_2, and five different carboxylic acid vapor groups were used as sintering atmospheres. The sintering temperature varied from 140 to 260 °C, and sintering times varied from 15 to 60 mins. Sintering temperatures were maintained below 260 °C to avoid any deformation and degradation of the substrate, considering the glass transition temperatures of the PI substrates.

Scanning electron microscopy (SEM) was used to analyze the shape and size of the Cu NPs, microstructure, and thickness using cross-section imaging. Then Avizo software was utilized to determine the size distribution and average particle size of the Cu NPs from the SEM images. Using a thermogravimetric analysis (TGA) with an N_2 gas flow rate of 100 ml/min and a temperature ramp of 10 °C/min to achieve 600 °C, the decomposition temperatures and metal weight contents of Cu NP ink were evaluated. The surface roughness of the sintered Cu NP pattern was measured with an atomic force microscope (AFM). Crystallinity and grain sizes of sintered Cu NP patterns were observed using X-ray diffractometry (XRD) with Cu Kα (1.5406A) radiation. Electrical characteristics were evaluated using a four-point probe. The hardness of the sintered Cu NP patterns was measured using micro indentation. An adhesion test was conducted following ASTM-D3359-09 standard cross-cut tape test. Folding tests evaluated the flexing or bending capabilities of the conductive lines. The electrical characteristics of the RFID antenna were evaluated in a 13.56 MHz band using a network analyzer.

The electrical performance of the Cu NP patterns was evaluated using RFID antenna fabrication. The antennas were printed and sintered using optimized sintering conditions of Cu NP ink. Three spiral and three-square patterns were designed with different dimensions, such as the number of turns, line width and spacing, inner/outer radii for spiral patterns, and inner/outer diameters for square patterns. Their resonance frequency, return loss (S_{11}), and quality factor (Q-factor) for each antenna were measured using a network analyzer. The Q-factor characterized the capability of the antenna to communicate with an RFID reader and an RFID antenna. 13.56 MHz RFID system was followed due to its excellent performance. Too low or too high a Q factor might result in not being able to read the frequency or narrow peak, along with interference between the RFID reader and RFID antenna. The Q-factors in the range of 5-20 are preferred for RFID antenna tags fabricated in the 13.56 MHz band.

9:50 AM EL18.17.08
Interfacial Events in Graphene-Based Technologies for Neural Interfaces Marta Delgà, Jose Antonio Garrido and Elena del Corro; ICN2, Spain

Active implantable neural interfaces have experienced great advances in the last years, partially thanks to the use of novel materials. Graphene is one of these new materials contributing to the recent progress thanks to its outstanding mechanical, electrical and electrochemical properties. Neural interfaces based on graphene have the potential to make these implants softer and more conformable, adapting better to the tissue morphology; furthermore, it is possible to prepare smaller devices while maintaining high performance, which can lead to improved spatial selectivity and specificity. Yet, this flourishing technology presents important challenges related to two-dimensional nature of graphene, in particular the impact of interfacial phenomena on its properties. Among the existing interfacial phenomena impacting on the graphene properties, and thus on the device performance and stability, in this work we explore two main phenomena: electrolyte intercalation between graphene and the substrate and residue deposition over graphene during fabrication.
To address water intercalation, we combine electrical and morphological (KPFM and Raman) characterization. We study the influence of different factors on the amount of water under graphene, including device size and aspect ratio, the passivation layer design or the cleanness of graphene surface. Furthermore, we will present a novel methodology to investigate the amount of residual charge on graphene; this approach is based on the response of graphene electronic properties to the electrolyte pH and ionic strength, which is monitored by immersion Raman spectroscopy.
Our results reveal the existence of trapped water between graphene and the substrate and of non-controlled residual charges on graphene after fabricated. Finally, graphene protection strategies are presented revealing promising improved capabilities of graphene-based device performance.

SESSION EL18.18: Virtual Session II
Session Chairs: Sihong Wang and Xuzhou Yan
Tuesday Morning, April 25, 2023
EL18-virtual

10:30 AM *EL18.18.01
Puncture-Resistant and Self-healing Multifunctional Electronic Skin Cheng-Hui Li; Nanjing Univ, China

Flexible electronic skins play a very important role in the development of human-machine interaction and wearable devices. To fully mimic the functions of human skin, electronic skins should better be able to perceive multiple external stimuli (such as temperature, touch and friction) and resistant to injury. However, both objectives are highly challenging. The fabrication of multifunctional electronic skins is difficult because of the complex lamination scheme and the integration of different sensors. The design of skin-like materials is hindered by the trade-off problem between flexibility, toughness and self-healing ability. In the past a few years, we designed and synthesized a series of polymer which have modulus similar to that of skins, and shows good flexibility, puncture-resistance, notch-insensitivity, and fast self-healing ability. Upon incorporating conductive filliers or liquid metals, the as compared conductive composites can convert changes in temperature and strain into electrical signal changes, thus leading to multifunctional sensing performance. Based on these superior properties, we have prepared a series of flexible electronic skin sensor, demonstrating its great potential in the wearable field and physiological signal detection.

11:00 AM EL18.18.02
Etching of Scandium-Doped Aluminum Nitride using Inductively Coupled Plasma Dry Etch and Tetramethyl Ammonium Hydroxide Zadid Shifat[1,2], Isaac Stricklin[1,2], Ravi Kiran Chityala[1,2], Arjun Aryal[1,2], Giovanni Esteves[3], Aleem Siddiqui[3] and Tito Busani[1,1,2]; [1]The University of New Mexico, United States; [2]UNM Center for High Technology Materials, United States; [3]Sandia National Laboratories, United States

Properties such as wide bandgap, higher electromechanical coupling, and low dielectric permittivity have made Scandium-Doped Aluminum Nitride ($Sc_xAl_{1-x}N$) a promising material for optoelectronics and RF applications. devices are challenging to fabricate because $Sc_xAl_{1-x}N$ films are complex to etch, especially with greater scandium concentrations. Our group has developed a process to etch of $Sc_xAl_{1-x}N$ (x=0.125, 0.20, 0.40) thin films (~ 730 nm thick), which results in vertical sidewalls that approach 90° (±0.2°) and reduces the degree of undercut. As part of this process, etching homogeneity among different Sc compositions is maintained by high-temperature annealing in nitrogen atmosphere, followed by a wet etching in a tetramethyl ammonium hydroxide (TMAH) bath. The wet etch step used a 25% concentrated TMAH (TMAH: Water in 1: 3 ratio) solution at 78°C~82°C to etch the films. The etching rate of $Sc_{0.125}Al_{0.875}N$, $Sc_{0.20}Al_{0.80}N$, and $Sc_{0.40}Al_{0.60}N$ was found to be 365 nm/min, 243 nm/min, and 81 nm/min, respectively. An identical etching profile can be obtained by TMAH vapor as well.

$Sc_xAl_{1-x}N$ etching was found to be independent of the SiO_2 hard mask thickness andwe have analyzed the prospective reasons behind the factors that affect verticality during etching. We also demonstrated how the annealing process significantly repairs the surface damage introduced into the $Sc_xAl_{1-x}N$ by the ion-bombardment effect caused during the SiO_2 hard mask dry etch step, thereby ultimately prevents lateral etching. We can also reduce sidewall roughness of a post etched $Sc_xAl_{1-x}N$ film with the combination of inductively coupled plasma (ICP) etch and annealing without affecting the sidewall verticality in all Sc compositions. Preliminary results of ongoing device fabrication that use this developed etch approach will also be presented.

11:15 AM EL18.18.03
P(VDF-TrFE)/ZnO Composite Film as a Wearable Piezoelectric Energy Harvester Sepide Taleb, Wiebren M. van Lingen and Mónica Acuautla; University of Groningen, Netherlands

This research reports a novel flexible wearable piezoelectric energy harvester made on copper textile. For fabrication of the piezoelectric energy harvester, the optimal concentration of ZnO nanoparticles in P(VDF-TrFE) is initially obtained by the fabrication of piezoelectric films with casting method. Afterwards, Ultrasonic Spray coating technique has been used for the first time to produce composite piezoelectric sensors. Such sensors are produced on conductive copper textile as substrate, to be worn comfortably, and easily on clothes for producing energy from daily activities. The experiments performed under simple movements on the elbow shows a peak-to-peak voltage of around 500 mV. This device can not only provide the electrical power for microelectronic devices or health monitoring systems, but it can also be used as a tactile sensor due to its high sensitivity and biocompatibility.
Several piezoelectric wearable energy harvesters and sensors have already been reported with high output voltage, most of them based on well-known lead-rigid PZT ceramics [1]. However, flexibility and biocompatibility of polymer piezoelectric materials, like P(VDF-TrFE), have motivated many researchers to apply these materials in wearable devices to bring more comfort for the users. Adding various fillers into P(VDF-TrFE) is one of the methods to enhance the piezoelectric coefficient of piezopolymers. One of the promising fillers used in this regard is ZnO nanoparticle, which is a piezoelectric material with wurtzite crystal structure. P(VDF-TrFE)/ZnO composite films have been already fabricated with different methods, like spin coating [2] and electrospinning [3]. To the authors knowledge, fabrication of P(VDF-TrFE)/fillers by ultrasonic spray coating system has not been reported. Though, this method can be advantageous for producing large-scale, high quality piezoelectric films with good reproducibility and control of the fabrication parameters [4].
In this research, initially the optimal concentration of ZnO nanoparticles in P(VDF-TrFE) for piezoelectric properties was obtained using a simple casting method. To do so, piezoelectric films from different concentrations of ZnO (0, 10, 20, and 30 wt%) in 5 wt% P(VDF-TrFE) solution were casted, and their crystallinity, morphology, ferroelectric, and piezoelectric properties were studied.
Higher Piezoelectric coefficient (d_{33}) and lower dielectric constant result in higher mechanical to electrical energy conversion, and therefore higher output voltage of the energy harvester. The 20 wt% ZnO in P(VDF-TrFE) provided the highest piezoelectric coefficient and peak-to-peak output voltage when a force of 100 N was applied by a mechanical testing system. Therefore, such concentration was used to make the ultimate energy harvester by ultrasonic spray coating method.
To improve comfort and compatibility with normal clothing, a conductive copper textile was used as a substrate, thus the energy harvester does not need to be firmly attached to the skin. The optimal solution has been sprayed on top of the copper textile, and annealed at 100 °C to obtain a 19-µm-thick piezoelectric layer. Then, a 15-nm gold layer was sputtered as top electrode and the energy harvester with copper wires were encapsulated in PDMS to protect the system. The wearable energy harvester produces the peak-to-peak output voltage of 250 and 500 mV, by bending the elbow with a small (~30°) and large angle (~90°), respectively.

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11:20 AM EL18.18.05
Preparation and Characterization of Epoxy-Siloxane-Silica Hybrid Hard Coating for Foldable Display Galbadrakh Altantsetseg, SeungCheol Yang, Yeon-Gil Jung, Huynhee Choi and Hye-Yeong Park; Changwon National University, Korea (the Republic of)

Surface protective coatings have been widely used in various applications, such as medical and surgical instruments, electronic displays, optics, antifouling, antifogging, energy storage devices, and automotive and aerospace coatings. The purpose of this study is to produce a protective hard hybrid coating material with high transparency and high scratch resistance for flexible display. For this work, a novel protective hybrid coating was fabricated by photo cationic polymerization of dispersion solution prepared with epoxy oligosiloxane resin and silica sol. The dispersion solution was prepared by simple mixing including ultrasonication. The property change of the epoxy-siloxane-silica composites were studied depending on their composition variation. The mixed solution showed good dispersion stability without precipitant after storage of the solution for 7 days. The 10µm thick transparent hybrid coating formed on PET film with 50 µm thickness had pencil hardness of 3H. The morphology and properties of the coating were characterized by SEM, FTIR, and UV-vis.

11:25 AM EL18.18.06
An Effective and Rapid Soldering of Electrical Components on Flexible Printed Circuits via NIR-Assisted Heating Venkat Kasi, Amin Zareei, Sarath Gopalakrishnan and Rahim Rahimi; Purdue University, United States

Achieving effective and rapid integration of electrical components onto digitally printed conductive traces on flexible substrates, without compromising the electrical and mechanical properties of temperature-sensitive components, has been one of the main challenges in the field of flexible hybrid electronics (FHEs). While convection oven-reflow soldering is the most widely applied method for connecting electrical components onto the traditional rigid printed circuit boards, this high-temperature method is not suitable for flexible substrates and digitally printed components. To address this challenge, we introduced a novel technology, near infrared (NIR) radiation-based technology, as an effective tool for rapid and effective soldering of a lead-free Sn-Bi-Ag solder paste for connecting electrical components onto conductive traces printed on flexible substrates. In this approach, the NIR technology utilizes the highest energy densities to heat certain materials, such as metal particles, via a selective thermal process, while keeping other materials such as polymers at relatively low temperature. Since many polymer substrates including PET have low or negligible absorbance in the near-infrared range, the NIR radiation specifically heats alloy particles in the solder paste and enables them to reach their melting temperature. The conditions such as NIR power and the time of exposure were optimized to obtain improved spreading and adhesion of solder on conductive traces and the substrate. The formation of interfacial region, which represents the degree of soldering process, was investigated using cross-sectional SEM and EDX analysis. As a proof-of-concept, we demonstrated the use of this technology in the fabrication of wearable FHE device that allows the remote assessment of the exudate absorption in wound dressings and indicates the appropriate time for dress change to prevent from any potential infection at the wound site.

11:40 AM EL18.18.07
Sustainable Processes to Produce and Scale-Up Metal Oxide Devices Emanuel A. Carlos, Rita Branquinho, Pedro Moreira, Asal Kiazadeh, Jonas Deuermeier, Alexandra Gonçalves, Ana Carolina Marques, Maria Morais, Joana Figueira, Joana Pinto, Elvira Fortunato and Rodrigo Martins; CENIMAT|i3N, Department of Materials Science, School of Science and Technology, NOVA University Lisbon and CEMOP/UNINOVA, Portugal

Nowadays, the number of electronic devices that each person has is quite impressive and it tends to increase exponentially in the next 30 years. This will lead to a high quantity of electronic waste accumulation that will not be recycled and will most likely end up in landfills in developing countries. To overcome this serious societal problem, it is necessary to rethink the production process of some electronic devices and to reconsider their life cycle assessment, more specifically their environmental footprint.

Coating and printing electronics can be a solution and its market is expected to have a compound annual growth rate of 18.3% from $9.9 billion in 2021 to $23 billion by 2026. By adopting more sustainable materials and processes electronics waste is reduced, leading to the reduction of the carbon footprint, and paving the way for green electronics.

In this presentation, we report suitable processes (blade and spray coating; inkjet, screen, and flexographic printing) and solution-based materials (In_2O_3, IGZO, ZTO, NiO and Al_2O_3) are developed to assure the scale-up of metal oxide-based devices, such as thin film transistors, diodes, memristors, thermochromics and transparent heaters to low-cost industry levels.[1-5] These devices will lead to great societal impact since they can power up the speed and efficiency of lighter and thinner wearables, as well as smart windows and packaging applications highly needed for the emergent IoT. To reach a real product soon these metal oxide devices should be combined with silicon integrated circuits, also called hybrid electronics. This will be crucial to achieve high performance and sustainability standards.

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(5) *Ongoing work, **2023***

11:45 AM EL18.18.08
Laser Processed Flexible Electronics Joana Pinto, Maria Morais, Jaissica Vassantrai, Ana Carolina Marques, Joao Coelho, Sara Silvestre, Tomás Pinheiro, Ricardo Correia, Elvira Fortunato and Rodrigo Martins; Department of Materials Science, School of Science and Technology, NOVA University Lisbon and CEMOP/UNINOVA, Portugal

The demand for flexible electronic devices has been increasing, mostly driven by the emerging markets of consumable electronics and the Internet of Things (IoT). Among several processing techniques, Direct Laser Writing (DLW) has been regarded as an alternative to conventional microelectronics manufacturing processes. DLW is a cost-effective, one-step, and mask-less technique enabling the production of flexible electronics for a variety of applications, such as PCB boards and other components.[1–3] Using laser processes, different materials and devices can be directly synthesized through precursors chemical reduction, or even the production of graphene through the conversion of carbon-based substrates, such as paper and cork.[1, 3, 4]

This work presents the capabilities and versatility of DLW writing for electronic components development. By this method were obtained silver, copper, and graphene conductive tracks exhibiting sheet resistances of 0.23 ohm.sq^{-1}, 0.53 ohm.sq$^{-1,}$ and 30 ohm.sq^{-1}, respectively. These conductive layers led to the production of radio-frequency antennas, micro-supercapacitors, and simple circuits on paper and cork, further demonstrating the relevance of this method. This technique is compatible with a set of recyclable and bio-compatible substrates, adding a layer of sustainability to the production method.[1–3, 5] Finally, DLW was also applied to synthesize metal oxide semiconductors (WO_3, ZnO, among others) broadening the prospect of fabricating sensors and other devices through this direct and simple technique.

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11:50 AM EL18.18.09
Defect Quantification of MOCVD Deposited Monolayer MoS_2 Using Kelvin Probe Force Microscopy Technique Moha Feroz Hossen[1,2], Olubukola Ayanbajo[1,2], Sachin Shendokar[1,2], Swapnil Nalawade[1,2] and Shyam Aravamudhan[1,2]; [1]Joint School of Nanoscience and Nanoengineering, United States; [2]North Carolina A&T State University, United States

Defects are unavoidable during synthesis of materials due to thermodynamical equilibrium. In the synthesis of two-dimensional transition metal dichalcogenide (2D TMDC), point defects emerge as a dominant defect due to the absence of chalcogen atoms in the lattice structure. Having the few or less than one nanometer level thickness of monolayer film of TMDC materials, the presence of defect states on the film surface changes the carriers concentration. The changing of carrier concentration in monolayer TMDC film shifts the position of fermi level towards either conduction band edge or valence band edge depending on the type of majority carriers. The shifting of fermi level changes the work function of the TMDC monolayer film. The conventional hall measurement is not feasible to measure surface carrier concentration of 2D materials films. Instead, kelvin probe force microscopy (KPFM) is used to measure surface carrier density. The carrier density is calculated by measuring the work function of the monolayer film using KPFM. Each point defect in 2D TMDC materials increases the certain amount of carriers concentration that facilitate the defect quantification. In this work, we tried to quantify point defect in metal-organic chemical vapor deposited (MOCVD) monolayer MoS_2 using kelvin probe force microscopy (KPFM) by measuring the position of the fermi level that is shifted due to the unbounded electrons of MoS_2.

11:55 AM EL18.06.59
Gigantic Effect Due to Phase Transition on Thermoelectric Properties of Ionic Sol-Gel Materials Jin Liu[1], Xiao-ming Tao[1] and Wei Zeng[2]; [1]Hong Kong Polytechnic University, Hong Kong; [2]Guangdong Academy of Sciences, China

Sol-gel phase transition in ionic thermoelectrical (i-TE) materials can induce large rapid changes in viscosity and ionic transport process. Based on these properties, the phase-transition is expected to give a drastic variation in thermoelectric properties, crucial in low-grade waste heat harvesting for Internet of thing (IoT) and wearable electronic applications. In this work, we prepare and examine four different types of i-TE materials featured with non-phase-transition, thermal sol-to-gel phase transition, thermal gel-to-sol phase-transition and UV-induced sol-to-gel phase transition. For the first time, we observe a significant rise of the thermopower by around 6.5 times during the sol-gel transition of the poloxamer/LiCl system (thermal sol-to-gel phase-transition system). In addition, due to the stable value of electrical conductivity and thermal conductivity during phase transition, an even greater ionic figure of merit by around 23 times is also achieved. These phenomena are found to be universal as the large variation in thermopower is confirmed in the other thermal gel-to-sol transitional and UV-induced transitional materials. We further reveal the mechanism based on the Onsager's relations and propose a model that can deal with the pre-, post- and during phase-transition processes. Finally, we probe six factors that can influence the huge variation of the thermopower during the phase transition and shed light on the possible gigantic changes in thermopower during the phase transition. This work indicates the gigantic effect that phase transition can have on thermoelectric properties in i-TE systems regardless of the type of phase transition and discovers a possible route to design and control the desired TE performances of materials, which can lead to a new sight in tunable i-TE devices for low-heat energy harvesting applications.

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Liu, J., Zeng, W., Tao, X., Gigantic Effect due to Phase Transition on Thermoelectric Properties of Ionic Sol–Gel Materials. *Adv. Funct. Mater.* 2022, 2208286. https://doi.org/10.1002/adfm.202208286

SESSION EL18.19/SB03.11/SB09.13: Virtual Session: Keynote Presentation
Session Chairs: Jia Liu and Xuzhou Yan
Thursday Morning, April 27, 2023
EL18-virtual

10:30 AM *EL18.19/SB03.10/SB09.13.01
Hybrid, Compliant Implantable and Wearable Neural Systems Stephanie P. Lacour; Ecole Polytechnique Federale de Lausanne, Switzerland

The introduction of soft materials and microtechnology provides an opportunity to tailor the design of neural transducers and explore interfaces with increased selectivity and improved biointegration. Soft carrier materials and elasticity engineering support neural devices with mechanical signature closer to that of the neural host tissue and potential for long-term biointegration. Microfabrication allows for customized electrode layouts with micrometric to millimetric electrode diameter, low to high (0.1 to >10 /mm^2) electrode density and small to large (mm^2 to 10s cm^2) surface area. Hybrid integration of conventional, rigid electronic hardware with the compliant neural transducers is explored to enable on-board signal processing, data transfer and powering. The design and processing of multilayered thin-film encapsulation are then required to hermetically package the thin form-factor neural systems.
This talk will review our advances in each of the four components, namely soft transducers, integrated LEDs, hybrid interfacing with customized electronics and telemetry and flexible yet hermetic organic-inorganic multilayers. We will illustrate these concepts with neural systems interfacing the central nervous system.

SYMPOSIUM

April 11 - April 28, 2023

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Supratik Guha, The University of Chicago
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SESSION EL19.01: Opening and Interconnects
Session Chairs: Paul Berger and Francesca Iacopi
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3020

10:30 AM OPENING REMARKS

10:45 AM *EL19.01.01
Material, Strucures, Devices and Architectures Paolo Gargini; IEEE-IRDS, United States

Electronics powered products have permeated all aspects of society and this trend is still accelerating. All of this has been made possible by the integration of larger and larger number of solid-state transistors that have continued to evolve absorbing new materials, morphing into new structures, and adapting to newer and evolving circuit architectures.
The first patents about forming a solid-state device by means of creating two separately spaced electron rich regions to be connected on demand by applying a voltage on an electrically isolated gate straddling between and above them were published between 1925 and 1935; however, actual demonstration of the transistor effect did not occur until 1947-48. It took however, another 20 years before the first silicon-gate planar process produced functional and reliable Metal Oxide Semiconductor (MOS) transistors and for the first time an economically viable Integrated Circuit industry took off. Between 1969 and 1971 multiple types on memories and logic products became a reality. Through the 70s, 80s and 90s integrated circuits were produced with transistors of smaller features that yielded better performance and lower costs from one generation to the next one. During this period, several new materials were introduced to further increase performance and reliability. By the beginning of this century, it became clear that the fundamental materials constituting the MOS transistor were reaching fundamental limits and a complete overall was necessary. Between 2003 and 2011 new dielectric and metal materials were introduced into the manufacturing process and for the first time the planar transistor evolved in an upright structure name FinFET since the new structure resembled a fin. The next structural transition is anticipated to occur around the year 2025 when individual layers transistors will be stacked on top of each other in what is called Nanosheet architecture. This however is not the end! Integration of new resistive materials and new magnetic materials is jut beginning to enter the manufacturing process. Many more exciting device transformations are also reaching the feasibility stage and so the combination of materials, structures, devices, and architectures will continue to produce and widely proliferate products that will make our lives better and more exciting than ever before.

11:15 AM DISCUSSION TIME

11:30 AM EL19.01.03
Low-Resistivity Molybdenum Nitride Thin Films Deposited by Atomic Layer Deposition for Cu Diffusion Barrier Min-Ji Ha, Jeong-Hun Choi, Na-Gyeong Kang and Ji-Hoon Ahn; Hanyang University, Korea (the Republic of)

As memory devices become ultra-miniaturized, the increase in the resistance of the metal line due to the decrease in the line width has become a very critical issue. Mo-based materials have been studied as candidates for next-generation metal line materials because of their low resistivity at low thickness and excellent oxidation resistance. However, the development of precursors suitable for vapor deposition methods (such as atomic layer deposition) is immature. In this study, we propose a low resistivity MoN_x thin film using a halogen-free liquid precursor as a new metal line and diffusion barrier candidate. Controlling the percentage of H_2 (0-10%) contained in N_2, MoN_x thin films were successfully deposited by PEALD. It was confirmed that the MoN_x thin films (H_2 0-10%) were uniformly and continuously grown on the SiO_2 substrate without an incubation period. Among the deposited MoN_x thin films (0-10%), MoN_x thin films using H_2 10% showed the lowest resistivity of 30-50 μΩcm and maintained the low resistivity even at the thinnest thickness of 4.15 nm. In addition, the diffusion barrier (~7nm) stability tests for Cu metallization were performed up to 600 °C because the thermal budget in the BEOL process was limited to 550 °C. The MoN_x thin films deposited using lower H_2% improved diffusion barrier ability because they form amorphous phase. The MoN_x thin films proposed in this study has the potential to be applied to various applications as a next-generation metal line materials in the semiconductor industry.

11:45 AM EL19.01.04
Poly(lactic) Acid and Highly Conductive Porous Copper Co-Printing via Fused Filament Deposition and Laser Sintering Hybridization Remi Rafael and Paddy K. L. Chan; Hong Kong University, Hong Kong

Additive manufacturing of electronic devices and 3D printed circuit boards (3D PCB) is a complex and challenging endeavor. The major reason is due to the high processing temperature of metals and the incompatibility with the classic polymer-based dielectric or printed materials. Although low temperature processes have been developed to print conductive materials like conductive thermoplastic composites and metal nanoparticle inks, these conductive composites are restricted by low conductivities, and direct ink writing or inkjet printing are often associated with high cost, complex chemical or thermal sintering steps and low throughput. A lot of time they are more suitable for the thin film printing rather than 3D printing. As a result, there is currently no additive manufacturing technology available on the market, capable of printing centimeter scale 3D PCB with embedded 3D vias.
In this work, we present a 3D printing method capable to print together dielectric poly(lactic) acid and a highly conductive porous copper material to produce 3D PCBs. We developed a copper/copper oxide/PLA thermoplastic composite filament which can be utilized for conductive printing in a fused filament deposition (FDM) and laser sintering hybridized setup. The composite, originally dielectric, is first printed using the classic FDM process, before being locally sintered by a laser diode. The sintering process degrades the PLA into volatile compounds and causes the reduction of the copper oxide into its native conductive state. The resulting material is a porous copper network of interconnected copper particles with low resistivity ($< 4 \times 10{-}4$ Ω cm) and high maximum current density (6 A/mm^2) without degradation. Using a custom-made hybrid 3D printer with two FDM extrusion heads and a laser head, those two processes (printing and sintering) are repeated until a complete 3D PCB is formed. To demonstrate the capability of this method, we will present a simple LED blinking circuit, integrating conventional electronic components by soldering, and a centimeter scale solid printed object with embedded 3D vias. The detailed electrical characterization of the printed porous copper will be presented.

SESSION EL19.02: Novel Materials Metrics and Metrology
Session Chairs: Pei-Wen Li and Tseung-Yuen Tseng
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3020

1:30 PM *EL19.02.01

ARES™ Autonomous Research Systems Control of Carbon Nanotube Yield and Structure Benji Maruyama; AFRL/RXA, United States

The current materials research process is slow and expensive; taking decades from invention to commercialization. The Air Force Research Laboratory pioneered ARES™, the first autonomous research system for materials development. A rapidly growing number of researchers are now exploiting advances in artificial intelligence (AI), autonomy & robotics, along with modeling and simulation to create research robots capable of doing iterative experimentation orders of magnitude faster than today. We will discuss concepts and advances in autonomous experimentation in general, and associated hardware, software and autonomous methods.

For Carbon Nanotubes (CNTs), we show progress in autonomous and data science methods to understand and control the fundamental mechanisms that drive CNT synthesis via CVD. We will explore the importance of the oxidizing or reducing nature of the CVD environment on nucleation and growth.

In the future, we expect autonomous research to revolutionize the research process, and propose a "Moore's Law for the Speed of Research," where the rate of advancement increases exponentially, and the cost of research drops exponentially. We also consider a renaissance in "Citizen Science" where access to online research robots makes science widely available.

2:00 PM EL19.02.02

Enabling Nanoscale Tomographic Materials Analysis with Multi-Probes Scalpel SPM Deepanjan Sharma[1], Matthew Tedaldi[1], A.D.L. Humphris[1], J.P. Hole[1] and Umberto Celano[2,3]; [1]Infinitesima Ltd., United Kingdom; [2]Arizona State University, United States; [3]imec, Belgium

The continuous advances of nanoelectronics device technology are creating an ever-increasing demand for customized chips. The rapid development of three-dimensional architectures such as FinFET, gate-all-around (GAA), and nanosheets requires the use of new approaches for their physical analysis that go beyond state-of-the-art metrology. A promising solution is offered by Scalpel SPM, a concept based on the contact-mode atomic force microscopy (AFM) where tip-induced material removal by abrasive wear has been re-imagined as a valid option to achieve tomographic sensing. Scalpel SPM uses a single asperity nanocontact capable of sub-nanometer material removal, thus enabling a three-dimensional segmentation by alternating sensing and removal scans. Here, we report on the development of a dedicated system – the Rapid Probe Microscope (RPM3D) – for the implementation of Scalpel SPM that leverages the use of three independent probes, alternating their operation on the same area of the sample surface. Thus, separating the scalpel and sensing responsibilities into multiple tips holds benefits both for further studies on the fundamental physics of nanomachining as well as the realization of a tomographic tool. First, we discuss the interlaced high data acquisition rate and an interferometric detection system providing sub nanometer spatial accuracy and automated probe switching and multi-probe sensing. Namely (1) the development of a synchronized multi-probe sensing method, and (2), the creation of an automated data acquisition scheme in which the rate of nanomachining is extracted during tomographic data collection. Second, we show a pathway for automatic extraction of the tip-induced material removal rate (RR) to be combined with automated multi-probe sensing. This is reported with multiple electrical contact-mode techniques including conducting atomic force microscopy (C-AFM) and scanning spreading resistance microscopy (SSRM) as a multiscale 3D analysis platform that does not compromise high-resolution imaging, we propose a specific design that can accomplish both accurate tip re-positioning and a simple technique for switching and using multiple probes.

2:15 PM EL19.02.03

Ge-rich Ge-Sb-Te Phase-Change Thin Films Under the Light of Synchrotron Radiation— Crystallization and Thermomechanical Behavior Philipp Hans[1,2], Cristian Mocuta[3], Yann Le-Friec[4], Philippe Boivin[4], Roberto Simola[4] and Olivier Thomas[1,2]; [1]Aix Marseille Universite, France; [2]CNRS IM2NP, France; [3]Synchrotron SOLEIL, France; [4]STMicroelectronics, France

Phase Change Memory is a very promising non-volatile memory that is being considered by several companies for a wide range of applications (storage-class memory, in-memory computing, neuromorphic computing, eNVM for microcontrollers …). At STMicroelectronics a new Ge-rich Ge-Sb-Te alloy (GGST) has been developed with a crystallization temperature above 350°C [1] for addressing the specific needs of the automotive market where high operating temperatures are needed. To investigate the crystallization and mechanical behavior of these GGST alloys we use X-ray diffraction as a function of temperature during annealing. Capped thin films are heated *in situ* under nitrogen atmosphere on the DiffAbs beamline of SOLEIL synchrotron facility. The incident beam is monochromatic (18 keV) and the incidence is fixed. A bidimensional detector collects the diffraction pattern and is corrected and integrated [2] to yield a 1D diffraction pattern. The diffraction peaks are then fitted with a Voigt function [3] that allows extracting the integrated intensity, integral breadth and position of the Bragg peaks. These parameters allow following the crystallization kinetics and the thermomechanical behavior [4] of thin films as a function of various parameters: doping, film thickness (5 nm – 50 nm), nature of surrounding layers … In addition, we will show that thanks to the high flux and penetrating power of synchrotron X-rays patterned and metallized structures close to real products can be investigated. The results obtained from such in situ investigations bear important consequences for the understanding of the crystallization process in memory cells.

Acknowledgments:
The authors gratefully acknowledge the SOLEIL Synchrotron for allocating beam time. P. Joly, is acknowledged for excellent technical support during the experimental campaign at SOLEIL Synchrotron on DiffAbs beamline. This research was supported by IPCEI/Nano 2022 program.

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2:30 PM *EL19.02.04

Scale-Dependent Mechanical Properties of Advanced Materials for Nanopatterned On-Chip Interconnect Structures Ehrenfried Zschech and Kristina Kutukova; deepXscan GmbH, Germany

The mechanical robustness of microelectronic products is an increasing challenge, particularly for microchips and chipsets operated in harsh environments, for use cases that require lifetimes much longer than in the past and for safety-critical applications [1,2]. Microcracks in nanopatterned on-chip interconnect stacks, e.g. introduced during dicing of the wafer, are a serious reliability concern since these they can grow and eventually cause catastrophic failure of the microchip. This reliability-limiting degradation process is pronounced by geometrical shrinking of metal interconnects, novel manufacturing technologies and integration schemes as well as new materials used for interconnect stacks of future electronics. In addition, advanced packaging technologies (e.g. hybrid bonding) can cause local thermomechanical stress on wafer or chip level. The risk of fracture is increased for BEoL stacks of microchips if metal interconnects are insulated with so-called low-k materials. These dense or porous CVD-deposited and UV cured organosilicate glass materials are characterized not only by a low dielectric permittivity but also low Young's modulus and cohesive strength, and consequently low fracture toughness [3]. The understanding of the kinetics of crack propagation provides valuable information for the evaluation of the risk of mechanical failure, however, a quantitative determination of the critical energy release rate for crack propagation is needed for the design of optimized, mechanically robust BEoL structures.

In this talk, the determination of the critical energy release rate in patterned interconnect structures of advanced microchips is described. The implementation of a micro-double cantilever beam (micro-DCB) test in an X-ray microscope allows a 3D imaging of the pathways of microcracks in fully integrated multilevel on-chip interconnect structures with a spatial resolution of about 100 nm [4]. Based on the measured geometric shape of the crack and cantilever bending lines at several loading steps during the micro-DCB test as input data and a data analysis based on the Euler-Bernoulli beam model, the determination of the critical energy release rate G_c for crack propagation was determined in different patterned regions of a wafer manufactured in 14 nm CMOS technology node with a Cu/low-k interconnect stack. The critical energy release rate G_c for crack propagation of a so-called guard ring structure, designed to stop the crack growth, is significantly larger than the respective values in patterned surrounding regions, and about one order of magnitude higher than the G_c values of the respective unpatterned dielectric thin films. These results show that, in addition to the materials properties of the dielectric materials, the geometry of the metal structures is playing an essential role for the fracture behavior of Cu/low-k interconnect stacks [2].

With the methodology described in this talk, conclusions for the robustness of on-chip interconnect stacks can be drawn and input for the design of guard ring structures can be provided. This new approach has important implications for on-chip interconnect technology development and for risk mitigation strategies in semiconductor industry.

The combination of micromechanics and nondestructive high-resolution 3D imaging of opaque materials opens a way for the fundamental study of the structure behavior of nanoscale structures and materials. One century after Griffith's fracture theory, it will cause a new era of fracture mechanics, namely fracture mechanics in small dimensions.

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3:00 PM BREAK

SESSION EL19.03: Novel Fabrication Methods
Session Chairs: Benji Maruyama and Ehrenfried Zschech
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3020

3:30 PM EL19.03.01
Precursor Development for Direct-Writing of Inorganic Nanostructures Sven Barth, Felix Jungwirth, Fabrizio Porrati and Michael Huth; Goethe University Frankfurt, Germany

Focused electron/ion beam deposition (FEBID, FIBID) allow the spatially controlled formation of nanoparticles, thin film patches, nanowires and free-standing complex nanoarchitectures on a wide range of substrate materials. Moreover, the method enables a growth on structured surfaces and the formation of predefined arrays by this maskless direct-write approach. However, the purity of the as-grown material is typically limited. Therefore, the method requires precursor development to provide chemical impetus driving the methods applicability. This contribution will highlight the precursor development for this nanoprinting approach.[1] Specific examples of precursors will be discussed that enable for the direct deposition of binary deposits. The knowledge gained is applied to the synthesis procedures for metal silicide and alloy formation as well as functional metal carbides.[2,3]

Acknowledgment: S.B. acknowledges generous financial support from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) project 413940754 and 413942347.

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3:45 PM EL19.03.02
Site- and Shape-Selective Synthesis of Heterostructures by Nano-Micro-CVD Fabrizio Porrati, Sven Barth and Michael Huth; Goethe University Frankfurt, Germany

Recent advancements in additive manufacturing enable the fabrication of free-shaped 3D objects with high accuracy using focused electron beam-and focused ion beam-induced deposition (FEBID and FIBID).[1] We demonstrate the formation of 3D core-shell heterostructures by combination of direct-write 3D FEBID scaffolds and the successive site-selective chemical vapor deposition (CVD). In particular, conductive 3D nanobridges are printed by FEBID and used as resistors allowing deposition induced by Joule heating. The successful combination of both approaches is demonstrated using two material systems of specific physical properties.[2] The fabrication of complex 3D core-shell heterostructures promises to add new functionalities by combining free-shaped 3D surfaces to layers of materials with different properties. Specifically, shape dependent physical properties can be investigated by this highly adaptable approach.

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4:00 PM EL19.03.03
Optical Micro-Patterning of Electronic Polymers for Device Applications Meghna Jha, Joaquin Mogollon Santiana, Tucker L. Murrey, Harishankar J. Manikantan and Adam J. Moule; University of California, Davis, United States

The largest need in organic electronic devices is a universal method to produce micro- to nano-scale features for devices from semiconducting polymers cheaply, and at scale. We recently developed a solution method to optically pattern conjugated polymers with sub-micrometer resolution. We examine the relationship between optical write intensity, write speed, and write wavelength on the resulting pattern fidelity. Finite element modeling reveals that nearly all polymer patterning occurs as a result of dissolution due to local optical heating. The dissolution rate as a function of light wavelength, intensity, and solvent quality can be quantitatively predicted with upper patterning rates of 5 m^2/hr possible. We demonstrate the fabrication of polymer nanowires with cross section of 250x40 nm, which demonstrates the efficacy of this process for device fabrication. We also demonstrate optical patterning of conjugated polymers using a cleanroom photolithography instrument (Alvéole PRIMO). This is significant because it means that every organic electronics group can pattern with similar resolution using their own local commercial equipment. This patterning technology enables a whole new class of patterned conjugated polymer devices.

4:15 PM EL19.03.04
Process Development and Material Characterization for ALD Indium Tin Oxide (ITO) Thin Films Qi Jiang[1], Nathalie Moreno[1], Shuhan Liu[1], Xinyi Wen[1], Kasidit Toprasertpong[2], Vijay Narasimhan[3], Graham J. Ewing[1], Michelle Rincon[4], Angelica Zacatzi[3], Swaroop Kommera[1], Ravi Kanjolia[3] and H.S. Philip Wong[1]; [1]Stanford University, United States; [2]The University of Tokyo, Japan; [3]EMD Electronics, United States; [4]Onsemi, United States

Indium Tin Oxide (ITO) is a conducting material widely used for transparent electrodes in various applications such as batteries, touch screens, and solar cells. When thinned down to sub-10nm, ITO can be used as the channel material for transistors because an applied electric field in the gate can completely deplete the channel and turn off the transistor. The common method to deposit ITO is sputtering; but sputtered ITO tends to be rough, non-uniform, and non-conformal. Besides, the ITO composition is pre-defined by the sputtered target and has little tunability for different needs. Atomic Layer Deposition (ALD) provides films that are generally better than sputtering in terms of roughness, conformality, and uniformity, as well as having better control in thickness and composition.
In this work, we developed the ALD ITO process, compared two different precursors, and studied how the process parameters affects the ITO thin film Characteristics. Tetrakis(dimethylamino)-tin (TDMASn) is used as the Sn precursor. As for the In precursor, both Indium Cyclopentadienyl (InCp) and Trimethylindium (TMI) have been used and compared for the ALD ITO films. Oxygen plasma is used as the source of oxygen. ITO films are deposited onto both SiO2/Si(100) and glass substrates and examined using ellipsometry, contactless sheet resistance mapping, X-ray photoelectron spectroscopy (XPS), etc. We have characterized how the ALD ITO resistivity changes with different In precursors, In: Sn composition ratio, film thickness, deposition temperatures, and annealing conditions, and have studied the underlying physics associated. We will present transistor results comparing the process conditions.

4:30 PM EL19.03.05
Additive Manufacturing of Amorphous Metal Soft Magnetic Composites Luis C. Delfin, Mingqi Shuai, Melody Wang, Kawin Surakitbovorn, Juan Rivas-Davila and Wendy Gu; Stanford University, United States

Soft magnetic composites (SMCs), consisting of metallic regions separated by insulating layers, have gained increased interest for power and electronic applications due to their excellent magnetic properties, low eddy current losses, and low coercivity. SMCs made of amorphous metal soft magnets are of interest for high-frequency applications. However, the brittle nature of amorphous metals limits their geometry to thin ribbons. This work presentsthe synthesis of Fe-based amorphous metal nanoparticles, which are then oxidized to achieve a core-shell structure. The synthesis method is scaled-up to the 100 g scale to be used as feedstock material in additive manufacturing processes such as Laser Powder Bed Fusion (LPBF). The small size of the nanoparticles is predicted to lead to low core losses, as well as improved ductility. Nanoindentation is used to determine hardness and elastic modulus. Through plane resistivity measurements and B-H curves were performed to evaluate their performance as SMCs. Then, single layers are printed to determine power, scanning speed, and hatch spacing for dense structure and optimized microstructure.

SESSION EL19.04: Sensors
Session Chairs: Paul Berger and Ricardo Donaton
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3020

9:00 AM EL19.04.01
Colorimetric Multigas Sensor Arrays-Based Artificial Olfaction for Volatile Organic Compounds Healin Im[1,2], Jihho Kim[3], Zakaria Al Balushi[1], Donghyuk Park[3] and Sunkook Kim[2]; [1]University of California, Berkeley, United States; [2]Sungkyunkwan University, Korea (the Republic of); [3]Inha University, Korea (the Republic of)

Artificial olfaction conceives multigas sensor arrays for gas-fingerprint pattern recognition, which is attributed to its specificity for multiple gases. It is a series of interactive sensor arrays compatible with electronic circuits and data analysis software from a sensor architecture perspective. It can sense and transform information on gas mixtures into readable digital outputs and compute their concentration based on statistical models. Herein, we develop colorimetric multigas sensor arrays assembling chemo-reactive fluorescent porous nanofibers and 10 <!--[if gte msEquation 12]><m:oMath><i style='mso-bidi-font-style: normal'><m:r>×</m:r></m:oMath><![endif]--><!--[if gte vml 1]><v:shapetype id="_x0000_t75" coordsize="21600,21600" o:spt="75" o:preferrelative="t" path="m@4@5l@4@11@9@11@9@5xe" filled="f" stroked="f"> <v:stroke joinstyle="miter"/> <v:formulas> <v:f eqn="if lineDrawn pixelLineWidth 0"/> <v:f eqn="sum @0 1 0"/> <v:f eqn="sum 0 0 @1"/> <v:f eqn="prod @2 1 2"/> <v:f eqn="prod @3 21600 pixelWidth"/> <v:f eqn="prod @3 21600 pixelHeight"/> <v:f eqn="sum @0 0 1"/> <v:f eqn="prod @6 1 2"/> <v:f eqn="prod @7 21600 pixelWidth"/> <v:f eqn="sum @8 21600 0"/> <v:f eqn="prod @7 21600 pixelHeight"/> <v:f eqn="sum @10 21600 0"/> </v:formulas> <v:path o:extrusionok="f" gradientshapeok="t" o:connecttype="rect"/> <o:lock v:ext="edit" aspectratio="t"/></v:shapetype><v:shape id="_x0000_i1025" type="#_x0000_t75" style='width:8.4pt; height:28.2pt'> <v:imagedata src="file:///C:/Users/LGE1/AppData/Local/Temp/msohtmlclip1/01/clip_image001.png" o:title="" chromakey="white"/></v:shape><![endif]--> 10 IGZO phototransistor arrays as a next-generation artificial olfactory platform to recognize five different volatile organic compounds (VOCs). Porous nanofibers, coupled with two different organic emitters and emitting fluorescence, rapidly respond to gas-phased VOCs and offer a prominent fluorescent alarm. In addition, the composition between fluorophores and polymers provides a selectivity against VOCs. The VOCs-induced variation in fluorescence of nanofibers is quantified and amplified by IGZO phototransistor arrays, resulting in the gas-fingerprint patterns in terms of electrical signals. Thus, the pattern library associated with VOCs and their concentration enables us to determine each airborne analyte as the artificial olfactory platform. Therefore, this system could achieve rapid, early quantitative recognition of hazardous gases and be applied as a preventative, portable, and wearable multigas identifier in various fields.

9:15 AM EL19.04.02
Low-cost, and Robust Printed Sensors for Monitoring Gaseous Oxygen Flux Through Soil John-Baptist Kauzya, Brenna Schwartz, Eloise Bihar, Catherine Crichton and Gregory L. Whiting; University of Colorado Boulder, United States

Oxygen content in soil has been shown to promote plant growth and crop production, therefore, it is important to monitor oxygen gas flux through the soil. In order to accurately perform such in-situ characterization of gas fluxes through soil, high spatial resolution in the sensing system is imperative. Printed gas sensors for monitoring oxygen content in the air have been designed and documented in the literature. In order to apply these technologies to soil, a harsh environment that experiences fluctuations in properties such as moisture, temperature, and density, we have modified/adapted the current devices' configuration. In this work, we demonstrate the design, construction, and testing of robust devices that utilize printed oxygen sensors to transduce gaseous oxygen flux through soil into a measurable signal, without succumbing to the negative impacts of its transient properties. The accuracy of these devices is explored alongside their sensitivity, stability, and longevity. By building these gas sensing systems for in situ monitoring of oxygen flux in soil, we can provide a better understanding of how farming and agricultural practices affect soil and crop health.

9:30 AM EL19.04.03
Organic Optoelectronic Components in a Smart-Integrated Miniaturized System for Plasmonic-Based Sensing Stefano Toffanin; CNR-ISMN, Italy

The continuous growth of the global population has been remarking the need of early detection systems to prevent the spread of epidemics as well as to improve the standards of living. The emerging demand of sensing technologies has prompted researchers and industrial companies to develop devices able to monitor medical, food, water, and environmental safety/quality indicators in an efficient, simple, and reliable way. While high sensitivity and selectivity must be guaranteed, compactness, user-friendliness and low-cost are key characteristics to enable the use of the sensing technology for point-of-care diagnostics without the need for trained personnel [1].

Among state-of-the-art methodologies for pollutants detection, optical sensing has emerged as one of the most simple, versatile, and powerful approaches for analytical purposes. However, a major obstacle towards the development of a portable system has been the use of bulky optical components (e.g. lasers and optical fibers), which are necessary to ensure a good sensing capability. In particular, huge interest has been attracted by functionalized metallic surfaces based on surface plasmon resonance (SPR), as extremely sensitive, label-free, quantitative systems for real-time detection of single or multiple analytes. However, the need of a fine and precise control of the angle of the incident light ended up in the use of not-portable optical components in the final sensor [2].

In this scenario, organic optoelectronic components might enable the definition of new miniaturized detection schemes to boost the advent of compact optical sensors for on-site analysis, given their inherent capability of smart monolithic integration in nm-thick multi-stack devices on almost any surface. Here, we report an unprecedented ultra-compact system endowed with optical and plasmonic sensing capabilities through the smart integration of (i) organic light-sources such as organic light-emitting diodes (OLEDs) or transistors (OLETs), (ii) an organic light-detector such as organic photodiode (OPD) and (iii) a sensing nanostructured surface such a nanoplasmonic grating (NPG) [3]. The components and the layout of integration were suitably designed to make the elements work cooperatively in a reflection-mode configuration. In particular, the OPD was vertically stacked onto the source electrode of the OLET thus providing electrical switching, light-emission and light-sensing capability in a single organic multilayer architecture. When coupled to the NPG, a multifunctional system with SPR-sensing ability was obtained at a remarkably high level of miniaturization, arising from the direct fabrication of the NPG onto the encapsulating cap of the light-emitting/-sensing platform.

The optimal size and relative positioning of the three elements, as well as the signal variation of the sensor under different conditions, were predicted by means of accurate 3D optical simulation tool. Accordingly, the effectiveness of the final miniaturized integrated system was validated by the dependence of the OPD output signal on the NPG exposure to liquid media with different refractive index, *i.e.* water, ethanol and sucrose solutions at different concentrations [4] by achieving a sensitivity up to 10^{-4} refractive-index units (according to the specific light source used) at a sensor size as low as 0.1 cm^3.

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9:45 AM EL19.04.04
Wearable Neural Sensors Based on Epitaxial Graphene on 3C-SiC on Silicon Shaikh N. Faisal[1], Tasauf Torzo[1], Tien Thong Do Nguyen[2], Daniel Leong[2], Chin-Teng Lin[2] and Francesca Iacopi[1,3]; [1]University of Technology Sydney, Australia; [2]Australian Artificial Intelligence Institute, Australia; [3]ARC Centre of Excellence in Transformative Meta-Optical Systems, Australia

Recent advances in Neuroscience and Artificial Intelligence, particularly in paradigms and related algorithms for evoking and decoding intent from “brain waves”, ie the low-frequency, collective oscillations of millions of brain neurons, have paved the path to the use of electroencephalography (EEG) as a non-invasive platform for brain-computer interface (BCI) [1]. Although the spatial-temporal resolution of EEG is inferior to the use of implanted interfaces, the wearable nature of such BCI is of great importance for most of the large -scale uses that do not involve mitigating severe disabilities. However, one of the main bottlenecks for EEG -based BCIs is now the availability of suitable dry sensors. Dry sensors tend to show a relatively high contact impedance with the skin, which hampers an accurate read-out of the ~μV amplitude biopotential signals to be read at scalp locations, because of their strong capacitive component in the contact [2]. In addition, their contact with the skin needs to be stable during movement and reliable over long-term usage outside lab settings, which is another key challenge due to corrosion, biocompatibility and slipping issues. The use of 2D materials for neural sensors open new promising possibilities in this application area [3].

We have pioneered the use of epitaxial graphene on silicon carbide on silicon as a low- contact impedance EEG sensor which is extremely reliable upon long-term usage [4]. The produced sensors are wafer- thin, biocompatible with the skin, and show a lower contact impedance as compared to bulkier commercial sensors. In particular, we observe that their contact impedance improves once in contact with the skin, thanks to a gradual wetting of the graphene’s surface [4]. In addition, we show that the sensors are remarkably resilient to corrosion as they do not delaminate and show minimal reduction of performance upon storage in a highly saline environment for up to one year. In this contribution, we will share the latest progress in the use of epitaxial graphene sensors mounted on a head helmet for the hands-free control of a remote robotic platform.

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Journal of Neural Engineering 18 (6), 066035, 2021.

10:00 AM BREAK

SESSION EL19.05: Neuromorphic and Quantum Computing I
Session Chairs: Mario Lanza and Pei-Wen Li
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3020

10:30 AM EL19.05.01
Stable Resistive Switching of Highly Polycrystalline Two-dimensional Molybdenum Ditelluride based Memristor Array Jihoon Yang[1], Soon-Yong Kwon[1], Zonghoon Lee[1,2], Donghyeok Lim[1], Hongsik Jeong[1], Aram Yoon[1,2], Donghyun Lee[1] and Iljohn Jung[1]; [1]Ulsan National Institute of Science and Technology, Korea (the Republic of); [2]Institute for Basic Science, Korea (the Republic of)

Two-dimensional (2D) materials have generated attention for neuromorphic computing applications, and are promising for use in low-power synaptic devices at the atomic scale. However, 2D material-based memristors are disadvantaged by the large stochastic forming process, which results in switching variability. In this study, we present a 2-inch wafer scale memristor array that contains nanometer-sized grains of highly polycrystalline 2H-$MoTe_2$ as an active medium and exhibits reliable resistive switching. The polycrystalline 2H-$MoTe_2$ films were synthesized on a 2-inch SiO_2/Si wafer by tailoring the Te flux through a Te vapor-confined method using a eutectic alloy. The synthesized films contain uniformly sized nanograins (~60 nm) and exhibit ultrahigh-density (1.37×10^{11} cm^{-2}) grain boundaries (GBs). These GBs provide confined defective paths to enable conduction, facilitating reliable resistive switching. Compared to single-crystalline 2H-$MoTe_2$-based memristors, the polycrystalline 2H-$MoTe_2$-based memristor (PMM) arrays show improved resistive switching uniformity and stable multi-level resistance states, along with high device yields (>83.7%), small device-to-device variations (<13.8%), and long retention times (>10^5 s). Finally, this PMM shows linear analog synaptic plasticity under repeated pulses more than 2,500 and exhibits a learning accuracy of 96.05% for MNIST handwritten digit classification. The introduction of nanograins in the PMM represents a novel route to accelerate the use of 2D memristors in practical neuromorphic computing applications.

10:45 AM EL19.05.02
Investigation of Resistive Switching Mechanism in High-Performance High Entropy Oxide-Based RRAM Jing Yuan Tsai[1], Hung-Yang Lo[1], Chun-Wei Huang[2], Jui-Yuan Chen[3] and Wen Wei Wu[1]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]Feng Chia University, Taiwan; [3]National United University, Taiwan

The application of high entropy oxide (HEO) attracts great attention in recent years, due to its unique structural characteristics such as excellent electrochemical properties and long-term cycling stability possibilities that HEO has been used as an anode active material in Lithium-ion batteries. Furthermore, transition metal (TM) oxides have been used as dielectric materials of resistive random access memory (RRAM) owing to the stable structure and variable oxidation state of transition metals. However, the switching mechanism of TM-HEO-based RRAM has not been fully investigated to date.
In this work, We grew the high entropy oxide $(Cr, Mn, Fe, Co, Ni)_3O_4$ on Nb: STO conductive substrate epitaxially, and deposited the Pt metal as the top electrode. The structure of the pristine dielectric layer is spinel. After cycled, we observed that some regions of spinel structure will transform into rock-salt structure by using advanced transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) characterization, and the result data of X-ray photoelectron spectroscopy (XPS) and Electron Energy Loss Spectroscopy (EELS) support this perspective. Only specific elements will change their valence state, which resulted in excellent resistive-switching properties with a high on/off ratio on the order of 10^4 times, and excellent endurance in the order of 10^3 cycles at room temperature.

11:00 AM DISCUSSION TIME

11:15 AM EL19.05.04
Regulated Conductive Filament Formation and Evolution for Improved Switching Uniformity in Embedded Metal-oxide Based Memristor - A Phase Field Study Kena Zhang and Ye Cao; The University of Texas at Arlington, United States

The extreme device-to-device variation of switching performance is one of the major obstacles preventing the applications of metal oxide-based resistive random-access memory (RRAM) in large-scale memory storage and resistive neural network. Recent experimental works have reported that embedding highly ordered metal nano-islands (NIs) can effectively improve the uniformity of the RRAM devices, but the underlying role of the ordered metal NI is not fully understood. In this study, to address this specific problem, we develop a physical model to understand the origin of the variability and how embedding metal NIs within the HfO_2 oxide can improve the electroforming and resistive switching performances of RRAMs by reducing this variability. We find that due to dimensional confinement, introducing NIs increases electric fields in their vicinity, leading to high vacancy concentrations even at low forming potentials, and hence a more deterministic formation of the CF from its vicinity, in contrast to the random growth of CFs in the absence of embedded NIs. This deterministic vacancy nucleation in the vicinity of the embedded metal NIs is not only found to reduce the initial electroforming but also the subsequent reset/set voltages, as well as enhance the uniformity of these operation voltages and current ON/OFF ratio. We further demonstrate that modifying the shapes of the metal NIs can modulate the field strengths/distributions around the NIs, and that choosing NI metals that chemically facilitate vacancy formations can further optimize the CF morphology, reduce operation voltages, and improve switching performance. Our work thus provides a fundamental understanding of how embedded metal NIs improve the resistive switching performance in oxide-based RRAMs, and could potentially guide the selection of embedded metal NIs to realize a more uniform RRAM that also operates at higher efficiency than present materials.

11:30 AM *EL19.05.05
Optoelectronic Synaptic Memristors for Bio-Inspired Computing Tseung-Yuen Tseng; National Yang Ming Chiao Tung University, Taiwan

Nowadays, technology is rapidly evolving. Artificial intelligence(AI) is one of the fascinating technologies in the modern world. AI has made significant technological progress in face classification, speech recognition, strategic game, and decision-making [Yao, et al., Nat. Commun., 8, 1, pp. 1-8, 2017;

Jarrahi, Bus. Horiz., 61, 4, pp. 577-586,2018]. The processing of AI computing heavily depends on big data availability and requires a large amount of computation. Bio-inspired neuromorphic computing is expected to develop a more proficient computing architecture that mimics biological neural networks. Neurons and synapses are the two fundamental elements of neuromorphic architecture, where synapse plays an important role in learning and memory(C. Mead, Proc. IEEE, 78(10), 1629–1636, Oct. 1990). Memristors can become a potential candidate to behave as synapse due to their chemical compositions and electrical properties. In the last few years, photonic memristors have attracted increasing attention for AI systems. Such memristive devices have excellent capabilities to reduce the von Neumann bottleneck issue [Indiveri et.al., Proc. IEEE, 103, 8, pp. 1379-1397, 2015]. Additionally, integrated system consists of arrayed optical memristors to accept as building blocks of biospired vision system.

This talk will present that the photonic oxide memristor has high potential for synaptic application. It will report the conduction mechanism of the memristor device and working principle of the synapse. The synaptic features including potentiation/depression, paired-pulse facilitation(PPF) and spike time dependent plasticity(STDP) will be briefly introduced. In our recent work, Zn_2SnO_4(ZTO) based memristor devices are fabricated. The SL device shows over 80% optical transparency for the entire visible region. Significant improvements in bipolar resistive switching properties of the device with low SET voltage and long DC endurance cycles are observed in the 200°C, N_2 annealed device. The linearity of such memristive synapse is improved for 350 training epochs with a total number of 175000 pulses. The STDP learning rule for the annealed device is demonstrated through the electric field. The optical sensing capabilities of this device including photonic potentiation, photonic PPF, learning experience behavior, and multilevel memory feature by the repetition of optical pulse are demonstrated under the blue light illumination. On the other hand, the linearity and on/off ratio of the optoelectronic synapse are further improved by employing ZTO/MgO DL device. Such device has improved reliability with stable endurance and synaptic characteristics. The nonlinearities of potentiation and depression of the device are 1.96 and 0.33, respectively. The device shows 300 training epochs with 300000 pulse numbers. The synaptic features of the ZTO-based memristors make it to be suitable for optoelectronic synaptic application

SESSION EL19.06: Neuromorphic and Quantum Computing II

Session Chairs: Inge Asselberghs, Paul Berger and Supratik Guha
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3020

1:30 PM EL19.06.01

Electrical Properties Optimization on Resistive Switching Characteristics in Nb_2O_5-based RRAM Devices Chien-Hua Wang and Wen Wei Wu; National Yang Ming Chiao Tung University, Taiwan

In recent years, resistive random access memories (RRAM) has the advantages of simple cell structure, fast switching speed, low cost and the possibility of becoming next-generation non-volatile memories. However, the switching behavior of RRAM device is still not having enough evidence to be confirmed to replace conventional random access memories. In order to improve endurance characteristics and reduce power consumption, we use two distinct transition metal oxides, NiO and Nb_2O_5 for the further study. The dielectric layer NiO served as oxygen reservoir, and the Nb_2O_5 acted as resistance switching layer. In this work, we fabricate two different device structures, the respective structures are single-layer dielectric devices: Pt/Nb_2O_5/Pt, and bilayer dielectric devices: Pt/NiO/Nb_2O_5/Pt. It is found that the single-layer RRAM devices are unipolar operation, and another bilayer RRAM devices are bipolar switching mode. In addition, the bilayer RRAM devices exhibit better on/off ratio and endurance compare to single-layer devices. Besides, both devices also possess long cycling endurance and great ON/OFF ratio ($>10^3$).
To realize the resistive switching mechanism of two different types of devices, the high-resolution transmission electron microscope (TEM) was used to observe the conducting filaments in both dielectric layers. Moreover, the results of energy dispersive spectrometer (EDS) were used to identify the elementary distribution and analyze the filamentary compositions, indicated that the filament type of both devices was composed by a stack of oxygen vacancies. Furthermore, the X-ray photoelectron spectroscopy (XPS) and the electron energy loss spectroscopy (EELS) are used to analyze the oxidation state, bonding condition, and reactive regions in RRAM devices. This study indicated that bilayer RRAM devices enhance the performance of electrical characteristics, and provide insights into the proper structure design to alter the electrical properties of the related RRAM devices.

1:45 PM EL19.06.03

Deterministic Activation of Resistive switching and Light Emission from TaOx with Nanoscale Resolution Olha Popova[1], Steven J. Randolph[1], Sabine M. Neumayer[1], Benjamin Lawrie[1], Olga Ovchinnikova[1], Liangbo Liang[1], Matthew Marinella[2], Bobby G. Sumpter[1] and Petro Maksymovych[1]; [1]ORNL, United States; [2]Arizona State University, United States

Resistive switching in thin films phenomena have by now been widely reported throughout an enormous range of material classes, almost making them a generic property of field and current induced [MM1] material response. However, the mechanisms behind resistive switching have been persistently difficult to control, not in a small part due to its non-equilibrium nature. Moreover, from a practical side, the need for “controlled breakdown” to initiate resistive switching, is undesired due to significant power dissipation, stochasticity as well as dramatic restructuring of the material. Such structural changes are the major reason why the structure-function paradigm for resistive switching materials is difficult to develop.
In present work we have advanced both the measurement and the conditioning of the resistive switching phenomena utilizing TaOx as a model system. On one hand, we introduced two microscopy techniques – microwave impedance microscopy and cathodoluminescence – for the characterization of electroresistive phenomena. The advantage of these methods is that they can directly probe the electronic structure and conductance of amorphous binary oxide materials down with nanoscale imaging resolution. Therefore, much more robust connection to theoretical methods can be established, that can then guide a design approach material optimization. Meanwhile, we utilized ion-beam irradiation as a path to activate conductivity of materials without the need for energy-intensive electroforming. Using model Ta2O5-x amorphous films we will demonstrate: (1) direct imaging of electronic structure and trap centers in thin amorphous TaOx films; (2) electronic, dielectric and conductive characterization of Ta2O5-x after He-ion irradiation. Although He-ions begin to modify the nature of the bond [MM2] centers even at the lowest doses, the films exhibit remarkable stability toward large displacive dose of He-ions and are driven to metallic state only at the limit of structural decomposition; (3) unexpected enhancement of luminescence yield with increasing damage of the binary oxide film. We attribute this effect to preferential injection of bright luminescing centers under the combined effects of He-irradiation and localized electric fields. Our techniques are directly compatible with device architectures, potentially allowing for a high-degree of on-demand tuning of neuromorphic circuitry and materials.

2:00 PM *EL19.06.05

Materials and Technology Elements for Scaling Quantum Processors Ricardo Donaton; IBM Quantum, United States

Quantum computing has the potential to be a new computing paradigm. At IBM Quantum we have been scaling the number of qubits, improving coherence

times and gate fidelities as seen through the evolution of our quantum processors: Falcon 27 qubits, Hummingbird 65 qubits, Eagle 127 qubits, and we are on track to deliver Osprey 433 qubits and Condor 1121 qubits. Throughout this process we are learning about materials, process integration and yield, mechanical aspects, superconducting flexible cables, cryogenic infrastructure, control electronics and more. However, we cannot continue to simply increase the chip size to accommodate more and more qubits. Because of that, we are developing processes and architectures to connect processors into modular systems.
In this talk we will discuss the architectures and materials used in integrating new technology elements such as superconducting interconnects, through-substrate-vias and advanced packaging techniques that are enabling us to scale up our quantum processors. We will also touch on how we are planning to continue scaling up and deliver 4000+ qubit processors in the near future.

2:30 PM BREAK

3:00 PM *EL19.06.06
Materials and Integration for Quantum Computing in Silicon Mark A. Eriksson; Univ of Wisconsin-Madison, United States

As much as possible, qubits for quantum computers must be isolated from their environment in order to preserve phase coherence and maintain entanglement. Remarkably, the techniques used to make classical silicon CMOS devices can be used to make qubits with excellent performance. The operation of these devices, on the other hand – from the required temperatures to the number of electrons comprising a typical qubit – is very different from what is found in even the most advanced classical integrated circuits. In this talk, I will present two recent advances in materials – and the integration of those materials – for quantum computing in silicon. Recent results have begun to demonstrate the remarkable properties of silicon quantum wells containing short wavelength oscillations in the concentration of added germanium atoms. This highly engineered material, which has concentration oscillations on the 1-2 nanometer scale, changes the band structure in ways that provide better protection for quantum states, by increasing the energy gap to energy levels outside the qubit basis. It also is predicted by theory to introduce spin-orbit coupling, which can be used to enable all-electrical control of spin qubits. I will also discuss the role of integration, including 3D integration, which enables readout of quantum dot qubits in silicon by measuring the microwave transmission of a superconducting resonator on a separate substrate, flip-chip bonded to the first.

3:30 PM *EL19.06.07
Cryogenic Electronics for Quantum Computing: From Materials to Devices Cezar Zota, Eunjung Cha, Alberto Ferraris, Mridula Prathapan, Peter Mueller and Thomas Morf; IBM Research, Switzerland

The impact of an advanced quantum computing technology on society will be transformative [1]. To realize such a quantum technology, the entire quantum system must evolve, from the qubit chip to the supporting readout and control electronics [2]. Integration of cryogenic electronics inside the cryostat may become necessary to reduce system cost, increase speed and improve the input-output bottleneck [3]. Significant efforts have already been made to develop cryogenic integrated circuits for the generation of qubit control signals inside the cryostat. One of the main design constraints of such circuits and their subsequent integration is the low available cooling power, which is in the order of a few W at the 3 K stage, and significantly less at the lower stages. Advanced cryo-circuits demonstrated today show power dissipation in the order of 5 mW/qubit [4]. This means that even with such solutions, scalability will remain challenging for advanced quantum computers. An approach to address this power challenge is to develop not only tailored cryogenic circuits, but also tailored cryogenic devices that can leverage the unique and beneficial properties of materials at low temperatures.

In this work, we will demonstrate the design and operation of a cryogenic qubit control circuit, an RF arbitrary waveform generator, based on commercial 14 nm FinFET technology. The circuit exhibits exceptionally low power dissipation and excellent noise performance. To plot a path towards even further reduce power dissipation, we study and model the comprising transistor technology at 4 K. The results indicate that a tailored cryogenic CMOS technology, leveraging the reduced subthreshold swing and enhanced mobility of the transistors, could achieve orders of magnitude reduction of DC power dissipation. Finally, we demonstrate cryogenic circuits based on III-V materials, such as InGaAs and InP, and show how these leverage the extremely high electron mobility of cryogenic quantum wells towards even further enhanced circuit performance.

[1] T. D. Ladd *et al.*, *Nature*, vol. 464, no. 7285, pp. 45–53, Mar. 2010.
[2] L. M. K. Vandersypen *et al.*, *Npj Quantum Inf.*, vol. 3, no. 1, p. 34, 2017.
[3] B. Patra *et al.*, *IEEE J. Solid-State Circuits*, vol. 53(1), pp. 309–321, 2018.
[4] J. C. Bardin *et al.*, *Dig. Tech. Pap. - IEEE Int. SSCC.*, pp. 456–458, 2019.

4:00 PM EL19.06.08
Characterizing Nanomagnets Used for Silicon Spin Qubit Operation Peter Rickhaus[1], Liza Zaper[1,2], Floris Braakman[2], Alexander Stark[1], Felipe Favaro de Oliveira[1], Mathieu Munsch[1], Patrick Maletinsky[2,1] and Martino Poggio[2]; [1]Qnami AG, Switzerland; [2]Universität Basel, Switzerland

Certain type of spin qubit implementations require the application of well-defined magnetic fields.[1] These are provided by nanomagnets. For the sake of reproducible qubit operation, it is key to ensure that the stray field, generated by the nanomagnets, has little variation caused by the nanofabrication technique. We use Scanning Nitrogen-Vacancy Magnetometry (SNVM) to map out the magnetic stray field generated by nanomagnets. Previously, we have successfully used this technique to characterize the very small stray fields that originate from CoFeB nanowires.[2] Here, we fabricate the nanomagnets using focused electron beam ion deposition (FEBID), a resist-free technique that potentially improves the magnetic homogeneity. We use the high sensitivity and spatial resolution of SNVM to characterize the magnetization, homogeneity and magnetic particles of the nanomagnets and to find improvements for the fabrication technique.[3]

[1] Neumann et al., Simulation of micro-magnet stray-field dynamics for spin qubit manipulation, J. Appl. Phys. 117 (2015)
[2] Celano U., et al., (2021) Probing Magnetic Defects in Ultra-Scaled Nanowires with Optically Detected Spin Resonance in Nitrogen-Vacancy Center in Diamond. Nano Lett. 2021, 21, 24, 10409–10415.
[3] Zaper, L. et.al., in preparation

SESSION EL19.07: Poster Session I
Session Chairs: Supratik Guha and Francesca Iacopi
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL19.07.03
Alternative Approaches to Purify As-Produced Boron Nitride Nanotubes from Thermal Induction Plasma Process Jingwen Guan, Yueying Li, Steven Walker, Robyn Iannitto, Liliana Gaburici, Keun Su Kim, Dean Ruth, Mark Plunkett, Christopher T. Kingston and Benoit Simard; Security and Disruptive Technologies Research Centre, Canada

Boron nitride nanotubes (BNNTs) are an engineered nanomaterial possessing a compelling set of intrinsic properties, including a stable broad band gap about 5.5 eV, therefore, being an electrical insulation material, excellent mechanical strength, high thermal conductivity, high oxidation resistance, and transparency in visible light. These properties make them perfect candidates for future nanocomposites in applications such as high-temperature and extreme environments, and transparent and protection materials. After the discovery of carbon nanotubes (CNTs), BNNTs were first theoretically predicted and then successfully synthesized in 1995 by an arc-discharge method. Subsequently, numerous other techniques for BNNT synthesis have been discovered, including the plasma-based Hydrogen Assisted BNNT Synthesis (HABS) method developed at the National Research Council Canada (NRC). Despite such advances in production, direct growth of highly pure BNNTs still remains challenging today, with most methods yielding varying mixtures of BNNTs, non-nanotube fragments and particles, and incompletely consumed feedstock. From the HABS method, the as-produced BNNT product consists of approximately 20 wt% elemental boron particles, and 25 wt% of non-nanotube B-N byproducts and unreacted h-BN feedstock. Removal of these impurities is essential to extract the full potential of BNNTs in nanocomposites. We will present three different approaches to post-synthesis purification of HABS-BNNT materials produced at the NRC, namely gas-phase halogen processing, non-covalent polymer extraction, and a three-stage solution process, and will discuss the advantages and disadvantages of each approach with respect to purity, efficiency and scalability.

5:00 PM EL19.07.04
Atomic Structure of Amorphous TiO_2 : GeO_2 Mixtures and its Evolution with Annealing Ruth Osovsky[1,2], Emmett Randel[1], Aaron Davenport[1], Samuel Castro Lucas[1], Michael Van Erdewyk[1], Justin B. Sambur[1] and Carmen S. Menoni[1]; [1]Colorado State University, United States; [2]Israel Institute for Biological research, Israel

Transparent amorphous oxide thin films are ubiquitous in photonics technologies. They are transparent over a broad wavelength range, from near ultraviolet to near infrared. Their refractive index in the near infrared offers high contrast with Si or among oxides, as is the case between (amorphous) *a*-Ta_2O_5 and *a*-SiO_2, which is exploited for light confinement in integrated Nano- and Si photonics devices. Amorphous oxide thin films are also extensively used in optical interference coatings for most demanding laser science applications. Tunable optical and mechanical properties are accessible by depositing mixtures of two or more cations. Recent research on ion beam sputtered (IBS) mixtures of 44% TiO_2 and 56% GeO_2 have been identified as prospective candidates for the high index layer in interference coatings for gravitational wave detectors, as their internal friction, when annealed to 600 °C for 100 hours, is ~4x lower than state-of-the art TiO_2 : Ta_2O_5 [1]. This work reports on a study of the evolution of atomic structure and bonding of mixtures of TiO_2 and GeO_2 through Raman and Infrared spectroscopies with annealing. Characteristic vibrational signatures of *a*-GeO_2 are altered in the mixtures, indicating the doping of Ti ions into the lattice of *a*-GeO_2 in substitutional mode, as evidenced by a larger distribution in inter-tetrahedral Ge-O-Ge bond angles and suggesting a more open and flexible network. Annealing causes structural reorganization on the TiO_2 : GeO_2 mixtures, as observed by the evolution in Ge-O-X (X=Ge, Ti) vibrational signatures in the mixture, which is more significant at temperatures ≥ 500°C. This work brings out a new understanding of the modifications in the atomic structure of TiO_2 : GeO_2 mixtures upon thermal treatment, which is critical to understand the mechanisms involved in affecting internal friction in this promising high refractive index materials for coatings of gravitational wave detectors [1].

[1] G. Vajente *et* al., "Low mechanical loss TiO_2 : GeO_2 coatings for reduced thermal noise in gravitational wave interferometers", *Phys. Rev. Lett.* 127, 071101 (**2021**).

This work is supported by the National Science Foundation LIGO program through grant No. PHY 2110101 and PHY 2012024.

5:00 PM EL19.07.06
Effects of Metal Diffusion on Electrical Performance and Reliability of Low Dielectric Constant Thin Films Fabricated by Plasma-Enhanced Chemical Deposition Method Under Thermal Stress Seonhee Jang, Rajib Chowdhury and Thomas Poche; University of Louisiana at Lafayette, United States

To reduce a resistance-capacitance (RC) time delay in the back-end-of-line (BEOL) interconnect is critical for advanced integrated circuit chips. Copper (Cu) and low-dielectric constant (low-*k*, *k*<4.0) interconnects can reduce the RC time delay by 30-50 %, compared to traditional aluminum (Al) and silicon oxide interconnects because Cu/low-*k* film combination provides lower metal line resistance and parasitic capacitance between metal lines. However, the migration and diffusion of metal into the low-*k* films become challenging during the integration of Cu/low-*k* film, resulting in degradation of electrical performance and reliability. One solution is to form metal barriers. With further scaling of technology node, the volume of Cu metal lines decreases and its resistance significantly increases because of Cu surface and grain boundary scattering and the metal barriers. The other solution is to employ different metals to reduce the surface and grain boundary scattering effect. Potential candidates to replace Cu can be determined by lower product value of bulk resistivity and electron mean free path than that of Cu. Based on this criteria, cobalt (Co) and molybdenum (Mo) were selected. In this study, the integration of Co or Mo with the low-*k* films was conducted and electrical characteristics and reliability of the low-*k* films were investigated.
In this study, low-*k* SiCOH thin films were fabricated on p-type Si (100) wafer by plasma-enhanced chemical vapor deposition (PECVD) of tetrakis(trimethylsilyloxy)silane (TTMSS, $C_{12}H_{36}O_4Si_5$) precursor at room temperature. The thickness of the low-*k* SiCOH film was in the range of 100-200 nm. Following, three different metals Cu, Co, and Mo were deposited on the low-*k* SiCOH film through a shadow mask using a DC sputtering method to fabricate metal-insulator-silicon (MIS) capacitors. All metal films were deposited at room temperature. The thickness of the films was approximately 50 nm. The fabricated MIS capacitors were then annealed in N_2 atmospheres at 400 °C for 2 h. The elemental composition changes were investigated by X-ray photoelectron spectroscopy (XPS). The electrical characteristics and reliability of the MIS structures were measured from capacitance-voltage (C-V) and current-voltage (I-V) curves using a semiconductor parameter analyzer.
The C-V curves of Cu-gate, Co-gate, and Mo-gate MIS capacitors were compared before and after thermal stress. The typical C-V curves were obtained with accumulation, transition, and depletion regions from the negative to positive bias application. Depending on the type of metal-gate, the accumulation capacitance was different, suggesting that the deposition of metal gate may affect the capacitance of the underlying low-*k* film. The thermal annealing reduced the accumulation capacitance of the MIS capacitors. The *k*-value was determined by the equation, $k=C_{acc}d/\varepsilon_0 A$, where C_{acc} is the accumulation capacitance, d is the thickness of the low-*k* film, ε_0 is he vacuum permittivity, and A is the gate area. An increase in the *k*-value suggests that the low-*k* thin film was damaged by plasma during metal sputtering deposition. After annealing, the *k*-values were reduced, indicating that plasma-induced damage to the film could be partially recovered by annealing process. A flatband voltage (V_{fb}) shift in the C-V curves could occur due to the presence of charges of fixed, interface, and mobile types. Another shift in the C-V curves was the evidence of the diffusion of metal ions into the low-*k* film by annealing process. An increased leakage current after annealing demonstrates that the diffusion of metal ions occurred in the low-*k* film. From the XPS elemental composition analysis, metal atoms diffused into the low-*k* film at the interface between the low-k film and each metal after annealing. A large V_{fb} shift was also

observed after annealing suggests that a thermal stress stimulated more metal ions to diffuse into the low-*k* film.

5:00 PM EL19.07.07
Colloidal Single Crystals Engineered with DNA in Lithographically Defined Microwells Alexa Wong[1,2], Kwanghwi Je[3], Cindy Zheng[1,3], Liban Jibril[1,2], Ziyi Miao[1,2], Sharon Glotzer[3] and Chad Mirkin[1,2]; [1]Northwestern University, United States; [2]International Institute for Nanotechnology, United States; [3]University of Michigan–Ann Arbor, United States

Lithographically-defined microwell templates are used to study DNA-guided colloidal crystal assembly parameters, including superlattice position, orientation, and size, in an effort to increase our understanding of the crystallization process. In addition to enabling the synthesis of arrays of individual superlattices in arbitrary pre-defined patterns, the technique allows one to study the growth pathways of the crystals via *ex situ* scanning electron microscopy. Importantly, a Volmer–Weber (VM) (island formation)-like growth mode is identified, which has been reproduced via simulations. Notably, both experiment and simulation reveal that the crystallites merge and reorient within the microwells that defined the crystal growth to form single-crystalline structures, an observation not common for VM pathways. The control afforded by this platform will facilitate efforts in constructing metamaterials from colloidal crystals as well as their integration into optical devices and applications.

5:00 PM EL19.07.09
Steady-State and Transient Electron Transport in the Two-Dimensional Electron Gas in Gallium-Aluminum-Nitride Heterojunctions with Gallium Nitride Yana Wang[1], Michael Shur[2], Walid A. Hadi[3] and Stephen K. O'Leary[1]; [1]University of British Columbia, Canada; [2]Rensselaer Polytechnic Institute, United States; [3]Florida State University, United States

At the interface of gallium-aluminum-nitride with gallium nitride, a two-dimensional electron gas will form. This electron gas can both enhance the low field mobility and influence the electron drift velocity for higher applied electric field strengths. Using a self-consistent Schrödinger-Poisson equation solver, we determine the concentration of electrons within such a two-dimensional electron gas as a function of the aluminum content. A comparison will then be made with results acquired using the analytical approach of Ambacher *et al.* [1]. The impact of this two-dimensional electron gas on the steady-state and transient electron transport that occurs within this material will then be critically examined. The device implications will be explored.

[1] O. Ambacher, B. Foutz, J. Smart, J. R. Shealy, N. G. Weimann, K. Chu, M. Murphy, A. J. Sierakowski, W. J. Schaff, L. F. Eastman, R. Dimitrov, A. Mitchell, and M. Stutzmann, J. Appl. Phys. **87**, 334 (2000).

5:00 PM EL19.07.10
Flexible Hydrogenated Amorphous Carbon Thin Films Fabricated by Plasma-Enhanced Chemical Vapor Deposition of Cyclohexane Precursor Thomas Poche, Rajib Chowdhury and Seonhee Jang; University of Louisiana at Lafayette, United States

The characteristics of the hydrogenated amorphous carbon (HAC) films can be determined by the composition of sp^3, sp^2, and sp^1 hybridized structures depending on the bond type of four valence electrons. The C-C bonds with sp^3 and sp^2 correspond to diamond and graphite, respectively, and a mixture of sp^3 and sp^2 determines the material properties. The sp^3 bond shows some advantages including mechanical strength, wide band gap, and chemical and electrochemical inertness, however it is unfavorable for a strip process after etching. The HAC films by adding hydrogen to a sp^3/sp^2 could possibly present an etching resistance. The HAC films are characterized according to the composition ratios among a sp^3, sp^2, and hydrogen. When the hydrogen content is large, polymer-like HAC films can be formed with low film density due to high content of sp^3. When the hydrogen content is small, the content of sp^3 becomes low, resulting in a diamond-like HAC with high film density and hardness. When the hydrogen content becomes smaller, the content of sp^2 is high and a graphite-like HAC can be obtained. Depending on the deposition conditions, the sp^2/sp^3 hybridization ratio can vary over a wide range of values. Flexible HAC thin films were fabricated by plasma-enhanced chemical vapor deposition (PECVD) of cyclohexane (CHex, C_6H_{12}) precursor on the substrate of indium tin oxide on polyethylene naphthalate (ITO/PEN). The sheet resistance of ITO was about 12 Ω/square. The transparency of ITO was ≥ 75 % with a haze of 3 %. The PEN substrate was DuPont Teijin film. Thicknesses of ITO and PEN layers were >180 nm and 0.125 mm, respectively. Gas molecules vaporized from the CHex precursor were carried by argon (Ar) with a purity of 99.999 % gas and delivered to the reactor. A base pressure was 0.53 Pa before deposition. The HAC films were deposited at room temperature of 25 °C with an operating pressure of 26.7 Pa. The RF plasma power with 13.56 MHz was chosen from 20 to 100 W. To characterize etching properties of the HAC films, dry etching with $Ar+CF_4+O_2$-based gas chemistry was conducted in an inductively coupled plasma-reactive ion etching (ICP-RIE) system. Tetraethyl orthosilicate (TEOS) oxide was used as the reference for calculating the etch rate and etch selectivity. The etch selectivity of the HAC film was calculated by t_{TAC}/t_{TEOS}, where t_{TEOS} and t_{TAC} are the thicknesses of the TEOS and HAC removed after dry etching. The thickness and extinction coefficient of the HAC films were measured by ellipsometer. Surface morphology of the films was observed by atomic force microscopy (AFM). The functional groups of the films were identified using Fourier transform infrared (FTIR) spectroscopy. The chemical composition of the films was determined by X-ray photoelectron spectroscopy (XPS). The structural arrangement of the carbon bonds was analyzed by Raman spectroscopy.
The prominent IR absorption consists of C–H stretching modes at 3300-2800 cm^{-1} and C=C and C–H bending modes below 2000 cm^{-1}. The C–H stretching mode can be deconvoluted into three: $sp^1\equiv$C–H modes centered at 3300 cm^{-1}, sp^2=C–H$_n$ modes at 3085-2975 cm^{-1}, and sp^3–C–H$_n$ modes at 2955-2850 cm^{-1}. The structural transformation could occur from the sp^3 to sp^2 depending on deposition conditions. Two carbon allotropes – diamond and graphite – can be distinguished by their Raman spectra. Typical D and G peaks were observed around 1350 and 1590 cm^{-1} in the Raman spectra, respectively. The Raman spectra of disordered carbons can be classified by the intensity ratio of the D and G modes, I(D)/I(G). To quantify the chemical bonding status, the ratio R is introduced as the peak area ratios of C–C to C–H$_x$. The etch-durability represented as the inverse of the film loss is related to the ratio R. Etching properties were strongly affected by deposition conditions and etching parameters.

5:00 PM EL19.07.12
TEM Investigation of Resistive Switching mechanism of $PbSnO_3$ Perovskite Oxide RRAM Device Meng Hsuan Yang and Wen Wei Wu; National Yang Ming Chiao Tung University, Taiwan

Resistive memristors with high density and nonvolatile have the significant potential for long-term data storage and development of artificial neural computing. Among most filamentary-type resistive switching(RS) memories, conventional binary oxides (MO_x) are extensively studied as RS materials in memristors.[1] However, there are few studies on ternary oxides and lack of stoichiometry information.
In this study, we introduced novel material $PbSnO_3$(PSO) as switching layer, which epitaxially grew on $SrRuO_3$ (SRO) bottom electrode and $SrTiO_3$ (STO) substrate. This work revealed the resistive switching mechanism by means of the formation nanochannel in the $PbSnO_x$ (PSO) matrix and the effect of oxygen deficiencies on its characteristics. High-resolution transmission electron microscope (TEM) was utilized to achieve a clear visualization of conducting path. Furthermore, the components and structures were analyzed by electron energy loss spectroscopy (EELS) and energy dispersive spectroscopy (EDS) equipped in TEM. PSO-based RS memory exhibited superior performance including high ON/OFF ratio, long data retention time, narrow distribution of switching voltage, and stable device-to-device uniformity, which provide great potentialities on the application of novel RRAM devices.

5:00 PM EL19.07.13
Deformable Carbon Atomic Film-based Etching Mask Jiwoo Kim, Dong Hoon Moon and Gwan-Hyoung Lee; Seoul National University, Korea (the Republic of)

Carbon-based materials have been studied in the various field such as semiconductor industry as potential materials due to their superior properties such as high electrical and thermal conductivity, chemical stability, and mechanical strength. Carbon-based materials have great potential not only as channel and electrode materials with their outstanding electrical properties, but also as sacrificial masks , etch stop, and barrier materials with their high chemical stability and excellent mechanical strength. Chemically stable carbon-based thin film can be a key to overcoming the conventional technological limit of enabling complex 3D stacking structure and nano-fabrication. Here, we synthesize carbon atomic film on silicon substrates and show mechanical properties and etching behavior of the carbon mask. Deformation of the carbon thin film occurs during etching and unique 3D structures can be fabricated with the carbon mask. Also, the kirigami pattern allows the fabrication of more complex 3D structures which is not available with conventional mask materials. Our work paves the path for the etching and fabrication technique for complex 3D structures.

5:00 PM EL19.07.14
A Novel Electrical Characterization Method for Simultaneous Extraction of the Grain Size, Single-Crystalline Grain Sheet Resistance, and Grain Boundary Resistivity of Polycrystalline Monolayer Graphene Honghwi Park, Jiyeong Yun and Hongsik Park; Kyungpook National University, Korea (the Republic of)

Among many kinds of graphene grown or synthesized by various methods, graphene grown on metal catalysts by chemical vapor deposition (CVD) has been the most widely used for device applications because large-scale monolayer graphene can be produced with a relatively good material quality. However, CVD graphene is typically grown as polycrystalline composed of multiple single-crystalline grains stitched by grain boundaries (GBs), and carrier scattering at the GBs could severely degrade electrical performance and uniformity. For the design and fabrication of electrical devices utilizing CVD graphene, therefore, it is very important to know the electrical parameters of single-crystalline grains and GBs as well as the average grain size, as these directly correlate to electrical performance of CVD-graphene devices. Accordingly, many approaches to dealing with them have been studied over the past decade; however, extracting the grain-related parameters (*i.e.*, the average grain size, grain sheet resistance, and GB resistivity) through a simple characterization method still remains as a great challenge because of the difficulty in observing graphene GBs and evaluating the electrical properties of the GBs and single-crystalline grains separately.

Here, we report for the first time an electrical characterization method that can extract the average grain size, grain sheet resistance, and GB resistivity of monolayer CVD graphene simultaneously through a simple transmission-line model (TLM) measurement. We found out that the electrical property of polycrystalline graphene (*i.e.*, sheet resistance) depends significantly upon the device dimension and such the dependence results from the GB density within the device channel region. By statistically investigating the distribution of GB density depending on channel dimensions, we developed an analytical resistance model that can explain the relation between the sheet resistance of polycrystalline graphene and its grain parameters. With this resistance model, we confirmed that the three-grain parameters can be extracted simultaneously with high accuracy (> 99%) from the dependence of the sheet resistance on the channel dimension. Furthermore, the developed analytical resistance model and its applicability for parameter extraction were experimentally validated by characterizing TLM patterns fabricated on monolayer CVD graphene. The result showed that the average grain size, grain sheet resistance, and GB resistivity of CVD graphene can be extracted simultaneously with high accuracy. This method of simultaneous extraction of the grain-related parameters from the sheet-resistance dependence on the channel dimension obtained from simple TLM measurements will provide a useful tool for the electrical characterization of CVD graphene and other poly-crystalline 2D materials, and their efficient device applications.

5:00 PM EL19.07.15
Control of Threshold Voltage of AlGaN/GaN FinFET by Monolayer Doping Linh Chi T. Cao[1], Shu-Han Hsu[1] and Chun-Lin Chu[2]; [1]Sirindhorn International Institute of Technology, Thammasat University, Thailand; [2]Taiwan Semiconductor Research Institute National, Applied Research Laboratories, Taiwan

Abstract:
With the evolution of modern society and economy, the demand for network applications, broadband network systems have been gradually grabbing significant attention in the high-tech industry. To meet the requirements of smart life, smart city, and unmanned devices and vehicles in the future, the standard of 6G could include wireless communication between low-orbit satellites combined with 5G cellular communication systems. For 6G wireless communication, wide bandgap and high-electron-mobility transistors of AlGaN/GaN (HEMTs) are emerging as excellent candidates for radiofrequency (RF) and microwave power amplifiers due to their high-power-handling capabilities and ability of small-scale fabrication to obtain minor and cheaper chip size. The conventional AlGaN/GaN HEMTs such as depletion-mode transistors with a negative threshold voltage (Vth) can limit the device application and their stability against temperature. Therefore, it is important to convert the gate-controlled channel from depletion- to enhancement mode. Herein, this study presents a method that can accurately control threshold voltages of AlGaN/GaN by using monolayer doping with fluoride-containing molecules without any lattice damage that can be created from conventional methods such as implantation or dry-etching. First, epitaxy of GaN/AlGaN/GaN was introduced over SOI substrate sequentially in CVD chamber. TEM shows the corresponding thickness for each layer (Figure 2). Using a self-assembly technique, a uniform and reproducible monolayer of 1H,1H,2H,2H-Perfluorooctyltriethoxysilane (POTS), fluorine-containing molecules, was immobilized onto surface of AlGaN/GaN substates by covalent bond Ga-O-Si. The XPS measurement observed fluoride signal with 56.48 % of atomic percentage that confirmed the formation of fluoride- self assembled monolayer onto AlGaN/GaN substrate. The doped concentration of fluoride atoms can be controlled by self-assembled time and the doses of POTS for assembled reaction. After forming a fluoride-containing monolayer, the device is then capped with SiO_2, spike annealed under high temperature to complete monolayer doping process. The AlGaN/GaN FinFET device composed of the P-type and N-type high-mobility carrier channels will be fabricated to further verify the performance and reliability characteristics for the novel Vth turning process. This can open more process possibilities for next-generation high mobility AlGaN/GaN FinFET to serve future related 6G communication and low-orbit satellite circuit development.
Keywords: Fluoride monolayer doping, 6G communication, AlGaN/GaN FinFETs, self-assembled monolayers (SAMs).

5:00 PM EL19.07.16
Selectively Self-Healing, Stretchable and Wirelessly Operatedsensor System Based on a Rubber-Modified Epoxy with High Toughness Somin Kim and Jeong Sook Ha; Korea University, Korea (the Republic of)

There has been extensive research on self-healing materials for extending the lifespan of wearable devices and for environmental friendliness. However, it is still in progress to get selectively self-healing functionality by specific stimulus such as heat or light for prohibiting the unintentional merging of materials to ruining the devices.

In work, we report on the synthesis of thermo-responsive self-healing epoxy and its application to fabricating self-healing strain and temperature sensors. Thermo-responsive self-healing epoxy is synthesized by using poly(tetramethyl glycol), 1,4-butanediol diglycidyl ether, aminophenyl disulfide, and dimethylglyoxime. Dimethylglyoxime and aminophenyl disulfide are highly thermo-responsive whose triggering temperature can be tuned by molecular structures. By heating, the disulfide bond exchange reaction and the regeneration of the oxime-carbamate bond can be initiated, resulting in self-healing. In addition to self-healing performance, the synthesized polymer exhibits high toughness and stretchability owing to the ring-opening reaction of the epoxy group and packing of poly(tetramethyl glycol). Using the synthesized self-healing epoxy film as a substrate, individual temperature and strain sensor is fabricated based on a mixture of the self-healing polymer and conductive materials, and NFC coil was patterned on the polymer substrate to transmit energy wirelessly. Then, a multi-sensor patch of vertically assembled sensor layers and NFC coil layer are made using deformable and self-healing liquid metal galinstan interconnections. Here, the layer-by-layer assembly is attributed to interlayer self-healing without delamination. Such fabricated multi-sensor patch can monitor bio-signals and can be charged wirelessly after attachment onto human skin and it can be fully self-healed by heating to recover the sensitivity even after multiple cycles of damage and healing.

5:00 PM EL19.07.17
Comparative Study of NiO_x/β-Ga_2O_3 p-n Heterojunctions on (-201) and (001) Free-Standing β-Ga_2O_3 Substrates Dinusha Herath Mudiyanselage, Dawei Wang, Ziyi He and Houqiang Fu; Arizona State University, United States

β-Ga_2O_3 is a wide bandgap (WBG) semiconductor material that has been extensively studied for power, optical, and RF electronics due to its large bandgap of 4.9 eV and high breakdown field of ~ 8MV/cm. It is expected that β-Ga_2O_3 can outperform its GaN and SiC counterparts. However, most of the demonstrated β-Ga_2O_3 devices are unipolar due to the lack of p-type Ga_2O_3, such as high electron mobility transistors (HEMTs) and Schottky barrier diodes. This is primarily attributed to the absence of shallow acceptors and holes trapped in localized polarons. To overcome these constraints, other p-type materials, such as p-type NiO_x, have been utilized to produce β-Ga_2O_3 based p-n heterojunctions. Several NiO_x/β-Ga_2O_3 devices, such as p-n diodes and junction barrier Schottky (JBS) diodes have been demonstrated so far. These devices show excellent properties, such as low on-resistance and high breakdown voltages. Moreover, due to its highly asymmetric monoclinic crystal structure, β-Ga_2O_3 exhibits anisotropic properties along different crystal orientations. However, the impacts of different β-Ga_2O_3 crystal orientations on NiO_x/β-Ga_2O_3 p-n heterojunction are still not clear.
In this work, we perform a comparative study of NiO_x/β-Ga_2O_3 p-n heterojunctions on (-201) and (001) crystal orientations. The edge-defined film-fed grown β-Ga_2O_3 substrates were acquired from Novel Crystal Technology, Inc Japan with a similar n-type doping concentration of [Sn] = 5 × 10^{18} cm^{-3} and thickness. First, the substrates were cleaned using acetone, isopropyl alcohol (IPA), and DI water. The Ti/Au (20/130 nm) back contacts were deposited by electron beam (E-beam) evaporation followed by rapid thermal annealing at 500 °C in N_2 environment. Then, standard photolithography was performed to define patterns for deposition of NiO_x and the anode. 200 nm NiO_x and the anode Ni/Ti/Au (20/15/100 nm) were deposited using E-beam evaporation, followed by a liftoff process to isolate individual devices. I-V and C-V measurements were performed using a 4200 SCS semiconductor parameter analyzer. Both devices show an excellent rectification with ON/OFF ratio of 10^{10}. The I-V measurements indicate a turn-on voltage of 1.9 and 2.6 V, an ideality factor of 1.3 and 2.5, and an on-resistance of 3.7 and 5.4 mΩ.cm^2 for (-201) and (001) devices, respectively. The (-201) device exhibited better performance compared with the (001) device in terms of low turn-on voltage, near ideality, and low on-resistance. C-V measurements indicated a doping concentration of 1.6 ×10^{18} cm^{-3} and 1.7×10^{18} cm^{-3} for respective devices. This indicates both devices have similar hole concentrations in the NiO_x layer. These differences in the device electrical properties are attributed to the different atomic configurations, the density of dangling bonds, and conductivity modulated hole injection into β-Ga_2O_3. Further investigation through annealing and temperature-dependent measurements will reveal more information about the anisotropic nature of NiO_x/β-Ga_2O_3 p-n heterojunctions. This work can be an importance reference for understanding the anisotropic electrical behavior of β-Ga_2O_3 heterojunction based bipolar devices.

5:00 PM EL19.07.18
Study on Switching Voltage of Silver Telluride Nanoparticle-Based Resistive Random Access Memory Won-Yong Lee and Jaewon Jang; Kyungpook National University, Korea (the Republic of)

In this study, we report on the change of the switching voltage of a silver telluride nanoparticle-based resistive random access memory (RRAM) device in accordance with the annealing temperature. Solution-processed Ag/silver telluride/Au RRAM was fabricated using synthesized silver telluride NPs. According to the annealing temperature, the change in the properties of the silver telluride thin-film was observed, and the change in the electrical properties of the RRAM devices was also observed. The fabricated silver telluride-based RRAMs have complementary resistive switching characteristics regardless of the annealing temperature. However, it was confirmed that the reset switching voltage was decresed according to the change of the thin-film as the annealing temperature increased. The reset voltage of the device annealed at room temperature was ±3~4V, whereas reset voltage of the device annealed at 200°C decreased to ±1V. This change in switching voltage is due to the change in the crystallinity and surface morphology of the thin-film.

5:00 PM EL19.07.19
Investigating Resistive Switching Mechanism in $PbHfO_3$ Based RRAM Device Che-Hung Wang and Wen Wei Wu; National Yang Ming Chiao Tung University, Taiwan

Recently, binary metal-oxide based resistive random access memory (RRAM) has become one of the popular candidate for future application in memory system due to its excellent characteristics, such as high switching speed, and trusting stability. In this work, the dielectric layer $PbHfO_3$ (PHO) films of 100 nm thickness have been epitaxially deposited on $SrRuO_3$ bottom electrode and then deposited Au as top electrode. PHO shows great electrical properties, which performs high cycling endurance (up to 400 cycles), uniform distribution of both low resistant state (LRS) and high resistant state (HRS), and long retention time (over 10^4 s). The high resolution TEM and STEM images demonstrate the PHO structure before and after the switching behavior. These results strengthen the switching mechanism and the detailed discussion of this switching behavior provide a novel aspect of the RRAM switching mechanism.

5:00 PM EL19.07.20
Atomic-scale Investigation of Structural evolution and Resistive Switching Behaviors in Lanthanum cobaltite -Based Resistive Random-Access Memory Yen Jung Chen and Wen Wei Wu; National Yang Ming Chiao Tung University, Taiwan

Resistive random-access memory (RRAM) is considered for next-generation non-volatile memory (NVM) owing to its simple devices, low cost and high storage density. Resistive switching occurs in a wide range of materials among the transition metal oxides (TMO). In this work, we utilize epitaxial ternary metal oxides layer, LaCoOx (LCO), which grows on Nb-doped SrTiO3 (Nb-STO) substrate as RRAM device. We deposited Au/Ti metal as the top electrode, and measured the SET and RESET process with more than 900 cycles. To reveal the resistive switching behaviors, we use the high-resolution transmission electron microscope (TEM) and Atomic-scale scanning transmission electron microscopy (STEM) to observe the structural evolution and oxygen-ion migration in LaCoOx. From the TEM results and the corresponding Fast-Fourier-Transform Diffraction pattern (FFT-DP), the functionalities of LaCoOx films can be manipulated by distinct voltage. It is clearly demonstrated that the structure changes from monocrystalline to polycrystalline. Further demonstrate structural evolution, we change the top electrode to Pt/Ag. According to previous study, we know that the topotactic phase transformation between perovskite and brownmillerite phases can be performed for epitaxial LaCoOx films. In recent years, topotactic phase transformation has attracted much attention owing to their potential physical and electronical properties for RRAM devices. Under negative bias, the

Pt/Ag/LCO /Nb-STO RRAM device can switch from the pristine high resistance state (HRS) to the LRS, which is known as the SET process. As we continuously applied voltages sweep cycles, the structure will transform from LaCoO2.67 to brownmillerite LaCoO2.5 with perovskite LaCoO3 regions. Additionally, we use X-ray photoelectron spectroscopy (XPS) to demonstrate the Co valence changed for further studying micro-structural evolution and the resistive switching behaviors. This study not only revealed the oxygen-ion migration of LaCoOx but also proved it to be the promising candidate for RRAM application.

5:00 PM EL19.07.21
High Figure of Merit Indium-Tin Oxide (ITO) Electrodes Based on Metal-Polymer Composites without Counter Anions Dongbeom Kim, Wonjeong Suh, Jaehyun Kim, Yebin Park and Unyong Jeong; Pohang University of Science and Technology, Korea (the Republic of)

In solution-based polymer-assisted deposition (PAD), high performance transparent conducting oxides (TCO) have been rarely reported compared to multicomponent inorganic thin films (metal-oxides, -carbides, -nitrides, and -chalcogenides). TCO fabrication requires i) removal of impurities, ii) high-density oxide film, iii) homogeneity in crystal structures and film morphology, and iv) controllable elemental doping. This study carries out a systematic investigation into preparation of stable multicomponent metal-polymer complex solutions by removing the counter anions in the solution. This study also performs accurate acid-base titration for each metal species in order to optimize the amount of PEI, thus maximize the density of the film. As a representative TCO, Sn-doped In_2O_3 (ITO) films have been fabricated. The ITO film has an excellent sheet resistance (24.5 Ω/sq), high transparency (93%), and a figure of merit of $2.1 \times 10^{-2}\ \Omega^{-1}$, which are comparable to the best.

5:00 PM EL19.07.22
Single-Acceptor Grain-Boundary Segregation for DC-Bias-Insensitive High Effective Permittivity and Ultralow Dissipation in Ceramic Capacitors Ji-Sang An and Sung-Yoon Chung; KAIST, Korea (the Republic of)

Class-II multilayer ceramic capacitors, a necessary component in many microelectronic and automobile devices, are based on polycrystalline $BaTiO_3$ with chemically heterogeneous core−shell-type grains with multiple dopants. Instead of using this conventional duplex grain structure, we utilize nonequilibrium atomic-scale grain-boundary segregation of an appropriate single acceptor additive in nanocrystalline $BaTiO_3$ to achieve unprecedented dielectric functionality. Composition analyses directly demonstrate that the distribution of each additive is strongly confined to grain boundaries within several unit-cell width together with no chemical heterogeneity in the bulk grains. The resulting dielectric loss is identified to be <1% up to 100 MHz and, in particular, the nominal high relative permittivity of a 10^3 order with exceptional temperature stability is preserved even under a large DC bias field. The present study emphasizes that the suppression of grain growth and the control of additive segregation at the atomic level are key approaches toward achieving better ceramic capacitors.

5:00 PM EL19.07.24
Tunneling Field-Effect Transistors Based on $MoS_2/MoTe_2$ and MoS_2/WSe_2 Heterostructures with Ion-Gel Dielectrics GuenHyung Oh[1], JinGi An[1], JaeCheol Shin[2], Jonghoo Park[3] and TaeWan Kim[1]; [1]Jeonbuk National University, Korea (the Republic of); [2]Dongguk University-Seoul, Korea (the Republic of); [3]Kyungpook National University, Korea (the Republic of)

Two-dimensional (2D) transition-metal dichalcogenide semiconductors have the potential to scale down for future electronics due to their atomically thin layer and sharp interface. The band-to-band tunneling (BTBT) carrier injection process in tunneling field-effect transistor (TFET) is a promising approach to solve the fundamental thermionic limit of subthreshold swing (SS) of 60 mV/dec at room temperature. In this study, we investigated the van der Waals 2D/2D vertical heterostructures grown by the metal-organic chemical vapor deposition (MOCVD) and CVD-grown. Molybdenum disulfide (MoS_2) was used n-channel materials, whereas molybdenum ditelluride ($MoTe_2$) and tungsten diselenide (WSe_2) were used p-channel materials. Those heterostructures exhibit the staggered gap type (type II), which was suitable for TFET applications. The electrical transport properties of the $MoS_2/MoTe_2$ (or WSe_2) heterostructures using an ion-gel top gate dielectric exhibit the minimum SS values as low as 9.1 (7.5) mV/dec. The BTBT process was confirmed by the negative differential transconductance, negative differential resistance behavior, and temperature *I-V* characteristics. This work demonstrates considerable promise for wafer-scale production of next-generation low-power consumption electronic devices.

5:00 PM EL19.07.25
Low-Temperature ALD Silicon Nitride for NAND Flash Memory with a Very High Frequency (60 MHz) Plasma Source Minjeong Rhee and Il-Kwon Oh; Ajou University, Korea (the Republic of)

Silicon nitride (SiN_x) thin film has been used as a charge trap layer in NAND flash memory devices. As the NAND flash memory devices are more nanoscale and more complex structures, SiN_x is mainly studied through atomic layer deposition (ALD) with a high step coverage, low deposition temperature, and thickness control as the atomic level.[1] Since thermal ALD requires a relatively high deposition temperature for SiN deposition, so that plasma-enhanced ALD (PE-ALD) has been suggested for a relatively low deposition temperature with high film quality. However, PE-ALD has issues of low step coverage and damage to the bottom layer due to additional plasma energy. In particular, damage to the SiN_x bottom layer can cause tunnel oxide deterioration and cause a reliability issue in NAND flash memory. [2] Therefore, research on a process with higher step coverage and less damage to the bottom substrate while maintaining the advantages of low deposition temp and high growth rate is required.
In this study, we suggest a SiN_x process with better film quality, higher step coverage, and less damage. We used bis-diethylamino silane ($H_2Si((N(C_2H_5)_2)_2)$) as a precursor and N_2 plasma in radio frequency (RF) or very high frequency (VHF, 60 MHz) as a reactant. As the first in comparing the characteristics of SiN_x in RF PE-ALD and VHF PE-ALD, the saturation curve according to precursor feeding time and the linearity curve of the thickness according to the increase in ALD cycle were investigated using an ellipsometer to investigate the suitability of the process. The chemical composition ratio and impurity content of the thin films were comparatively analyzed through X-ray photoelectron spectroscopy (XPS). In addition, to check the step coverage in each process, a cross-sectional transmission electron microscope (TEM) after focused ion beam (FIB) treatment was checked after depositing SiN_x on a substrate that has a 1:5 aspect ratio. The damage to the substrate was measured through the average lattice constant change rate of the lower substrate before and after SiN_x deposition, which was calculated through TEM measurement. Through the above analysis, we analyzed that VHF PE-ALD has better characteristics than RF PE-ALD in terms of thin film quality, damage, and step coverage, showing its applicability in NAND flash memory. To analyze the characteristics of the device, after fabricating a metal-oxide-nitride-oxide-semiconductor (MONOS) capacitor with a control gate/gate oxide/floating gate/tunnel oxide/Si structure, the C-V curve was measured through a probe station. Through the electrical property measurement, the effect of SiN_x deposited with VHF PE-ALD as a charging trap was analyzed. By adjusting the frequency of PE-ALD from RF to VHF, this study showed applicability in NAND flash memory, which requires high step coverage, low damage, and high capacity.

SESSION EL19.08: Low-Dimensional Materials I
Session Chairs: Mark Eriksson and Pei-Wen Li
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3020

8:30 AM EL19.08.01
Establishing Magneto-Elastic Coupling in a Spin-Crossover Molecular Network Grown on 2D Surfaces Shatabda Bhattacharya and Hirokazu Tada; Osaka University, Japan

Spin-crossover (SCO) complexes show bistability of spin states under various actuation parameters including temperature. This bistability along with hysteresis loop has potentiality of using them as binary units for information storage application. However, despite of cooperativity in SCO complexes, they remain non-magnetic. This is probably due to the reason that the microscopic origin of cooperativity has been primarily described by means of elastic interactions in pristine SCO. Apart from elastic coupling, long range magnetic interaction must be given equivalent importance. The spin-crossover phenomenon originates from the competition between the mean spin pairing energy (Δ), which favors the high-spin (HS) paramagnetic state and the ligand field parameter (10Dq), which favors the low-spin (LS) diamagnetic state. In addition to non-magnetic spin state transitions, the magnetic interaction can be alternatively introduced via substrate incorporation. In comparison to molecular crystals with isolated units, 3D molecular network are better candidates for extending the interaction through chemical bridges. Hybrid heterostructure based on SCO/2D surfaces remain a sensitive tool for detecting spin transitions. The fragility of SCO materials upon interfacing them on 2D surfaces is an unsolved issue. Hence, determining the ultimate scale limit with suitable 2D substrate at which cooperativity becomes effective is of major interest. Here, we showcase an easily processable, robust SCO/2D hybrid heterostructures that show long range magnetic ordering through exchange interactions. Fe-Triazole based SCO complex has been chosen for this types and chemically synthesized reduced graphene oxide (rGO) was used as the 2D substrate. Due to presence of large number of functional groups on the surface of rGO, it is a promising candidate for anchoring SCO molecular network epitaxially on rGO. Theoretically, it has been found that energy stabilization of SCO/rGO is better than Graphene/SCO. After formation of the heterostructure, interfacial charge transfer (CT) between SCO and rGO has been evidenced by means of various characterization techniques. The CT changes the high spin (HS) and low spin (LS) transition states of the molecular network which is of fundamental importance. With enough number of HS states and via superexchange interaction between the Fe-centers, a long-range magnetic ordering has been established during the spin state transition which favors like spin pairings (HS-HS or LS-LS). We have found that hysteresis width (ΔK) and transition temperatures ($T_{1/2}^{up}$, $T_{1/2}^{down}$) can also be controlled in a vast way by tuning the thickness of the SCO molecular network on rGO surface. Depending on layer number, ferromagnetic (cooperative) to antiferromagnetic (anti-cooperative) ordering has been evolved. This makes a magnetically ordered SCO/2D hybrid which could perform plethora of applications in nanomagnetics. Apart from magnetic characterization, the spin state dependence of electrical conductivity in SCO is also arrested through transport measurement due to the presence of highly delocalized π-surface electrons of 2D rGO. While pristine SCO remain insulating ($\sim 10^{-11}$ S) due to weak intermolecular interaction of van der waals nature, after attachment to highly conducting rGO surface, the conductance enhances in many folds ($\sim 10^{-5}$ S). While the overall transport is mediated via rGO surface, the epitaxial SCO network acts as scattering potential with the itinerant conduction electrons. Since the LS/HS states of SCO also depend on magnetic field in this case, the SCO/2D heterostructure shows magnetoresistance which is the main prototype for magnetoresistive- switching application. The conductance changing along with enhanced magnetic coupling could be utilized for switching application in spintronics using SCO/2D material.

8:45 AM EL19.08.02
High-Performance Junction-Free Field-Effect Transistor Based on Blue Phosphorene Shubham Tyagi, Paresh C. Rout and Udo Schwingenschlögl; King Abdullah University of Science and Technology, Saudi Arabia

Two-dimensional semiconductors have great potential in high-performance electronic devices. However, the common way of contacting them with metals to inject charge carriers results in contact resistance (leading to poor current delivering capability) and remains a bottleneck in the scaling of modern devices. We will discuss a junction-free field-effect transistor consisting of semiconducting monolayer blue phosphorene as channel material (with high carrier mobility) and metallic bilayer blue phosphorene as electrodes. The junction-free design minimizes contact resistance. Employing first-principles calculations along with the non-equilibrium Green's function method, we demonstrate an ultra-low contact resistance, a high I_{on}/I_{off} ratio of up to 2.6×10^4 and a remarkable transconductance of up to 811 μS/μm.

Acknowledgement: This research was supported by funding from King Abdullah University of Science and Technology (KAUST). For computer time, this research used the resources of the Supercomputing Laboratory at KAUST.

9:00 AM EL19.08.03
Graphene-Enabled Practical Molecular Electronics—Charge Transport in Junctions Between Molecules and 2D Materials Bhartendu Papnai[1,2] and Mario Hofmann[3]; [1]Academia Sinica, Taiwan; [2]National Tsing Hua University, Taiwan; [3]National Taiwan University, Taiwan

The idea of producing functional elements on atomic length scales has become a recent focus of research since the scaling of conventional electronics is reaching the molecular domain. The tailoring of individual molecules to impose electronic functionality has the promise of large-scale production of high-performance structures with novel properties. Devices can be created by using molecules in such a way that a new property emerges.
The concept to build a device within a molecular scale by exploring the properties of 2D materials is one of our primary goals. This work demonstrates the fabrication of the Vertical Molecular Field-Effect transistor in which the molecular layer of desired thickness is been used to form a junction. The thickness of the molecular film can be tuned by the use of Langmuir Blodgett techniques which we have used for making a homogeneous and uniform film of the molecule over graphene. The study of layer formation and deposition of tunable thickness (i.e. 1nm to several nm) molecular layers is achieved in this project. The Brewster Angle microscopy technique for imagining the Langmuir Blodgett film during its different stages has been used. The study of molecular junction formation was confirmed by electrochemical impedance spectroscopy. The characteristics of molecular field-effect transistors have been studied in this project and it has been observed that the current-voltage measurements of the devices show a decrease in current on further increase in voltage in a device. This is termed Negative Differential Resistance (NDR) and NDR peak are observed at 0.15V and 0.11V respectively with 5.2nA and 2.6nA are the Peak-to-Valley Current Ratio (PVCR) for the devices. Hundreds of molecular vertical FET devices have been measured and the device performance was assessed according to output and transfer characteristics. The formation of a junction between graphene-molecule and graphene-SiO2 was also observed. As NDR has been observed in devices of different channel lengths which shows that our devices have a significant NDR and this can be further used for various applications in logic gates and memory devices.
The discovery of graphene in 2004 gave birth to a new arena of 2D materials having exciting optical and electrical properties. Graphene having a honeycomb monolayer structure is interesting because of its excellent flexibility and mechanical strength. Graphene with excellent electronic properties that can be synthesized into large-area, flexible and conductive films suitable for electrodes. In molecular junctions, graphene film can be used as an interlayer electrode. which showed that the device has a high yield and long-term stability has been fabricated. In recent years the use of graphene as electrodes in molecular devices provides a high yield and stability because of their unique electronic structure and transport characteristics. We here

combine graphene's enabling properties with robust self-limiting deposition techniques to achieve the ultimate scaling of vertical graphene transistors to atomic dimensions.

9:15 AM EL19.08.04
Integration of Free-Standing Ultrathin High-κ Native Oxide for High-Performance Two-Dimensional Transistors Kongyang Yi and Zheng Liu; Nanyang Technological University, Singapore

As the current semiconductor technology based on silicon is facing increasing challenges below 5 nm nodes, the emerging two-dimensional (2D) transistors based on 2D semiconductors such as 2D transition-metal dichalcogenides (TMDCs) are attracting more and more attention. However, despite the variety of channel materials, the dielectric materials, which are equally important to the fabrication of high-performance 2D transistors, are still limited. So far, the majority of preparation methods of dielectric materials are realized through deposition, where the requirement of nucleation points is intrinsically contradictory to the high-quality dangling-bond-free surface of 2D semiconductors. Alternatively, native oxides of 2D semiconductors are being studied, but the performance is far below expectation compared with silicon dioxide (SiO_2) for Si, and the dielectric is restricted by the category of the parent semiconductors. Here, an ultrathin high-κ native oxide is integrated in 2D transistors as a free-standing dielectric material. Subthreshold swing down to 60 mV/dec at room temperature and on-off ratio over 10^8 is obtained in top-gated molybdenum disulfide (MoS_2) transistors. This work thus highlight the successful integration of a native oxide with desired dielectric properties in a non-native system.

9:30 AM *EL19.08.05
The Role of Native Defects in Ultra-Scaled h-BN Devices Mario Lanza; King Abdullah University of Science and Technology, Saudi Arabia

Two-dimensional (2D) layered hexagonal boron nitride (h-BN) might have multiple applications in electronics, such as anti-scattering substrate, passivation film, gate dielectric, and lateral thermal heat spreader (in-plane) or blocker (out-of-plane). However, when the h-BN is synthesized at the wafer scale with industry-compatible techniques, such as chemical vapour deposition (CVD), the presence of local defects impoverish its dielectric properties, as well as the figures-of-merit of the devices. In this talk I will discuss the role of native defects in CVD h-BN as observed via cross-sectional transmission electron microscopy (TEM) and conductive atomic force microscopy (CAFM). I will present data gathered in samples from the companies Graphene Supermarket and Grolltex and compare them with home-made CVD h-BN. We will also benchmark the data by comparing with additional measurements conducted in mechanically exfoliated h-BN from the National Institute for Materials Science (NIMS), which is the state-of-the-art in terms of crystallinity quality.

10:00 AM BREAK

10:30 AM *EL19.08.06
Bringing 2D-Materials from Lab to Fab - Maturing Processes to Enable Upscaling Inge Asselberghs; IMEC, Belgium

It turned into a never-ending success story, the discoveries with layered 2D-materials have led to a good understanding of the material properties and the identification of a broad range of potential application zones like sensors, photonics, spintronics and electronics [1, 2]. One of the most challenging approaches of having 2D-based circuits for high-performance logic is considered [3, 4]. While the list of material options keeps increasing, the request to demonstrate manufacturability is ramping up fast. The performance gap between synthetic materials and natural crystals is decreasing rapidly. Recently, a paper by Liu et al. [5] shows the mobility improvement up to 120 cm2/Vs for bilayer MoS2. This emphasis the urge to enable pathfinding experiments to close the gaps associated to identified process challenges [3, 6] and conduct pathfinding integration exercises in a 300 mm fab environment [7].

Therefore, a simplified single transistor test vehicle in a 300mm fab is required to allow the exploration of material selection and process condition identification at single device level. Here, wafer scale assessment provides insights in device-to-device, die-to-die and wafer-to-wafer variability. Combined with inline metrology, a unique insight can be given on the individual process steps and their impact on the channel properties. For example, acoustic wafer maps provide a unique way to reveal adhesion related effects. Once this exploration is done, a more elaborated integration route can be conducted.

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11:00 AM EL19.08.07
Damage-Free Deposition of Aluminum-Based High-κ Dielectrics on Graphene by PEALD Ardeshir Esteki[1], Alwin Daus[1], Sarah Riazimehr[2], Harm Knoops[2,3], Federico Fabrizi[4,1], Maryam Mohammadi[4], Martin Otto[4], Gordon Rinke[4] and Max C. Lemme[1,4]; [1]RWTH Aachen, Germany; [2]Oxford Instruments Plasma Technology UK, United Kingdom; [3]Technische Universiteit Eindhoven, Netherlands; [4]AMO GmbH, Germany

Graphene has great potential for heterogeneous integration with modern electronics [1]. One of the remaining challenges is the damage-free deposition of dielectrics on graphene and control of its doping level [2]. Plasma-enhanced atomic layer deposition (PEALD) is a production-ready technique for depositing high-κ dielectrics, but it often damages graphene due to highly reactive and energetic species formed during plasma activation. This problem has been circumvented by using thin interlayers such as hexagonal boron nitride to protect graphene [3], with the drawback of complicating fabrication by adding a second 2D material. In this work, we investigate a direct PEALD process using an Oxford Instruments Atomfab™ PEALD system. Our process provides a high-κ dielectric directly deposited onto graphene without detectable damage. Furthermore, we can systematically tune the doping level of graphene by varying the dielectric thickness.
Pd bottom contacts were deposited onto Si substrates with 90 nm thermally grown SiO_2 and structured by lift-off. Graphene was dry-transferred onto the samples and patterned by reactive ion etching. Aluminum-based dielectric layers with thicknesses of $t_{de} \approx 7$, 12 and 17 nm were deposited by PEALD at 200 °C in a low-power nitrogen plasma process employing trimethylaluminium as the precursor. Ti/Pd top-gates were fabricated by electron-beam evaporation and lift-off.
The effect of dielectric deposition onto graphene was investigated by Raman spectroscopy. A statistical analysis of the D to G peak intensity ratios and the full-width-half-maxima of the 2D peaks indicate no measurable process damage, in contrast to the standard Al_2O_3 plasma deposition process performed as a control experiment.

A “doping” effect of the graphene channel is observed in back-gate voltage-dependent drain current measurements (I_D vs. V_{BG}) in a four-point (4p) configuration. Measurements in air performed for ten devices show strong p-doping of graphene before deposition, with Dirac voltages of V_D ~30 V. After dielectric deposition, V_D shifts in a negative direction by ~25, ~35 and ~44 V for t_{de} of 7, 12 and 17 nm, respectively. The maximum electron and hole mobilities were extracted using the direct transconductance method [4], which excludes contact resistance effects due to the 4p configuration. The dielectric capping layer increases the maximum hole mobility from ~1500 to ~2300 cm^{2}V^{-1}s^{-1} and the maximum electron mobility from ~150 to ~1600 cm^{2}V^{-1}s^{-1}. After depositing top-gates, we performed double-gate current-voltage measurements and extracted a dielectric constant of ~35 for the PEALD dielectric [5]. This high value was further verified through separately fabricated metal-insulator-metal structures suitable for capacitance-voltage measurements. The top-gate 4p measurements (I_D-V_{TG}) yielded V_D of ~0.6 V and hysteresis below ~1% of the gate-source voltage sweep range. We further investigated the origin of the high dielectric constant in our PEALD dielectrics through material and structural analysis such as transmission electron microscopy, atomic force microscopy, energy dispersive x-ray spectroscopy and x-ray diffraction.

In summary, we demonstrate a scalable, low-damage PEALD process for direct deposition of high-κ dielectric films on graphene which can be used to tune V_D. This work opens new pathways for heterogeneous integration of devices with two-dimensional materials preserving material quality and controlling their doping.

Acknowledgments: The European Union's Horizon 2020 research and innovation program under grant agreements 2D-EPL (952792) and Graphene Flagship Core 3 (881603) and the German BMBF project GIMMIK (03XP0210).

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11:15 AM EL19.08.08

Atomic Layer Deposition of Conformal Wafer-scale WS$_2$ Films: a Promising Liner and Barrier Alternative for Back-end-of-Line Applications

Muhammed Juvaid Mangattuchali[1], Tan Hao[1], Hippolyte P. Astier[1], Soumyadeep Sinha[1], Chandan Das[2], John Sudijono[2] and Silvija Gradečak[1]; [1]NUS Singapore, Singapore; [2]Applied Materials, Inc., Singapore

The continued scaling of silicon integrated circuits makes it crucial to find substitute materials for both the front-end-of-line (FEOL, transistors) and back-end-of-line (BEOL, interconnects) applications. Currently, approximately 4-nm thickness is required for conventional liners and barriers to be effective. In forthcoming sub-5 nm technology nodes, these would occupy a substantial share of the interconnect cross-section and consequently increase the resistivity of Cu interconnects. Conversely, downscaling the thickness of the liner and barrier layers would result in poor Cu blocking efficiency. Two-dimensional (2D) transition metal dichalcogenides (TMDs) have been recently identified as promising candidates for Cu diffusion barrier and liner applications at the sub-nm scale. However, most 2D TMDs are grown using chemical vapor deposition processes at high temperatures (>800°C), making them incompatible with BEOL applications. Plasma-assisted growth can reduce growth temperatures, but poor conformality and plasma-induced defects remain challenges. Here, we report a complete thermal (no plasma assistance) atomic layer deposition (ALD) process for the deposition of crystalline WS$_2$ growth at <450 °C, suitable for BEOL integration. The process yields layer-controlled conformal (>95%) growth of WS$_2$ on an 8-inch wafer scale. Raman spectroscopy and transmission electron microscopy measurements were used to elucidate the quality and number of layers in WS$_2$, whereas x-ray photoelectron spectroscopy and energy dispersive x-ray spectroscopy were used to assess the stoichiometry and compositional uniformity, respectively. We further show that as-grown single and multilayer WS$_2$ grown *via* ALD are promising candidates as a liner layer: Cu interconnects with thickness of 10—20 nm show 50% reduction in resistivity when deposited on WS$_2$ compared to the reference SiO$_2$/Si substrate. In addition, thermal stress measurements of Cu/WS$_2$ layers show that WS$_2$ is a potential diffusion barrier alternative as it effectively blocks the diffusion of Cu into the surrounding dielectric. Our results demonstrate that 2D TMDs grown *via* thermal ALD are promising building blocks for BEOL applications beyond the 5 nm nodes.

11:30 AM *EL19.08.09

Large-Area Synthesis of 2D Transition Metal Dichalcogenides Using Plasma-Enhanced Atomic Layer Deposition Ageeth A. Bol; University of Michigan, United States

2D materials have been the focus of intense research in the last decade due to their unique physical properties. This presentation will highlight our recent progress on the large-area synthesis of two-dimensional transition metal chalcogenides for nanoelectronics using plasma-enhanced atomic layer deposition (PEALD). In particular, we demonstrate wafer-scale deposition of polycrystalline MoS2 thin films at very low temperatures down to 100 °C using PEALD. ALD is a scalable, semiconductor industry compatible gas-phase method producing uniform, high-quality thin films with accurately controlled thickness. Our PEALD process is based on self-limiting, alternating surface reactions of a metalorganic molybdenum precursor Mo(NtBu)2(NMe2)2 and mixed H2S/H2/Ar plasma. We have identified the critical role of hydrogen during the plasma step in controlling the composition and properties of molybdenum sulfide films. By increasing the H2/H2S ratio, we are able to deposit polycrystalline MoS2 films at temperatures as low as 100 °C. To the best of our knowledge, this represents the lowest temperature for crystalline MoS2 films prepared by any chemical gas-phase method.[1]

ALD-grown 2D films typically exhibit a high density of out-of-plane 3D structures in addition to 2D horizontal layers. While the out-of-plane 3D structures are ideal for catalysis applications, the presence of such 3D structures can hinder charge transport, which hampers device applications. In this presentation I will show how we used mechanistic insight obtained by HRTEM to tune the shape and density of the 3D structures during plasma-enhanced ALD. The obtained morphology control was further confirmed by electrical measurements.[2]

Earlier [3] we have shown that ALD is an excellent technique to make MoxW1-xS2 alloys with precise control over the alloy composition. Here, I will focus on how (plasma-enhanced) atomic layer deposition can aid in synthesizing p-doped 2DTMCs with precise control over the doping concentration, which is an asset for 2D TMD based device applications.

[1] M. Mattinen *et al., Chem. Mater*. (2022), **34**, 5104
[2] S. Balasubramanyam *et al. ACS Appl. Mater. Interfaces* (2020), **12**, 3873
[3] J. J. P. M. Schulpen *et al. 2D Mater.* (2022), **9,** 025016

SESSION EL19.09: 3D Integration
Session Chairs: Supratik Guha, Francesca Iacopi and Ehrenfried Zschech
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3020

1:45 PM EL19.09.01
High-performance and CMOS-BEOL compatible AlScN/MoS$_2$ FE-FET array KwanHo Kim, Jeffrey Zheng, Roy H. Olsson and Deep M. Jariwala; University of Pennsylvania, United States

3D Monolithic integration of memory/storage devices with front-end-of-line (FEOL) logic transistors has been a critical issue in computer hardware. This integration is important for reducing computational power consumption simultanously with improved energy efficiency in big-data and Internet of things (IoT) applications such as artificial intelligence. Despite decades of effort, it is still highly challengeing to demonstrate reliable, compact, back-end-of-line (BEOL)-compatible, energy-efficient, and scalable memory/storage devices. Ferroelectric Field Effect Transistors (FE-FETs) are one of the most promising candidates that can meet the strict requirements. Recent advances in CMOS-compatible ferroelectric materials such as Zr-doped HfO$_2$ (HZO) have attracted more attention to FE-FET as a promising candidate for small energy-efficient nonvolatile memory. Over a decade, while HZO-based FE-FETs have made great advances, highly notable ferroelectric properties have recently been discovered in aluminum scandium nitride (AlScN) in 2019. AlScN shows a high remnant polarization (P_r) of > 110 µC/cm2, which is two to three times higher than that of HZO, and has a BEOL-compatible deposition temperature of 350 °C. These merits make AlScN a very promising candidate for BEOL-compatible FE-FETs. However, despite these remarkable ferroelectric properties, scalable FE-FETs using thin AlScN ferroelectric have not yet been demonstrated. Here, scalable BEOL-compatible FE-FETs based on CVD grown two-dimensional (2D) MoS$_2$ channel and 20, 45 and 100 nm ferroelectric AlScN are presented. The large array of FE-FETs statistically showed very large memory windows of >7.8 V, ON/OFF ratios of $>10^7$, and ON current density >250 µA/um, all at highly scaled ~80 nm channel lengths. In addition, the FE-FET shows a stable retention measured up to 10^5 seconds and 10 years by extension, and endurance up to 2×10^4 cycles. Finally, due to the large memory window, the FE-FETs shows multi-bit (2, 4 and 7-bit) pulse programmable threshold and conductance states, opening a path towards scalable 3D hetero-integration of 2D channel/AlScN memory device with Si CMOS logic.

2:00 PM *EL19.09.02
3D MOSAIC of N3XT Chips—Domain-Specific Technology for Future Systems H.S. Philip Wong; Stanford University, United States

Future electronic systems will continue to rely on, and increasingly benefit from, the advances in semiconductor technology as they have had for more than five decades.

Three dimensional integration is one of the major technology directions for integrated circuits. A key technology direction is CMOS + X, where X can be memory, photonics, spintronics, power electronics, nanomechanics, sensors and actuators, RF/mm-wave, and even quantum computing. Nanosystems of 3D integrated “X” technology (N3XT) is a key concept at the chip level. We must also go beyond a single chip from a wafer and focus on integrating chips into systems using MOSAIC (MOnolithic Stacked Assembled IC).

MOSAIC systems may enable a wide spectrum of compute throughput, energy efficiency, and memory capacity to be simultaneously realized within the same hardware to support emerging workloads for edge machine intelligence. Accelerators addressing a variety of workloads can be reconfigured for application-level flexibility. Intelligently partitioning and co-designing the logic, memory, and interconnect with new design space made possible by CMOS + X can be key to such new capability.

I will give an overview of the new materials, device technologies, and design concepts that may need to be developed to realize this vision.

Acknowledgments: Prof. Haitong Li (Purdue University), Prof. Subhasish Mitra (Stanford University), Prof. Priyanka Raina (Stanford University)

2:30 PM BREAK

3:30 PM *EL19.09.03
Challenge Of 3D Stacking Technology For Advanced System Integration Masaaki Niwa[1,2]; [1]The University of Tokyo, Japan; [2]Research Association for Advanced Systems (RaaS), Japan

Cloud and MEC servers in post-5G information communication systems are required to realize advanced and diverse computational processing. On the other hand, it is becoming more difficult year by year to improve the performance of semiconductor devices due to the demise of Moore's Law, which has long supported technological innovation as a development index for semiconductor devices. To achieve even higher performance, miniaturization technology must be combined with cutting-edge packaging technology that integrates peripheral devices such as chiplets (memory, sensors, AI chips, RF, etc.) into a single package.
To materialize this, 3D integrated semiconductor devices, which are further miniaturized and consume less power, are expected to become a mainstream that will meet the requirements of many applications in the future. And it is necessary not only to develop the package designs that meet the demands of applications, but also to develop the consistent semiconductor manufacturing technology from materials to processes and devices to a level that can be mass-produced, while further advancing system and technology co-optimization (STCO).
Along with the changes and new creations in semiconductor manufacturing process due to the evolution of advanced packaging, the distinction between front- and back-end processes tends to disappear. System integration using 3D integrated packages and chiplets will be a mainstream in the future. Under such circumstances, the 3D integrated package will become a choke point for future semiconductor supply.
This time, the technological trends of advanced packaging as well as its manufacturing (including equipment) and material technology will be reviewed, focusing on advanced 3D hybrid direct bonding which is a potential candidate for ultra-fine devices.
In order to bond two wafers, the following two types of bonding must be achieved with high alignment accuracy.
1. Low resistance connection between Cu in TSV (Through Si Via) and Cu pad
2. Strong bond of each Si area other than Cu area.
For the hybrid bonding, it is necessary to realize these bonds at the same time.
A hybrid bonding method currently in practical use is a fusion bond that forms hydroxyl groups on the Si surface. However, this has an unfavorable problem of requiring high temperatures for the Cu atoms to break through the oxide layer on the Cu surface to inter-diffuse during the Cu–Cu bonding process in addition to achieve hydrophilic bonding in the Si region. One of the important issues in directly bonded hybrid bonding is the state control of Cu-Cu and Si-Si interfaces during bonding. And the surface activation [1] before the bonding is essential to achieve this.
At Research Association for Advanced Systems (RaaS), as a national project, wafer-on-wafer (WoW) and chip-on-wafer (CoW) technologies by means of low-temperature surface activation [2] are under development with Japanese companies and national research institute.
In this presentation, technologies for the hybrid bonded 3D system integration by WoW, CoW will be discussed including the studies under the national project/NEDO* performed at RaaS.
(*: New Energy and Industrial Technology Development Organization)

A part of this presentation is based on results obtained from a project JPNP20017, subsidized by the New Energy and Industrial Technology Development

Organization (NEDO).

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4:00 PM *EL19.09.04
Advanced Logic Scaling Using Monolithic 3D Integration Marko Radosavljevic; Intel Corporation, United States

Transistor scaling has been one of the key engines driving semiconductor industry for many decades now. Beyond traditional (Dennard) scaling of physical dimensions and supply voltages, innovations such as new materials and new architectures are being constantly and regularly deployed to enabled introduction of new technology nodes.
Main new architectural changes revolve around moving from planar device geometries to more 3D – first finFETs and most recently gate-all-around (GAA). These changes provide significant opportunities for scaling both due to (1) enabling gate pitch scaling because of improved short channel effects and (2) higher performance because device width is decoupled from planar area. To enable these architectures, technology teams delivered many materials and process innovations due to increased physical aspect ratios as well as need for very conformal depositions.
Extending further into this third dimension, researchers in academia, consortia and industry are very interested in exploring device stacking as means of increasing both functionality and logic scaling. While this appears as a natural next step, it also provides an open wide space ripe for new materials, integration approaches and applications. As such much of the early work has been focused on both (1) design technology co-optimization (DTCO) to identify needed ingredients to enable scaling and (2) demonstrating those ingredients into physical implementations in Si.
In this presentation, I will provide general overview of monolithic 3D integration options, will focusing on material centric aspects of this approach by highlighting experimental status and challenges.

SESSION EL19.10: Poster Session II

Session Chairs: Paul Berger and Pei-Wen Li
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL19.10.01
How Changes in the Crystal Temperature and Doping Concentration Impact Upon the Steady-State and Transient Electron Transport Within Gallium-Aluminum-Nitride/Gallium Nitride Heterojunctions Yana Wang[1], Michael Shur[2], Walid A. Hadi[3] and Stephen K. O'Leary[1]; [1]University of British Columbia, Canada; [2]Rensselaer Polytechnic Institute, United States; [3]Florida State University, United States

Noting that at the interface of gallium-aluminum-nitride with gallium nitride, a two-dimensional electron gas will form, we examine how the electron transport characteristics within such a gas vary in response to changes in the crystal temperature and the doping concentration. For the purposes of this analysis, Monte Carlo electron transport simulations are pursued. A critical comparison with results corresponding to bulk gallium nitride is considered. The device implications of these results then will be explored.

5:00 PM EL19.10.02
Testing the Compatibility of Photothermal Lithography with Commercial Lithography Equipment Meghna Jha, Joaquin Mogollon Santiana, Aliyah Jacob, Kathleen Light, Michael Lau, Megan Hong and Adam J. Moule; University of California, Davis, United States

Semiconducting Polymers (SPs) have received widespread attention due to their promising qualities like superior absorbance/emission, easy chemical tunablity, low-temperature solution processing, lightweight and flexible substrates, and low environmental toxicity. A significant obstacle for the industrial development of SPs is the lack of a patterning technology that is inexpensive, rapid, and viable and capable of producing sub-micron features. Photomask lithography is impossible because the SPs cannot withstand the processing steps. The Moule group recently developed a new photopatterning concept that enables micropatterning of SPs. We present a novel solution based optical patterning method that is compatible with any non-cross-linked SP, termed Photothermal Lithography. Selective polymer domains are removed as a photo-induced temperature gradient enables selective dissolution in a combination of solvents. In this study we test the compatibility of this technique with the Alvéole PRIMO. Alvéole PRIMO is a commercially available cleanroom equipment that enables Micropatterning, hydrogel polymerization and microfabrication, all in a single device. We were able to use this equipment to enable and test out Photothermal patterning technique on P3HT at various solvent concentrations and laser fluences. In this study we analyze the effect of depth of field, solvent concentrations, and laser fluences that effect the pattern size and resolution. This proves that Photothermal Patterning is compatible with available commercial Lithography equipment and this can be the way forward to fabricate patterned electronic devices with SPs.

5:00 PM EL19.10.03
Single Crystalline Ge Thin Film Grown on C-Plane Sapphire by Molecular Beam Epitaxy Emmanuel Wangila, Calbi Gunder, Subhashis Das, Nirosh Eldose, Hryhorii Stanchu, Fernando Oliveira, Chen Li, Shui-Quing Yu and Gregory Salamo; University of Arkansas, Fayettiville, United States

Germanium (Ge) film was grown on c-plane sapphire with and without a 10 nm AlAs buffer layer using molecular beam epitaxy. The samples were characterized using high-resolution X-ray diffraction (HRXRD) and atomic force microscopy (AFM). The samples grown directly on sapphire exhibits 2 germanium orientations, the (111) and (220) while samples grown using the AlAs buffer layer had only (111) orientation at 27.5 degrees. Samples that were grown with the AlAs buffer were investigated further and at different temperatures were observed to relax the compressive strain as the temperature was increased. From the Phi scan, the peaks with high intensity appear after every 60 degrees while lower intensity peaks can be seen at 30 degrees between the high intensity peaks. We also investigate the impact of different the thickness (50nm, 100nm,150nm and 200 nm) of the Ge layer. In this case the ratio of the high to low intensity Phi scan peaks was less with 100 nm thick Ge sample. This sample also had the lowest XRD rocking curve linewidth of 633 arcsec. This sample is prepared for epitaxy growth of SiGe and GeSn and we will discuss initial efforts at these growths.

5:00 PM EL19.10.04
Cubic Boron Nitride's Electron Transport John Chilleri[1], Poppy Siddiqua[2], Michael Shur[3] and Stephen K. O'Leary[2]; [1]New Mexico Institute of Mining and Technology, United States; [2]University of British Columbia, Canada; [3]Rensselaer Polytechnic Institute, United States

Through the use of a semi-classical three-valley Monte Carlo electron transport simulation analysis, the character of the electron transport that occurs within the cubic phase of boron nitride is examined. For the purposes of this particular analysis, both steady-state and transient electron transport processes are examined. For the steady-state analysis, the dependence of the electron drift velocity on the applied electric field strength is examined. For the transient electron analysis, however, we study how an ensemble of electrons, initially in thermal equilibrium, i.e., zero-field, responds to the sudden application of a constant and uniform applied electric field. A critical comparison, of these electron transport results with those corresponding to a variety of other semiconductor materials, is offered. The device implications of these results are explored.

5:00 PM EL19.10.05
Ultrawide Bandgap BN based Vertical Power Diodes via TCAD Simulation Ziyi He[1], Kai Fu[2], Mingfei Xu[3], Jingan Zhou[3], Tao Li[3], Yuji Zhao[3] and Houqiang Fu[1]; [1]Arizona State University, United States; [2]The University of Utah, United States; [3]Rice University, United States

Boron nitride (BN) material is an emerging ultrawide bandgap (UWBG) semiconductor with great promise for applications in power electronics, ultraviolet (UV) photonics, and quantum photonics. The current most mature phase of BN, hexagonal BN, has a large bandgap of 6.0 eV and has attracted a lot of interest owing to its unique physical properties. Due to its high thermal conductivity of 390 W/(K●m), high breakdown electric field of ~12 MV/cm, and high carrier mobilities, h-BN is also an attractive candidate for high-performance high power high voltage power electronic devices. However, it is still very challenging to produce high quality thick h-BN layers due to the technical difficulties in materials epitaxy and doping, which has hindered the development of BN devices. Furthermore, vertical architecture is usually adopted in high voltage power devices due to high current and voltage handling capability, immunity to surface issues and degradation and excellent heat dissipation. However, there are very few reports on BN vertical power devices and the performance limit of these devices is still not clear.
In this work, we use technology computer-aided design (TCAD) simulation to theoretically investigate the electrical performance of ultrawide bandgap BN-based vertical power diodes. Three configurations of h-BN power diodes were investigated, including vertical h-BN Schottky barrier diode (SBD), vertical h-BN PN diode, and vertical h-BN/AlN PN diode. The electrical properties of the three diodes were comprehensively investigated, including the band diagrams, forward and reverse characteristics for different doping concentrations and layer thicknesses. The h-BN material properties were defined in Silvaco Atlas, including bandgap, effective masses of electron and hole, permittivity, impact ionization coefficient, electron affinity, mobilities, carrier lifetimes, donor and acceptor activation energies from the previous reports of h-BN. All the substrates' doping concentrations were set to be 5×10^{18} cm^{-3} as ohmic contact layers for P-type and N-type. The h-BN power diodes showed excellent performance, especially for breakdown behaviors. The h-BN SBDs with a 5 µm drift layer showed a turn-on voltage of 0.5 V for Pt Schottky contact and breakdown voltages over 450 V. The h-BN PN diode with a 2.5 µm drift layer showed a turn-on voltage of 6.2 V and a breakdown voltage over 3 kV, the critical electric field is calculated to be 13.6 MV/cm. The h-BN/AlN heterojunction PN diode with a 2.5 µm AlN drift layer showed a turn-on voltage of 5.8 V and breakdown voltages over 2 kV. This work provides a theoretical understanding on the device principles of vertical BN power diodes, which can serve as a useful reference for the future development of efficient and robust BN power electronics.

5:00 PM EL19.10.07
Design and Fabrication of AlGaN/GaN Multiple p-Channel Schottky Barrier Diodes Dawei Wang, Dinusha Herath Mudiyanselage and Houqiang Fu; Arizona State University, United States

Wide bandgap GaN holds great promises for high-efficiency power conversion systems. To realize GaN power integrated circuits (ICs), peripheral logic circuits based on GaN are necessary, such as controllers, drivers, protection circuits. By using the AlGaN/GaN high electron mobility transistors (HEMTs) platform, all these components can be integrated on a single chip, dramatically reducing parasitic effects, such as gate ringing and false turn-on of power transistors. Currently, most GaN logic circuits still rely on only n-channel devices. This is because it is challenging to realize high-performance GaN p-channel devices due to much lower hole mobilities and sheet carrier density. Recently, multi-channel heterostructure is proposed to address the tradeoff between carrier mobility and density. But there are still few reports on GaN multi-channel p-type devices partly due to the difficulty in buried p-GaN activation, unknown doping concentration and thickness of the inserted p-GaN layers, and the acceptor-holes separation process.

In this work, we perform the design, modeling and fabrication of GaN-based vertically stacked 2DHG (two-dimensional hole gas) multiple p-channel Schottky barrier diodes (SBDs). The device epilayers were grown by metal-organic chemical vapor deposition (MOCVD) on a sapphire substrate, consisting of a thick GaN buffer layer, a 300 nm UID-GaN layer, and multiple layers for p-channels that are composed of a 40 nm p^+-GaN layer, a 20 nm UID-GaN layer, and a 15 nm $Al_{0.2}Ga_{0.8}N$ layer. In order to effectively activate the buried p-GaN layers, trenches with different geometric patterns between the anode and cathode were etched by 400 nm of depth. The devices were then annealed at 800 °C for 1 hour to break the Mg-H bond and allowed the [H] to diffuse to the ambient through the etched sidewall. Moreover, these trenches are also geometrically designed as edge terminations that can eliminate high electric field crowding at reverse bias, which is necessary due to the vulnerability of the etched trenches. Finally, the two electrodes and passivation layer were deposited on top of the devices. The distance between the anode and the cathode is from 15 um to 25 um. The device's electrical properties will be measured. For the simulation, the impacts of doping concentration and thickness of p-GaN layers and the thickness of UID-GaN layers of the multi-channel heterostructure will be comprehensively investigated. And the ionization energy of [Mg] in GaN was set to be 300 mV. 3-D simulation will be also introduced to design the structure of the trenches. It is shown that the ON-current densities at an anode voltage of -3.5 V for the SBDs with 1, 3, and 5 p-channels were extracted as 0.12, 0.26, and 0.365 mA/mm, respectively. With the doping concentration of acceptor increasing from 1×10^{19} to 3×10^{19} and 6×10^{19} cm^{-3} in each p-GaN layer, the ON-current has a slight increase from 0.35 to 0.365 and 0.38 mA/mm at an anode voltage of -3.5 V, indicating that the doping concentration of p-GaN is not critical dominant in the sheet carrier density of 2DHG channels. With the thickness of each UID-GaN between p-GaN and AlGaN increasing from 2 to 5, 10, and 20 nm, the ON-current is also increased from 0.24 to 0.265, 0.3, and 0.365 mA/mm. These results can provide critical references for the future development of GaN multiple p-channel devices such as multiple p-channel diodes and FETs for integrated power and logic circuits.

5:00 PM EL19.10.08
Growth of Germanium on GaAs (001) Substrates via Molecular Beam Epitaxy (MBE) Calbi Gunder, Emmanuel Wangila, Hryhorii Stanchu, Solomon Ojo, Sudip Acharya, Mohammad Z. Alavijeh, Shui-Quing Yu and Gregory Salamo; University of Arkansas, United States

In this report the growth of Germanium (Ge) has been investigated on GaAs (001) substrates via molecular beam epitaxy (MBE). Ge was grown both on GaAs and AlAs buffer layers to compare the difference in film quality, surface morphology and optical characteristics via photoluminescence (PL). From this investigation we were able to achieve higher-quality Ge layers when grown on a 30 nm AlAs buffer. In addition to this we have observed atomic steps of Ge when the growth temperature is between 500-600°C. Developing a high-quality Ge layer on III-V opens the possibility of it being used as an additional surface to investigate the growth of high tin content GeSn and or SiGeSn systems which are of significant interest in the study of microwave photonic applications.

5:00 PM EL19.10.10
Memory Characteristic of Organic/Inorganic Hybrid Synaptic Transistor with Silk Fibroin Gate Insulator Hyunjoo Hwang, Wonwoo Kho and

Seung Eon Ahn; Tech University of Korea, Korea (the Republic of)

According to the development of the 4th industry such as Artificial Intelligence (AI) and Internet of Things (IoT), needs to process large amounts of data is exploded. The conventional Von Neumann computing system is facing challenges of a bottleneck between data processing and memory unit. To overcome this issue, a neuromorphic computing system inspired by the human brain using parallel processing has appeared. Therefore, neuromorphic devices have been introduced based on various materials. Also, flexible and biocompatible organic synapse devices is studied a lot for wearable artificial intelligence systems.
In this study, we introduce organic/inorganic hybrid synaptic transistor with Silk fibroin from *Bombyx mori* cocoon as gate insulator. Silk fibroin is an electronic biomaterial that has light transmittance, good bio-compatibility and high mechanical flexibility. The dielectric constant (k) of silk fibroin is around 6, which is higher than SiO_2's. The potentiation and depression characteristics of hybrid synaptic transistor were investigated based on various pulse scheme. Artificial neural network (ANN) simulation with experimental results of silk fibroin synaptic device shows high recognition accuracy (>95%) for handwritten digit database in MNIST. It will be discussed working mechanism of synaptic transistor with silk fibroin and the possibility of the application of silk fibroin for synaptic devices.

5:00 PM EL19.10.11
ALD-prepared Metal Nitrides with Tunable (Super)conductivity by Ion Energy Control Erwin Kessels[1], Silke Peeters[1], Marc Merkx[1], Mariadriana Creatore[1], Adrie Mackus[1] and Harm Knoops[1,2]; [1]Eindhoven Univ of Technology, Netherlands; [2]Oxford Instruments Plasma Technology, United Kingdom

Metal nitrides find applications in numerous devices ranging from state-of-the-art field-effect transistors in logic to superconducting qubits in emerging quantum circuits. In many cases these metal nitrides need to be closed films with thicknesses < 10 nm which makes atomic layer deposition (ALD) often the method of choice. There are also increasingly strict demands on the (super)conductivity of these films, which makes it necessary to explore novel approaches to control their properties. In addition, there is growing interest to prepare the films with a selectivity towards specific materials and surface orientations.

In this contribution we will report on the preparation of conductive metal nitrides using plasma-enhanced ALD with precise ion energy control through rf substrate biasing. From results on TiN_x, HfN_x and TaC_xN_y, it is demonstrated that the conductivity can be accurately tuned by controlling the energy of the ions. The highest conductivities, approaching the values of the bulk materials, can be reached by increasing the ion energy to ~100-150 eV whereas higher energies lead to deterioration of the film properties though ion damage. A similar maximum in the critical temperature T_c is observed when evaluating the superconductivity. The conductivity results are correlated with compositional and structural properties of the films demonstrating the important role of energetic ions in reducing the O incorporation in the films and enlarging the polycrystalline grain sizes. Given the directional nature of the ions, the conformality of the films on 3D structured surface is also addressed. Moreover area-selectivity on prepatterned surfaces with different materials is demonstrated when employing ALD cycles with small molecule inhibitor dosing. These and other features enabled by ion energy control during ALD will allow for an extended set of applications of metal nitrides in next generation electronic devices.

5:00 PM EL19.10.12
Universal Ligands for Dispersion of Two-Dimensional MXene in Organic Solvents Tae Yun Ko[1], Daesin Kim[1], Arun Nissimagoudar[1], Seung-Cheol Lee[1], Xiaobo Lin[2], Peter Cummings[2], Yury Gogotsi[3], Insik In[4], Chong Min Koo[5] and Tufail Hassan[5]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Vanderbilt University, United States; [3]Drexel University, United States; [4]Korea National University of Transportation, Korea (the Republic of); [5]Sungkyunkwan University, Korea (the Republic of)

Ligands can control the surface chemistry, physicochemical properties, processing, and applications of nanomaterials. MXenes are the fastest growing family of two-dimensional (2D) nanomaterials showing promise for energy, electronic, and environmental applications. However, complex oxidation states, surface terminal groups, and interaction with the environment have hindered the development of organic ligands suitable for MXenes. Here, we demonstrate a simple, fast, scalable, and universally applicable ligand chemistry for MXenes using alkylated 3,4-dihydroxy-L-phenylalanine (ADOPA). Owing to the strong hydrogen bonding and π electron interactions between the catechol head and surface terminal groups of MXenes and the presence of hydrophobic fluorinated alkyl tail compatible with organic solvents, the ADOPA ligands functionalize MXene surfaces under mild reaction conditions without sacrificing their properties. Stable colloidal solutions and highly concentrated liquid crystals of various MXenes, including Ti_2CT_x, Nb_2CT_x, V_2CT_x, Mo_2CT_x, $Ti_3C_2T_x$, Ti_3CNT_x, $Mo_2TiC_2T_x$, $Mo_2Ti_2C_3T_x$, and $Ti_4N_3T_x$, have been produced in various organic solvents. Such products offer excellent electrical conductivity, improved oxidation stability, and excellent processability, enabling applications in flexible electrodes and electromagnetic interference shielding.

5:00 PM EL19.10.13
Magnetic Edge Doping of Chalcogenide-based Topological Insulators via Solvothermal Methods for Intrinsic Time Reversal Symmetry Breaking Gabriel Marcus, David Carroll and Timothy W. Carlson; Wake Forest University, United States

Topological insulators (TIs) represent an intriguing class of materials that possess time symmetry- protected spin currents at their edge. Application of a magnetic field to such systems causes symmetry breaking and establishes a persistent charge current that circulates around the TI perimeter. Although external magnetic fields are typically discussed in the context of TI time reversal symmetry breaking, doping with magnetic materials might generate intrinsic fields that yield symmetry collapse while simultaneously allowing for donation of carriers that strengthen the charge current. Here, we present our work undertaken to produce chalcogenide-based TIs and subsequently achieve edge modulation doping with magnetic metals like iron or nickel. A versatile and straightforward solvothermal wet chemistry approach was used to synthesize high yields of bismuth telluride (Bi_2Te_3) platelets which have the potential for nanoparticle growth at reactive edge sites. Different concentrations of iron and nickel dopants were added to solutions of Bi_2Te_3 and the resultant materials were characterized to assess the extent of magnetic edge doping. A variety of techniques including electron microscopy (TEM, SEM, SAED), spectroscopy (XPS, EDS, XRD), Hall Effect measurements, and magnetic force microscopy were used to visualize nanoparticle formation, quantitatively assess material composition, confirm host material doping, and determine magnetic response. Preliminary results indicate that edge nanoparticle formation is taking place; experiments to optimize dopant growth, verify carrier injection from dopant to host and understand the influence of such dopants on the host material's properties are ongoing. If magnetically doped chalcogenide TIs become a reality, they may play significant roles in quantum device and quantum information applications thanks to enhanced persistent charge currents that could maintain entanglement at relatively high temperatures.

5:00 PM EL19.10.14
Ultra-thin Hafnia-based Ferroelectric Tunnel Junction Synaptic Device for Neuromorphic Computing Application Wonwoo Kho, Hyunjoo Hwang and Seung Eon Ahn; Tech University of Korea, Korea (the Republic of)

IDC, a U.S. market intelligence firm, predicts that the global digital information volume to be 80 ZB (1 ZB equals 1 trillion GB) as of 2022. This massive information has a high proportion of unstructured data such as voice and video. Current serial von Neumann computing has limitations in processing and storing a large amount of unstructured data produced. The solution to this issue may be found in neuromorphic computing, a parallel processing technique. An efficient spike-based artificial neural network is needed for neuromorphic computing. Accordingly, a synapse device capable of spike-based learning is attracting attention, and studies to reduce the size of the synapse device are becoming active.

HZO-based ferroelectric tunnel junction (FTJ) is a simple MFM structure optimized for scaling down. It is also a promising memristor device that can be used as an analog synapse device for neuromorphic computing. The synapse device corresponds to ~10^{15} biological synapses in an artificial neural network that mimics the neural network of the human brain, hence miniaturization is essential. In addition, as it has recently been experimentally found that the learning method of biological synapse is Spike Timing Dependent Plastics (STDP), many studies are being conducted on this. However, research on STDP learning of ferroelectric-based synaptic devices is lacking.

We effectively implemented Long-term Potentiation (LTP) and Long-term Depression (LTD) with STDP learning methods by fabricating HZO FTJs with ultra-thin films of 3 nm level. Using the Cross-sim simulator and extracted LTP and LTD, the accuracy of pattern recognition of a handwriting image was assessed. In conclusion, we propose that our 3 nm extreme thin film HZO FTJ might be applied to artificial neural networks for implementing neuromorphic computing.

5:00 PM EL19.10.15

Redesigning Micro-Electromechanical Systems for Additive Manufacturing Emily Huntley[1], Kyler Kunzler[2], Georgia Kaufman[1], Michael Gallegos[1], Tim Dallas[2] and Bryan Kaehr[1,3]; [1]Sandia National Laboratories, United States; [2]Texas Tech University, United States; [3]Center for Integrated Nanotechnologies, United States

Micro-electromechanical systems (MEMS) are devices that sense and actuate at the microscale. Typically, MEMS devices are fabricated using multi-step, clean-room techniques that are time consuming in both design and fabrication and thus cost prohibitive for prototyping or small-lot production. Recently, simple MEMS actuators have been fabricated in a single-step approach using the micro-scale 3D printing technique of multi-photon lithography. Subsequent thin-film metal deposition produced dynamic MEMS that move through applied electrical power. In our work, we aim to adapt tried-and-true MEMS devices such as chevron actuators—traditionally fabricated using, for example, the SUMMiT V process—to be compatible with additive manufacturing, and ultimately develop complex multicomponent systems and functions. The design for additive manufacturing approach employed here required many iterative design/test cycles to adapt planar, multi-level assemblies into more 3D free form fabricated objects. Following this iterative process, we demonstrate rotation of a 300-micron, 100-toothed gear via a linear thermal actuator coupled to a long-spanning cantilever. Overall, this work extends the capabilities and knowledge surrounding the use of microscale 3D printed structures for producing dynamic MEMS and has the potential to displace traditional microfabrication techniques that require dozens of process steps.

5:00 PM EL19.10.16

Optimizing the Contact Structure for Scaled 50 nm-Channel MoS_2 and IGZO Field Effect Transistors Yuchen Zhou, Chankeun Yoon, Kelly Liang and Ananth Dodabalapur; The University of Texas at Austin, United States

A novel idea of replacing conventional flat-edge electrodes with an array of spike-shaped electrodes has been implemented and proved useful for overcoming short-channel effects and improving charge injection. 50 nm-channel MoS_2 field effect transistors (FETs) with nanospike array electrodes demonstrated improved gate control relative to flat edge electrode devices. By using the nanospike array electrodes with 5 nanospikes and a 1:3 spike-to-spacing ratio, a high on/off ratio (~10^7), negligible drain-induced barrier lowering (0.1 V/V), and a steep subthreshold swing can be achieved. While this design has worked well for amorphous metal oxide and organic semiconducting materials, the physics behind the nanospike electrodes is material dependent. Therefore, the structure of the nanospike needs to be optimized to realize the full potential for 2D materials such as MoS_2. We also hypothesize that the optimized nanospike electrodes work well for CVD grown MoS_2, which is more suitable for industrial-scale fabrication.

The nanospike array electrodes were patterned onto 90 nm of SiO_2 using electron beam lithography and 17 nm of Cr and Au were thermally evaporated. 3 nm and 20 nm of MoS_2 and hBN flakes were mechanically exfoliated respectively and transferred onto the patterned contacts. The top gate with a width of 3 mm was patterned with 100 nm thick Cr and Au. The tips of the nanospike are 200 nm wide equilateral triangles with a 1mm long rectangular base protruding vertically between the conventional flat electrodes. The channel length between the tips of the source/drain nanospikes is 50 nm.

Ideally, charge nanoribbons are formed at high drain biases between the spikes of the source and drain, resulting in the higher charge injection in a narrower semiconducting channel for each pair of the nanospikes. However, the spacing between each nanospike on the source/drain electrodes can have different effect on the formation of charge nanoribbons. We have examined various ratios of the nanospike vs. spacing including 1:2, 1:4, and 1:5 and compared with the established 1:3 ratio. As expected, the current magnitude is at its highest for 1:5 ratio (~ 70 mA vs. 20 mA for $V_d = 1$ V) due to larger channel width, but the subthreshold swing degradation was observed as well. Another configuration of the nanospike array electrodes that has worked well for organic materials is the one-sided nanospike electrodes. In this configuration, instead of using the nanospike electrodes for both the source and drain, the nanospikes are implemented on the source side only. The highest current magnitude (~160 mA), on/off ratio (~10^9), and the steepest subthreshold swing (~100 mV/dec) were achieved in this configuration with a 1:3 spike-to-spacing ratio. Since the source electrode plays the main role of charge injection, having the nanospikes on the source side facilitates charge injection, while more charges are received by the drain side compared to the double-sided nanospike configuration, resulting in a higher drain current. A optimized structure for the nanospike array electrodes can be carefully selected by pairing the single-sided nanospike electrodes with the best spike-to-spacing ratio. The two-dimensional charge nanoribbons formed by this structure provides an alternative to the three-dimensional nanowire semiconducting channels that are currently being investigated by industry.

Nanospike electrodes are also useful in flexible and printed electronics in which the contact metallization can be defined with nanoimprint lithography resulting in small channel lengths. Results with IGZO indicate that excellent transistor performance can be achieved with nanospike electrode devices even when the channel length is less than the gate insulator thickness, which is common in flexible and printed electronics.

5:00 PM EL19.10.17

1D Transition Metal Chalcogenides: Novel van der Waals Metals for Microelectronic Applications Jing Jin, Danial Coyle, Thomas Empante, Michelle Wurch and Ludwig Bartels; University of California, Riverside, United States

Micron-scale single-crystal nanowires of metallic $TaSe_3$, a material that forms -Ta-Se_3-Ta-Se_3- stacks separated from one another by a tubular van der Waals (vdW) gap, have been synthesized using chemical vapor deposition (CVD) on a SiO_2/Si substrate, in a process compatible with semiconductor industry requirements. Their electrical resistivity was found unaffected by downscaling from the bulk to as little as 7 nm in nanowire width and height, in striking contrast to the resistivity of copper for the same dimensions. While the bulk resistivity of $TaSe_3$ is substantially higher than that of bulk copper, at the nanometer scale the $TaSe_3$ wires become competitive to similar-sized copper ones. Moreover, we find that the vdW $TaSe_3$ nanowires sustain current densities in excess of 10^8 A/cm^2, an order of magnitude more than copper, and feature an electromigration energy barrier twice that of copper. The results highlight the promise of quasi-one-dimensional transition metal trichalcogenides for electronic interconnect applications and the potential of van der Waals materials for downscaled electronics.

Recent work has extended the preparation strategies to $ZrTe_3$ and related materials. Patterning of the substrate prior to CVD growth can encode the location and alignment of the CVD-grown nanowires resulting in a network of connections on the substrate.

5:00 PM EL19.10.18
Evolution of Electronic States During *In Situ* Transformation of Lanthanide Intermetallic $Pr_2Co_3Ge_5$ Ellis Kennedy[1], Trent Kyrk[2], Mary Scott[1,3] and Julia Chan[2]; [1]University of California, Berkeley, United States; [2]Baylor University, United States; [3]Lawrence Berkeley National Laboratory, United States

Recently identified low-dimensional intermetallic homologous series with the formula $A_nB_{n+1}X_{3n+1}$ consisting of rare-earth (A), transition metal (B), and tetrels (X) have potential as novel quantum materials [1]. Members of the series exhibit strongly correlated electron behavior, including superconductivity [2], Kondo lattice behavior [3], and vying antiferromagnetic and ferromagnetic states [4]. One member of the series, $Pr_2Co_3Ge_5$, exists in multiple polymorphs, each with unique magnetic and electronic properties. Single-crystal monoclinic m-$Pr_2Co_3Ge_5$ was grown using the flux growth method with tin as a metallic non-reactive flux. XRD confirmed the monoclinic structure and *C2/c* space group.

Electron-transparent lamellae prepared from the bulk *m*-Pr2Co3Ge5 were analyzed using monochromated probe-corrected electron energy-loss spectroscopy (EELS) and a direct electron detector. EELS provides information about the atomic coordination, electron interactions, and elemental identification [5]. The Co and Pr ionization edges were recorded from an edge portion of the lamella, approximately 50 nm thick. The lamella was tilted off-zone to avoid channeling effects in the EEL spectra and the energy resolution was 0.24 eV based on the zero-loss peak. The bulk average Pr valency is dominated by the Pr^{4+} cation, with the M_4 ($3d_{3/2} \rightarrow 4f_{5/2}$) edge exhibiting a lower energy shoulder on the main peak. A bulk in situ heating holder was used to increase the sample temperature from room temperature (20C) to 80 °C to induce a transformation from the monoclinic to orthorhombic *o*-Pr2Co3Ge5 (*Ibam*) phase in 10 °C steps. The temperature range was selected based on a previous in situ XRD study that placed the transformation between 40 and 60 °C. A change in the ionization edges began around 55 °C (with potential calibration error of a few degrees) as the Pr edges changed to reflect a 3+ dominant state in which the M_5 ($3d_{5/2} \rightarrow 4f_{7/2}$) edge developed a high energy shoulder and the M_4 edge split into two peaks separated by 3.3 eV. The Pr and Co EEL spectra of the lamella after heating was compared to a *o*-Pr2Co3Ge5 standard to confirm it had undergone a full structural transformation. Ionization edges captured between the initial and final structures show a mixed Pr valency, falling between the +4 state of the monoclinic phase and +3 state of the orthorhombic phase.

The use of dual EELS enabled analysis of the Co edges in tandem with the Pr edges during heating. The Co L_3 edge onset shifted to a higher energy between the *m*-Pr2Co3Ge5 and *o*-Pr2Co3Ge5 phases; however, the $L_{2,3}$ maximum peak positions are downshifted by 1 eV. Changes in both the Pr and Co edges indicate compensating electron behavior between the two cations.

The change in Pr valency and the observation of intermediate valencies suggests an instability of the *f*-electron valence that is possibly advantageous in materials with strong electronic correlations. Understanding the behavior of the *4f*-electrons and their relation to the Co *3d*-electrons that are largely responsible for the complex magnetic properties of materials in the series will improve their use as quantum materials [6].

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5:00 PM EL19.10.19
Feature Size Dependence of Semiconducting Polymer Films Based on Molecular Weight Distribution Joaquin Mogollon Santiana, Adam J. Moule and Meghna Jha; University of California - Davis, United States

Semiconducting Polymers (SPs) have received widespread attention due to their promising qualities like superior absorbance/emission, easy chemical tunability, low-temperature solution processing, lightweight, and flexible substrates, and low environmental toxicity. A major obstacle to the development of SPs devices is the lack of patterning processes, most traditional lithography methods done for inorganic semiconductors damage the SPs. Recently the Moule group developed a process named Projection Photothermal Lithography (PPL) that enables patterning in SPs films based on solubility compatible with non-crosslinked polymers. The method works by placing a thin SP film inside a cell with a semi-poor solvent, a binary mixture of a strong and weak solvent that will not dissolve the film at room temperature but will spontaneously dissolve as the temperature rises. Light is projected onto an area which will generate heat. The local temperature will increase until it surpasses the dissolution temperature (DT) causing the polymer to dissolve allowing us to pattern the film. Previous work was done using P3HT where it was found that tunning the semi-poor solvent ratio had a direct relationship with the DT. Using PPL with a homemade microscope set up rapid (~ $4cm^2hr^{-1}$), large single exposure area (0.21 mm^2), sub-µm patterns can be obtained optically In order to generalize this concept a different semiconducting polymer (PDPP3T) was used. It was determined that the PDI for this polymer is much broader than P3HT resulting in a significant difference in dissolution temperature for smaller and larger chains of polymers in the film. Knowing this our goal was to determine how PDI distribution and molecular weight affect the size of features made using the PPL method. With the PDPP3T data, it was determined that a larger molecular weight and small PDI are ideal for this patterning technique, as dissolution will occur more uniformly, which agrees with the P3HT results.

5:00 PM EL19.10.20
Direct Laser-Induced Hierarchical Mesoporous Copper Oxide on Copper Surface for Electrochemical Sensing Sotoudeh Sedaghat, Sina Nejati and Rahim Rahimi; Purdue University, United States

In this work, we demonstrate a novel a one-step rapid laser-processing approach for the fabrication of electrochemically active copper oxide mesoporous structures directly on copper metal surfaces. The effect of laser processing power on the composition, crystallinity, microstructure, wettability and color of the laser-induced oxide on the copper surface was systematically studied using optical microscopy, scanning electron microscopy (SEM), grazing incidence X-ray diffraction, Raman spectroscopy, and water contact angle measurements. The created ratio and percentage of crystalline Cu2O [111] and amorphous CuO with different laser processing conditions was confirmed by GI-XRD and Raman spectroscopy. Results of these studies confirmed clear decrease in size of created copper oxide nanostructures and increase in overall crystallinity of the final surface with increase in laser power processing conditions. The optimized copper oxide electrodes with the highest surface area and crystallinity showed the ability to be used for nonenzymatic glucose and hydrogen peroxide sensing with a unique ultrahigh sensitivity, fast response/recovery time, and selectivity. This rapid laser-induced oxidation technique can be potentially applied for scalable fabrication of wide range of electrochemically active metal oxide micro/nanostructures directly onto different metal surfaces for potential used in other electrochemical and biochemical sensing applications.

5:00 PM EL19.10.21

Understanding Oxygen Migration due to Contacts and Gate Bias-Stress in Indium Tin Oxide Transistors Sumaiya Wahid[1], Mahnaz Islam[1], Christopher Perez[1], Timothy D. Brown[2], Michelle Chen[1], Matthew Marcus[3], Hendrik Ohldag[3], Suhas Kumar[2] and Eric Pop[1]; [1]Stanford University, United States; [2]Sandia National Laboratories, United States; [3]Lawrence Berkeley National Laboratory, United States

Field-effect transistors with semiconducting oxide channels are promising candidates in several applications due to their low-temperature deposition, ultralow leakage current, as well as processing compatibility with silicon technology [1-3]. However, their stability is under question and their performance can degrade after long-term operation, an effect which is poorly understood. In this work, for the first time, we use *in-situ* x-ray absorption spectroscopy to probe the instability of indium tin oxide (ITO) transistors by looking into oxygen migration in metal-insulator-semiconductor-metal (MISM) test structures. To fabricate the MISM devices, we e-beam evaporate ~30 nm Pd as the back (gate-like) contact, followed by ~13 nm Si_3N_4 (as the insulator) with conductively-coupled plasma-enhanced chemical vapor deposition at 350 °C. This nitride is used to avoid interference from any oxygen species other than in the ITO. Next, we deposit ~4 nm thick ITO (as the semiconductor channel), using radio-frequency magnetron sputtering at room temperature, 100 W power and 5 mTorr pressure. Finally, the ~30 nm top metal contact (four types of samples with Ti/Pt, Ni, Pd, or Pt) is deposited using e-beam evaporation. To utilize *in-situ* scanning transmission x-ray microscopy, these MISM devices are fabricated on SiN_x membranes.

From the spectral absorption measurement of samples with four different workfunction metals, we demonstrate, for the first time, that metal contacts scavenge oxygen from ITO according to a trend consistent with their reactivity. Such oxygen scavenging from the ITO channel in a transistor creates more oxygen vacancies, which in turn generate more carriers in the channel, causing a negative threshold voltage shift, especially at short channel lengths [4] where the contacts are closer together. The observed trend with metal reactivity agrees well with our previous reports of ITO transistors with Ni *vs.* Pd contacts, where Ni contacts caused a more negative threshold voltage shift at shorter channel lengths *vs.* Pd contacts [5,6].

To investigate the microscopic physics during device operation and understand the gate bias-stress effect in ITO transistors, we perform *in-situ* x-ray absorption spectroscopy while applying voltage bias to the MISM structures with Ni contacts, and observe oxygen migration near both the ITO/dielectric and ITO/Ni interfaces. To correlate this effect with transistor behavior, we fabricate transistors using the same composition as the MISM structure and observe a similar trend. Notably, the device behavior upon gate-bias stressing is different with Si_3N_4 dielectric from our previously reported works with Al_2O_3 or HfO_2 dielectrics [7], which reinforces the impact of dielectric material on the stability of ITO transistors.

In short, our results provide new insight of device operation and threshold voltage (in)stability of ITO transistors using *in-situ* x-ray characterization. Both metal contacts and the gate insulator play major roles in oxygen migration, and are therefore instrumental for optimizing transistor performance and reliability.

This work is partly supported by the Stanford Graduate Fellowship (S.W., M.I.) and the SystemX Alliance.

Refs: [1] M. Si *et al.*, *IEEE Trans. Electron Dev.* 68, 3195 (2021). [2] S. Li *et al.*, *Nat. Mater.* 18, 1091 (2019). [3] W. Chakraborty *et al.*, *IEEE Trans. Electron Dev.* 67, 5336 (2020). [4] S. Subhechha *et al.*, *Symp. VLSI Tech*. (2021). [5] S. Wahid, E. Pop *et al.*, *IEDM* (2022). [6] S. Wahid, E. Pop *et al.*, *DRC* (2022). [7] L. Hoang, E. Pop *et al.*, *DRC* (2022).

5:00 PM EL19.10.22

Ultrafast Colorimetric Humidity Sensors with Mesoporous Titania Microspheres Nutpaphat Jarulertwathana, Syazwani Mohd-Noor and Jerome Hyun; Ewha Womans University, Korea (the Republic of)

Fast humidity monitoring is becoming increasingly important for a wide range of applications including emerging healthcare solutions and fuel cell engineering. However, most commercially available sensors suffer from slow response times ranging from seconds to minutes, limiting their use. Herein, we propose mesoporous solid and yolk-shell titania microspheres as ultrafast colorimetric humidity sensors. Different microsphere morphologies were synthesized through a solvothermal process with varying reaction times, and their performances were compared to determine the optimal structure for humidity sensing. We found that the pore volume, pore diameter and crystallinity, respectively, determine the responsive RH range, response time and stability of the materials. The optimal mesoporous solid microsphere had a fast response time of 20 ms and was structurally-stable for at least 180 days, which was the duration of this study. These microspheres were integrated into a prototype sensor system, consisting of a pair of LEDs and a photodiode. The system was sensitive and fast enough to detect unique humidity profiles generated from human speech, demonstrating an alternative approach to speech recognition. These results suggest that mesoporous titania microspheres are promising for ultrafast humidity detection.

5:00 PM EL19.10.23

Transparent and Flexible Memristor Utilizing Copper-Iodide Based on Low Temperature Solution Processing Yongin Cho, Arindam Bala and Sunkook Kim; Sungkyunkwan University, Korea (the Republic of)

This study proceeds with the utilization and process of binary halides, which is a representative candidates, to discover an active layer suitable for memristors. Herein, the solution-based Copper Iodide (CuI) thin film is used an active layer of the memristor which shows high performance of memory device from the point of endurance and retention. To implement of a transparent memristor, indium tin oxide (ITO) is deposited as a bottom electrode on the polyethylene terephtalate (PET) substrates. The CuI thin film is formed by dissolution-recrystallization solution-treatment at 80°C and silver electrode is deposited thereon to have a sandwich structure. The memristor having a high transparency of 90% or more has a current difference of 10 times between a low-resistive state (LRS) and high-resistive state (HRS). The memristor has a steady endurance of 100 cycles at low voltage range (-2.5V to 2.5V) and a constant read voltage of -0.5V, and the CuI-based memory remains stable for 10^4s in rentention characteristic. Additionally, the device also exhibits the same level of resistance state difference and current under bending stress. The CuI film is used as the active layer of a stable memristor introduced with transparent and flexible memory applications.

5:00 PM EL19.10.24

Two-Dimensional Field-Effect Transistors with a Reconfigurable Floating Gate for Logic-in-Memory June-Chul Shin, Hyun Young Choi and Gwan-Hyoung Lee; Seoul national University, Korea (the Republic of)

Recently, machine learning applications, such as artificial intelligence, neuromorphic computing, and autonomous vehicles, are attracting extensive attention. However, the von Neumann architecture consisting of the separated parts of data processing and data storage has weaknesses in real-time processing and consumes large power. Therefore, there has been a need for energy-efficient electronic hardware without data transport between logic and memory units. In this regard, two-dimensional (2D) materials are considered promising candidates for logic-in-memory. Owing to the atomic thickness and electrostatic controllability, the conductance of 2D field-effect transistors (FETs) can be precisely modulated so that they can be used for reconfigurable logic circuits. However, the logic-in-memory in previous works still shows a large power loss because the used 2D memory devices have only n-type transport. Therefore, it has been required to develop a CMOS-based circuit consisting of p-type and n-type memory devices, which have a low static power consumption and high noise margin. Here, we demonstrate 2D FETs with a reconfigurable floating gate based on the van der Waals heterostructure. By using WSe_2 as an ambipolar channel, the WSe_2 FETs exhibit not only reconfigurable memory operation of n- and p-type polarity but also multiple conductance states. The inverters and circuits based on the WSe_2 FETs show multi-functionality in logic operation with low power consumption. Our work highlights the great potential of atomically thin semiconductors for next-generation low-power electronics.

SESSION EL19.11: Low-Dimensional Materials II
Session Chairs: Ageeth Bol and Supratik Guha
Friday Morning, April 14, 2023
Moscone West, Level 3, Room 3020

8:30 AM *EL19.11.01
Dielectric, Magnetic, and Contact Properties of Two-Dimensional Materials William Vandenberghe[1], Madhuchhanda Brahma[1], Emeric Deylgat[1], Massimo Fischetti[1], Akash Laturia[1], Mehrdad Rostami Osanloo[1], Bart Sorée[2,3,4], Sabyasachi Tiwari[1] and Maarten Van de Put[1]; [1]The University of Texas at Dallas, United States; [2]imec, Belgium; [3]KU Leuven, Belgium; [4]University of Antwerp, Belgium

Two-Dimensional (2D) Materials have received an enormous amount of attention in the past decade. Modeling and simulation have also advanced dramatically and many materials properties can be determined from first-principles. Here, we present an overview of our recent progress in modeling dielectric, magnetic, and contact properties of 2D materials.
We first highlight how the dielectric properties can be calculated in a robust way. We show that in hexagonal boron-nitride, the out-of-plane dielectric constant changes minimally when going from monolayer to bulk. We show how leveraging materials databases, 32 novel candidate 2D dielectrics with a large band gap can be identified. For practical applications as an insulating dielectric, the band alignment with adjacent materials must be determined as well. Calculating the electron affinity and bandgap of all 32 materials, we estimate the leakage current and identify oxyhalides like LaOBr and LaOCl as promising 2D “high-k” future dielectrics.
Next, we show how magnetic properties can be determined from first principles while accounting for long-range interactions and the anisotropy of the exchange interaction. We apply our method on known 2D ferromagnets like CrI_3, and $CrGeTe_3$ to verify good agreement with experiments. We subsequently study the magnetic order of doped transition-metal dichalcogenides (TMDs) and identify V-doped $MoSe_2$ as the most promising doped TMD-based 2D ferromagnet. We also present how magnetic switching can be simulated atomistically by coupling quantum transport with Monte Carlo simulations. We further show how we can screen materials databases for the most promising 2D magnets.
Finally, we show our progress in understanding electrical contacts to semiconducting 2D materials like TMDs. We compute image-force barrier lowering in a 2D material surrounded by a dielectric. Calculating the current flowing from the metal to the semiconductor, we show that when the 2D material is surrounded by a “low-k” dielectric, the contact resistance is dramatically improved. The recipe we identify for making low-resistance contacts is: low Schottky barrier, high doping concentration, and low dielectric constant of the surrounding dielectric.

9:00 AM EL19.11.02
Enhancing the Nucleation of Dielectrics on MoS_2 by Atomic Layer Deposition Alexander Shearer, Jung-Soo Ko, Eric Pop and Stacey F. Bent; Stanford University, United States

Recently, 2D transition metal dichalcogenides (TMDCs) have received significant attention due to their unique optical and electrical properties, lending themselves to exciting applications such as microelectronics, sensing, catalysis, photonics, and more. In order to be used in these applications, TMDCs generally must be incorporated into nanoscale material stacks composed of other 2D materials or more often 3D materials including metals or metal oxides. Due to the uniformity and angstrom-level thickness control that it provides, as well as its widespread use in the semiconductor industry, atomic layer deposition (ALD) has become a promising candidate for depositing those metals and metal oxides on the TMDCs to form the requisite stacks. However, because of both the inert nature and low surface energy of the basal plane of TMDCs, it is difficult to deposit thin films upon these materials using techniques like ALD – often leading to films of poor quality with pinholes, voids, and rough surfaces.

Numerous techniques have been employed to improve ALD nucleation onto 2D materials: pretreatment of the surface with various absorbates, addition of both metal and molecular seed layers, and use of physisorption-assisted ALD by means of low temperature processing. The latter technique is particularly interesting because it still provides the benefits of ALD – namely the thickness control – and is a non-destructive mild treatment that does not lead to the incorporation of impurities from chemical pretreatments. While it has been employed before, little is known about how the approach can be further leveraged to lead to the growth of better films.

In this work, we investigate how various ALD parameters – such as temperature, purge time, and precursor – impact nucleation behavior and film quality of dielectrics, like Al_2O_3 and HfO_2, on MoS_2, a prevalent TMDC. Using atomic force microscopy (AFM), we study film nucleation and continuity as a function of ALD cycle number to better understand the impact of each ALD parameter. Additionally, using x-ray photoelectron spectroscopy (XPS) and reflection electron energy loss spectroscopy (REELS), we investigate the interfacial properties of the dielectric on MoS_2. Our results show that by selecting a low temperature, short purge process, with as few as 15 cycles of Al_2O_3 ALD, we can create a seed layer upon which high temperature ALD can be performed – resulting in a continuous, smooth film. Furthermore, according to AFM and Auger electron spectroscopy data, under the same operating conditions, different ALD Al_2O_3 and HfO_2 precursors exhibit distinct nucleation and growth behavior on MoS_2, indicating varied wetting of the TMDC surface and altered reaction kinetics by the precursors. The dependence of the deposited film properties on the ALD precursor choice and the process parameters will be discussed.

9:15 AM EL19.11.03
Anti-Ambipolar Phototransistors Based on 1D GaAsSb/2D MoS_2 Heterojunctions Wei Wang and Johnny C. Ho; City University of Hong Kong, Hong Kong

The incapability of modulating the photoresponse of the assembled heterostructure devices has remained a challenge for developing optoelectronics with multi-functionality. In this presentation, we report a gate-tunable and anti-ambipolar phototransistor based on 1D GaAsSb nanowire/2D MoS_2 nanoflake mixed-dimensional van der Waals (vdW) heterojunctions.[1] The resulting heterojunction shows asymmetric control over the anti-ambipolar transfer characteristics, possessing the potential to implement electronic functions in logic circuits. Meanwhile, the anti-ambipolar device allows the synchronous adjustment of band slope and depletion regions by gating in both components, thereby giving rise to the gate-tunability of the photoresponse. Coupled with the synergistic effect of the materials in different dimensionality, the hybrid heterojunction can be readily modulated by the external gate to achieve a high-performance photodetector exhibiting a remarkable on/off current ratio of 4×10^4, fast response of 50 μs and high detectivity of 1.64×10^{11} Jones. Due to the formation of type-II band alignment and strong interfacial coupling, a prominent photovoltaic response is also explored in the heterojunction. Finally, a visible image sensor based on this hybrid device is demonstrated with excellent imaging capability, suggesting promising applications in future optoelectronic systems.

9:30 AM *EL19.11.04

Advanced Epitaxial Si/SiGe Stacks for Nanowire Applications Andriy Hikavyy, Roger Loo, Yosuke Shimura and Naoto Horiguchi; imec, Belgium

A decade has passed since semiconductor industry had a major shift in the design paradigm of the field effect transistor (FET) moving from the so-called planar transistors to fin FETs or 3D transistors. Since then, this technology was perfected and currently reaching its limits. As scaling progresses the next shift is around the corner. After many years of R&D by many research groups, last year the major semiconductor players introduced a move from fin FET to gate all around (GAA) or nanosheet transistors in their scaling roadmaps. Looking further downstream, at VLSI 2021, imec introduced the forksheet and complementary FET (CFET) device architectures to extend the scalability of the nanosheet transistor family towards 1nm and beyond logic nodes.

In a CFET architecture, n- and p-MOS devices are formed on top of each other, removing the n-p spacing, allowing further maximization of the effective channel width and, hence, the drive current. This architecture can be realized in two ways: a monolitic and a sequential approach. In the first one both n- and p-MOS transistors are built on the same wafer. In the sequential approach the bottom device is built up to the contacts, next, a blanket semiconductor layer is bonded and top devices are formed. Both approaches have their pros and contras and are being currently intensively investigated.

One of the main building blocks of a GAA (nanosheet) transistor is a SiGe/Si stack with multiple SiGe and Si layers which act as active or sacrificial layers in the further processing. Growth of SiGe/Si stacks with relatively low Ge concentrations (<30%) is very well known for Group IV epi community which works with such stacks for decades. The situation changes significantly when we move to CFET architecture. One of the difficulties of the monolitic CFET is the integration of bottom and middle dielectric isolation (BDI and MDI) in order to cut-off a parasitic channel of the bottom device and to physically separate bottom and top devices. This complicates the initial SiGe/Si epi stack considerably and makes the final epi growth challenging.

In this contribution we will present typical schemes for manufacturing nanosheet devices and motivate SiGe/Si stacks needed in each case. Next, we will discuss strategies for epitaxial growth, choice of precursors and temperature ranges. Finally examples of the devices with integrated SiGe/Si stackes will be demonstrated.

10:00 AM BREAK

SESSION EL19.12: Breaking News
Session Chairs: Francesca Iacopi and Pei-Wen Li
Friday Morning, April 14, 2023
Moscone West, Level 3, Room 3020

10:30 AM EL19.12.01

Area-Selective Atomic-Layer Deposition of Carborane Thiols on Copper for Patterning and Interconnect Applications Sai Siva Kumar Pinnepalli[1], Raja Sekhar Bale[1], Rupak Thapa[2,1], Vamseedhara Vemuri[3], Nathan A. Oyler[1], Nicholas Strandwitz[3], Sean King[2] and Michelle M. Paquette[1]; [1]University of Missouri Kansas City, United States; [2]Intel Corporation, United States; [3]Lehigh University, United States

Miniaturization of components in an integrated chip follows Moore's law to advance computing capabilities for future technological needs. In the grand scheme of chip manufacturing, complex fabrication methods involving atomic-layer deposition (ALD) with precise control over atomic or molecular dimensions are envisioned to realize more than Moore's vision. Advanced chip-making further requires robust materials to develop miniaturized and scalable patterning processes. Boron carbide compliments silicon-based materials with its distinct chemical and physical properties and has potential applications as dielectric layers, hard masks, diffusion barriers, etch-stop, and patterning-assist layers. Carboranes are unique ALD precursors for boron carbide due to their three-dimensional icosahedral structure that produces densely packed, defect-tolerant, and cross-linkable monolayers over high-aspect ratio surfaces. Specifically, thiol-derivates of carboranes show intrinsic substrate selectivity towards copper and can assist in patterning processes.

The current study explores the vapor-phase ALD of the *ortho*-carborane-9,12-dithiol (9O12) and *meta*-carborane-1-thiol (M1) on copper surfaces. The process conditions for the 9O12 and M1 precursors—substrate temperature, precursor dose, and pressure—are optimized to obtain a higher substrate coverage. The films are characterized by X-ray photoelectron spectroscopy (XPS) and dynamic in-situ ellipsometry to gain insights into the kinetics of deposition mechanisms. Stability and structural changes as a function of temperature are evaluated to understand the robustness of the films. An overview of the 9O12 and M1 monolayer deposition and their applications to patterning will be presented at the eminent gathering.

10:45 AM EL19.12.02

Electrical Resistivity Evolution of Electrodeposited Ruthenium- and Molybdenum-based Nanowires for Interconnect Application Jun Hwan Moon, Seunghyun Kim, Taesoon Kim and Young Keun Kim; Korea University, Korea (the Republic of)

It is challenging to achieve historically anticipated improvements in the performance of integrated circuits (ICs) because the cost and complexity of the associated technology increase with each generation. As downscaling accelerates, the electrical resistance and diffusion to low-k dielectrics of conventional Cu/Ta/TaN interconnect become a major problem [1]. The reduction in the cross-sectional area of the interconnect causes an increase in the resistance of the interconnection structure, which causes RC delay and energy consumption. A liner/barrier whose thickness cannot be reduced any further drastically reduces the volume of the conductor in the trench structure, accelerating RC delay and making the process difficult [2]. Consequently, the demand for advanced interconnect metallization has increased. Therefore, the microelectronics industry is searching for new materials and processes [3].

This study investigates the electrical properties and microstructural evolution of nanoscale Ruthenium (Ru) and Molybdenum (Mo)-based metallic nanowires prepared via template-assisted electrodeposition. Most previous studies on advanced interconnect materials were carried out based on thin films. However, the actual structure and scale of interconnects, including vias and trenches, are nanowires with a high aspect ratio; thus, they exhibit properties significantly different from those of thin films owing to the confinement of low-dimensional systems.

In addition to material properties, nanopore engineering is required to fill the confined pores at the nanoscale with metallic materials. We provide an electrochemical strategy for synthesizing Ru- and Mo-based nanowires in nanopores and characterize the effects of microstructure and phase differences on the electrical properties of nanowires in situ. We find that the electrical resistivity was affected by the composition and microstructural changes, such as the diameter of nanowires, crystallite size, and phase. Properly designed alloys of advanced interconnect materials (e.g., Co, Ru, and Mo) show superior characteristics to existing materials in various characteristics that interconnect will have. We investigate the degree of thermal diffusion into a low-dielectric material by imitating a structure similar to an actual interconnect structure. First-principles calculations show that a corresponding liner/barrier is required as a new central conductor emerges.

Reference

[1] D. Gall, *J. Appl. Phys*, 127, 050901 (2020)
[2] C. Lo *et al., J. Appl. Phys*, 128, 080903 (2020)
[3] J. H. Moon *et al., J. Mater. Sci. Technol.*, 105, 17 (2022)

11:00 AM EL19.12.03
A Highly Efficient and the Smallest AAA Battery-Powered Pocket X-Ray System Based on Carbon Nanotube Amar P. Gupta[1,2], Taewon Kim[2], Jinho Choi[1], Mrinal Bhusal Sharma[2], Seung Jun Yeo[2,1], Jeung Sun Ahn[1] and Jehwang Ryu[1,2]; [1]Kyung Hee University, Korea (the Republic of); [2]CAT Beam Tech Co., Ltd, Korea (the Republic of)

One of the most common types of radiological device on earth is the X-ray machine. From the airport to the hospital, X-rays are used at least once on both the person and their belongings. Even though X-ray machines are used a lot, they are among the least efficient machines, with a ratio of less than 1%. In conventional hot cathode filament-based portable X-ray machines, 75% of the energy is used to accelerate electrons, and 20% is used to heat the filament (cathode) to generate electrons inside the vacuum tubes. Thus, there are two types of electrical power sources needed: a) a low-voltage, high-ampere source to heat the filament and make electrons, and b) a high-voltage, low-ampere source to speed up the electrons and make X-rays. However, we have made the first X-ray system that fits in a pocket and is smaller than our palm. It doesn't use a filament and has a high-voltage module that can be used for both making electrons and accelerate them up. This is possible because the X-ray system uses a Carbon Nanotube (CNT) cold cathode digital X-ray tube, it doesn't make any heat, doesn't have a complicated structure for filament feedthroughs, and can be powered by 2 AAA batteries. Our X-ray system is one of the smallest in the world. It weighs about 80 grams and is about 40 mm X 30 mm X 25 mm. An X-ray survey meter can detect a soft X-ray with a voltage of up to 7 kV. It gives off 50 mSv/hr of radiation dose at a distance of 10 cm from the X-ray source, proving that this smallest X-ray system can be used for cell irradiation experiments and possibly as an alternative to all the hazardous radioactive materials used for QC testing and calibration of X-ray survey meters. It can also take X-ray pictures of soft things like plant leaves when it is powered by a Lithium ion battery that is smaller than an AAA battery. We are certain that this new Nanotube innovation will assist researchers all around the globe in making the X-ray machine more compact, portable, energy efficient, and environmentally friendly.

11:15 AM EL19.12.04
Multi-Dimensional Driven Verification Platform of Chemical Vapor Compositions Yun Ji Hwang, Iman Shackery and Seong Chan Jun; Yonsei University, Korea (the Republic of)

Since gas molecules do not exist in a single state in nature, future gas sensing technology will have to move toward predicting and determining the state of the gas mixture itself, rather than being limited to a specific single gas in the air. In this study, we propose a platform that detects gas in a mixed gas state under humidity conditions like human exhaled gas and predicts the type and mixture state of the gas. Our subminiature sensor is a multi-dimensional nano-electrode sensor. For each channel, six different ssDNA functionalized graphene are arranged, enabling multi-dimensional sensing at the same time. Our sensor confirmed the reactivity to the chemical vapor composition under the mixing conditions of various ratios of NO, NO_2, NH_3, and H_2S gases under low and high humidity conditions, and showed high reactivity even under high humidity conditions. Chemical vapor in a mixed state is simultaneously detected in multiple dimensions by our sensors, and the data is input in the form of electrical signals to our artificial intelligence model. Our convolutional neural network-based deep learning model is a very fast and efficient model that can process multi-dimensional data simultaneously and is trained and optimized through experimental data. Our artificial intelligence model can recognize the detected electrical signal, determine the type and ratio of gas included in the chemical vapor composition at the time of detection, and determine the status of harmful gases in the air. Our chemical vapor composition determination platform has verified its performance by achieving a recognition rate of over 99% in both low and high humidity conditions. Our research results are not limited to human expiratory gas diagnosis but are expected to serve as an excellent research background in various fields such as manufacturing, aerospace, and personal air management systems that require detection of harmful gases in real environments.

11:30 AM EL19.12.05
Area-Selective Atomic Layer Deposition using Aminosilane Precursors to Confer Oxide versus Nitride Selectivity Jinseon Lee[1], Jeong-Min Lee[1], Hongjun Oh[2], Bonggeun Shong[2], Tae Joo Park[1] and Woo-Hee Kim[1]; [1]Hanyang University, Korea (the Republic of); [2]Hongik University, Korea (the Republic of)

Area-selective atomic layer deposition (AS-ALD) offers tremendous advantages in comparison with conventional top-down patterning processes in that atomic-level selective deposition can achieve in a bottom-up fashion on pre-defined areas in multi-dimensional structures. Inherent AS-ALD of oxide thin films on SiO_2 versus SiN surfaces is highly relevant to manufacturing of 3D-structured memory devices, but little is known about inherent AS-ALD on such surfaces. For example, in accordance with the continuous demand for higher memory density, the number of stacked SiO_2/SiN layers in 3D V-NANDs is increasing, resulting in an increased aspect ratio and decreased SiO_2/SiN tier size in the vertical direction. Accordingly, when NAND cells with an information storage layer are formed by a conventional top-down lithography/etching process, inter-cell non-uniformity and interference problems inevitably occur. This suggests that AS-ALD of SiO_2 thin film as an interlayer dielectric is required only on SiO_2, not on SiN, for NAND cell formation with discontinuous SiN CTL to prevent crosstalk between adjacent cells. For this purpose, AS-ALD of SiO_2 thin films on SiO_2 versus SiN substrates are investigated. Theoretical screening based on density functional theory (DFT) calculation is performed to identify Si precursors which maximize adsorption selectivity, results indicate that an aminosilane has the potential to function as a highly chemo-selective precursor as compared with a halosilane. Application of the aminosilane precursor to SiN and SiO_2 substrates result in inherent deposition selectivity of ≈4 nm without the aid of surface inhibitors. Furthermore, deposition selectivity is enhanced using an ALD-etch supercycle in which an etching step inserts periodically after a certain number of ALD SiO_2 cycles. Thereby, enlarged deposition selectivity greater than ≈10 nm is successfully achieved on both blanket-and SiO_2/SiN-patterned substrates. Therefore, this approach for performing inherent AS-ALD expands the potential utility of bottom-up nanofabrication techniques for next-generation nanoelectronic applications.

SESSION EL19.13: Virtual Session
Session Chairs: Paul Berger and Supratik Guha
Tuesday Afternoon, April 25, 2023
EL19-virtual

1:00 PM EL19.13.01
Template-Mediated Well-Defined Nanostructures for Optical, Optoelectrical, and Magnetic Applications Rui Xu[1], Yong Lei[2] and Denys Makarov[1]; [1]Helmholtz-Zentrum Dresden-Rossendorf (HZ, Germany; [2]Ilmenau University of Technology, Germany

Advanced devices play a critical role for sustaining the ever-growing demands of our society for energy, information, health care, etc. To achieve high performance, devices with nanoscaled features are attracting more and more attentions by virtue of their unique and promising effects emerging at nanoscale. Structural design and engineering of materials provides a verstile platform to optimize the device performance and improve the commercial competitivity[1]. Regarding the structural engineering, controlling the geometrical parameters (i.e., size, shape, hetero-architecture, and spatial arrangement) of nanostructures have been the central aspects of investigations and practical applications. By using anodic aluminum oxide template, we realized well-defined controlling of nanostructures over the size, in-plane/out-of-plane shape, hetero-architecture, and spatial arrangement[2]. With such well-defined nanostructures, the optical, optoelectrical, and magnetic performance of nanodevices can be obviously enhanced.
References:

1. Rui Xu et al, *Adv. Energy Mater.* 11, 2001537, 2021.
2. Rui Xu et al. *Nat Commun* 13, 2435, 2022.

1:15 PM *EL19.13.02
Supply Chain Challenges to Advancing BEOL Scaling and Materials Development Sean King; Intel Corp, United States

Innovations in back-end-of-line (BEOL) interconnects over the past several decades have been driven primarily by both Moore's law mandated dimensional scaling of Cu wiring and permittivity scaling of low dielectric constant (i.e. low-k) interlayer dielectrics (ILDs) to mitigate increased resistance-capacitance (RC) delays. While the need for both dimensional scaling and RC delay mitigation has not diminished, the physical limits of ILD dielectric permittivity scaling has now been reached with the introduction of air-gap technologies, and the industry now instead faces limitations in thickness scaling for the Cu barrier materials needed for yield and reliability considerations. The latter combined with Cu resistivity size effects has led to an exponential increase in interconnect metal line resistance and created an intense interest for identifying alternate materials and fabrication methods for BEOL metallization.

In this address, we overview some of the new materials and processes of current interest for BEOL metallization with a focus on supply chain considerations that may limit or prohibit implementation. We will specifically examine technical considerations and supply chain challenges for the consideration of platinum group metals (PGM) as Cu replacement conductors, PGM recovery and recycling, and supply chain challenges for novel precursors for flowable and area-selective deposition (ASD) of low-k dielectric materials.

1:45 PM *EL19.13.03
The Electromigration Characteristics of Copper Pillars with Increased Solder Christine Hau-Riege, Kevin Caffey and Dongming He; Qualcomm Technologies, Inc., United States

Copper pillars are the interconnect of choice for first-level connections for high density flip-chip packaging and second-level connections for 2.5D/3D packages due to fine pitch capabilities, leading to smaller devices and lower costs. However, the presence of Cu-Sn intermetallic compounds is a reliability concern due to its increased brittleness relative to copper and solder, which has been well-studied through various aging tests. To mitigate mechanical failure, two approaches have been reported: the inclusion of a Ni barrier layer to slow down the formation of intermetallic as well as an increase in solder volume to reduce fracture. This paper focuses on the implications of increased solder on electromigration reliability. Full transformation of the solder is not achieved in these copper pillars, so that Cu-Sn continually forms through prolonged electrical and thermal acceleration. This paper will report the electromigration performance of such interconnects in terms of current direction and pillar configuration as well as examines electromigration-induced failure mechanism and failure criteria selection.

2:15 PM *EL19.13.04
Epitaxial Growth of Transition Metal Dichalcogenide Monolayers and Heterostructures for Large Area Device Applications Joan M. Redwing; The Pennsylvania State University, United States

Wafer-scale epitaxial growth of semiconducting transition metal dichalcogenide (TMD) monolayers such as MoS_2, WS_2 and WSe_2 is of significant interest for device applications to circumvent size limitations associated with the use of exfoliated flakes. Epitaxy is required to achieve single crystal films over large areas via coalescence of TMD domains with the same crystallographic direction.

The prospects and challenges associated with the epitaxial growth of wafer-scale TMD monolayers and heterostructures for the development of large area 2D devices will be discussed. Metalorganic chemical vapor deposition (MOCVD) has emerged as an enabling growth technology for TMDs due to its ability to achieve a combination of high growth temperatures (>700ºC) and large chalcogen overpressures which are needed to obtain stoichiometric epitaxial films. The unique aspects of van der Waals epitaxy of TMDs on sapphire substrates will be presented including the effects of crystallographic orientation of the substrate on nucleation density and domain orientation and the role of surface passivation and steps on domain alignment and defects. Techniques for wafer-scale 2D layer transfer for device integration will be reviewed and applications for wafer-scale TMD monolayers in nanoelectronics, sensing and photonics will be presented.

2:45 PM EL19.13.05
Impact of Impurities and Annealing Conditions on Structural and Optical Properties of Hafnia-Based Thin Films Manuel Alejandro Garcia Andrade[1], Tetyana v. Torchynska[1], Georgiy Polupan[1], Larysa Khomenkova[2,3] and Fabris Gourbilleau[4]; [1]Instituto Politecnico Nacional, Mexico; [2]V. Lashkaryov Institute of Semiconductor Physics at NASU, Ukraine; [3]National University "Kyiv-Mohyla Academy",, Ukraine; [4]CIMAP, UMR CNRS/CEA/ENSICAEN/UNICAEN, France

HfO_2 based materials offer high refractive index and high transparency in UV-NIR spectral ranges that are promising for photonic applications. For this purpose, the stabilization of HfO_2 structure is required to minimize the optical losses in the HfO_2 based optical materials. It is known that stabilization of tetragonal/cubic structure can be achieved via HfO_2 doping with trivalent atoms, such as rare-earth (RE) elements. In this case, the electrical neutrality is achieved via formation of oxygen vacancies, i.e. one vacancy for two dopant atoms. At the same time, the interaction between different ions and their redistribution upon high temperature annealing were not well addressed.
In this report structural transformation of HfO_2 thin films co-doped with silicon and lanthanides (Pr) is considered in terms of the evolution of optical and light emitting properties of these materials. The films were grown on Si substrates by radio frequency magnetron sputtering in argon plasma and annealed at T_A=1000ºC for t_A=15-60 min in inert atmosphere. The transformation of film properties was studied by means of SEM, EDS, XRD, XPS, Raman scattering and photoluminescence (PL) techniques. For HfO_2 films doped with Pr ions, the stabilization of the tetragonal HfO_2 phase in annealed films was observed contrary to the monoclinic structure of pure HfO_2 films. The main reason responsible for this phenomenon is the formation of oxygen vacancies. For Pr-doped HfSiOx films, the phase separation between SiOx and HfO_2 occurs upon annealing and the Pr ions appeared in the HfO_2 phase. The shape of RE-related PL spectra followed the structural transformation. Narrow RE-related PL peaks were detected in the samples annealed at 1000 fr 30-60 min that

confirms the location of RE ions in the phase with a high crystal field. The peculiarities of PL spectra and the mechanism of PL excitation and its changes with the phase separation for different films are discussed.

2:50 PM EL19.13.06
Structural, Magnetic, and Magnetocaloric Study of Rare-Earth Doped $Pr_{0.5}RE_{0.1}Ca_{0.4}MnO_3$ (PRECMO) (*x*=0.1; RE = Y, Nd, Sm, Eu, and Gd) Manganite Nanoparticles Synthesized via Autocombution Method Jolaikha Sultana[1,2]; [1]The University of Memphis, United States; [2]The University of Arkansas, United States

Perovskite manganites having the general formula, $R_{1-x}A_xMnO_3$ (where R is a rare-earth ion and A is an alkaline-earth ion) have been considered as potential candidates for magnetic refrigeration based on MCE because of the large magnetic entropy change at moderate fields. Also their extraordinary chemical stability and tunable phase transitions are also added advantages to choose manganites for magnetic refrigeration applications. The study reports the structural, magnetic, and magnetocaloric effect in rare-earth-doped Perovskite manganite $Pr_{0.5}RE_{0.1}Ca_{0.4}MnO_3$(*x*=0.1; RE=Y,Nd, Sm, Eu,Gd), PRECMO. The powder samples were prepared by a facile autocombution method followed by annealing at 1100 degree celsius for 12 hours. Structural characterization was done through XRD, SEM, and FTIR analysis. XRD pattern reveals that all the PRECMO samples crystallize in the perovskite phase with an orthorhombic structure (space group Pnma). The lattice parameter of the powder samples was calculated from the XRD pattern refinement, which showed a decrease in lattice parameter and volume upon rare-earth substitution in Nd<Sm<Eu<Gd<Y order. This systemic change in the lattice volume is the result of the lanthanide contraction of RE ionic radii. FTIR spectra identify the characteristic Mn–O bond stretching vibration mode near 600 cm^{-1}which shifts toward high wavenumbers due to distortion of the MnO6 octahedron with RE substitution. Field-cooled (FC) and zero-field cooled (ZFC) magnetization were measured at 100 Oe. The magnetic phase transition temperature for all RE^{3+} doped manganite lies below 100 K. Isothermal magnetization curves were investigated in the temperature range of 5-300 K in fields up to 5T. All RE^{3+} doped samples showed paramagnetic behavior at RT and ferromagnetic behavior at 5K. Nd-doped PRECMO showed maximum magnetization of 65 emu/g, followed by Eu, Gd, Y, and Sm. The purpose of this work is to investigate the magnetocaloric effect for low-temperature magnetic refrigeration applications. The magnetic isotherms are being investigated to derive the compound's maximum entropy change and relative cooling power.
Authors: J. Sultana, Santosh Karki Chhetri, Dr. J. Hu, Dr. S. R. Mishra.

2:55 PM *EL19.13.07
Advanced 3D Printing Techniques for Future Electronics Yang Yang; University of Technology Sydney, Australia

The race to develop next-generation wireless electronics is accelerating at a rapid pace. Thanks to additively manufactured electronics (AME) technology, fast-prototyping, low-entry-cost, and in-house short-run manufacturing empower millions of start-ups and companies with demanding confidentiality and accelerated innovation. We aim to build a new class of multi-beam packaged antennas and miniaturized circuit designs to advance the knowledge for next-generation (5G) mobile devices. Compact and low-cost 3D printed antennas and circuits will be delivered to circumvent the limitations of today's mobile antennas, which are usually bulky and not compatible with future ultrafast wireless communications. The proposed AME antennas and microwave circuits should be easily integrated into mobile devices linking billions of high-speed wireless systems in a dynamic environment. New antenna prototypes with multiple dynamic beams will be created for emerging intelligent and immersive technologies, e.g. unmanned vehicles, ultra-low latency virtual reality, smart cities, and seamless telepresence on the move.

SESSION EL19.14: On-Demand Presentation
Friday Morning, April 28, 2023
EL19-virtual

8:00 AM EL19.07.11
Threshold Voltage and Memory Window Engineering of Surface Modified $Ti_3C_2T_x$ Mxene Memristor for Memory and Neuromorphic Computing Navaj B. Mullani and Jun Hong Park; Gyeongsang National University, Korea (the Republic of)

Mxenes, a new type of two-dimensional material, have attracted extensive interest in memory and artificial synaptic device application because of its excellent electrical and chemical properties. In this work, the conductivity of Mxenes is engineered to enhance the switching of the device with addition of functional groups, via the etching and oxidation processes. The exceptional properties of partially oxidized MXene ($Ti_3C_2T_x$) memristors have shown a large memory window and decreased threshold bias; on the nanosecond scale, we emulated the complex spike time-dependent plasticity-dependent synaptic rules using electrical pulses. The low threshold voltage, steady retention time (10^4 s), clearly distinguishable resistance states and high ON/OFF rate ($>10^6$) are the main memory-related attributes of this device. Furthermore, the physical origin of electronic transport in this device is found to occur by a filamentary resistive switching mechanism, as determined by analyzing the atomic/kelvin probe force microscopy and modelled electrical fittings. The image edge detection ability of the synaptic device is also revealed by using a convolutional neural network. Therefore, the present functionalization method for Mxene memristors can facilitate the essential manufacturing complexity of high-density non-volatile memory storage and artificial synapse system.

SYMPOSIUM

April 11 - April 13, 2023

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SESSION EL20.01: Radiation I
Session Chairs: Ardalan Armin and Nicola Gasparini
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3010

10:30 AM *EL20.01.01
Enhancing Functionalities of 2D and 2D/3D Hybrid Perovskite Films as Ionizing Radiation Detectors Beatrice Fraboni[1,2]; [1]Univ of Bologna, Italy; [2]INFN, Italy

The demand for large area, low cost and flexible high-energy radiation detection systems for medical imaging and public security, has pushed the research to develop novel detectors combining high sensitivity and low-cost fabrication processes. Recently, lead-halide perovskites emerged as a very promising novel class of materials for X- and gamma-ray detection. Their success can be attributed to the excellent perovskite optoelectronic properties. The presence of heavy elements like Pb, Br or I inside the lead-halide perovskite structure ensures a high effective atomic number, resulting in a high absorption coefficient in the ionizing radiation energy range. For efficient detection, high absorption is not enough, the charge transport properties of the material also play a crucial role. Diffusion length of over 1µm and long lifetime of carriers have been attributed to perovskite even in polycrystalline form. Moreover, perovskites can be fabricated also in thin-film form at low temperature from solution opening the possibility to low-cost, large-area and flexible detectors. Flexible detectors are extremely appealing because they open completely new and unexplored functionalities and markets such as wearable electronics, smart walls, and nuclear waste pipe testing for industrial and citizens' security, cultural heritage, and space applications.

We discuss how to improve the functionality as ionizing radiation detection of high-performing metal halide perovskites, targeting in both cases tens of microns perovskite active layer thickness and easily assembling onto flexible substrates: i) 3D perovskites, methylammonium lead triiodide (MAPbI3) and methylammonium lead tribromide (MAPbBr3), pure or in blends; ii) 2D/3D blends obtained by mixing 3D MAPbBr3 and 2D (based on larger organic ammonium cations) structure perovskites such as (PEA)2PbBr4; iii) 2D layered perovskites, (PEA)2PbBr4. Simple planar devices were fabricated on flexible substrates with the above detailed materials and their performances as ionizing radiation detectors have been tested under 40-150kVp X-ray beams and under MeV proton irradiation, also assessing their behaviour and stability for continuous operation at constant irradiation and bias.
We report on a detailed study on the relation between composition and electronic transport at the nanoscale, a key factor in polycrystalline thin films, carried out by comparing simultaneously acquired XRF (X-Ray Fluorescence spectroscopy) and XBIC (X-Ray Beam Induced Current). Finally we will discuss preliminary results on deep electronic levels in 2D (PEA)2PbBr4 obtained by Photo-Induced Current Transient (PICTS) analyses, a powerful tool to understand the role of electrically active defects in optoelectronic grade materials

11:00 AM EL20.01.02
Highly Efficient Organic Metal Halide Hybrid Scintillator Tunde B. Shonde[1], Maya Chaaban[1], He Liu[1], Oluwadara J. Olasupo[1], Azza Ben-Akacha[1], Fabiola G. Gonzalez[1], Kerri Julevich[1], Xinsong Lin[1], J.S. Raaj V. Winfred[1], Luis M. Stand[2], Mariya Zhuravleva[3] and Biwu Ma[1,1]; [1]Florida State University, United States; [2]The University of Tennessee, Knoxville, United States; [3]University of Tennessee, Knoxville, United States

Scintillators, which could convert high energy ionizing radiations to visible light photons, have recently seen surges of applications in various areas, ranging from nuclear substance monitoring to medical imaging and many industrial control systems. While a variety of materials, including inorganic single crystals, organic molecules, and plastics, have been developed for radiation scintillation, all of them have their own drawbacks and there is not yet a single material that possesses a combination of high radiation absorption, high light yield, fast responsivity with short decay lifetimes, and low cost of mass production.
In this talk, I will introduce a new design concept for the development of organic-inorganic hybrid scintillation materials that could be facilely prepared via low-temperature processes and exhibit high light yields with short decay lifetimes. For the proof of concept, a zero-dimensional (0D) organic metal halide (4-(4-(diphenylamino) phenyl)-1-(propyl)-pyrindin-1ium zinc bromide (TPA-P)$_2$ZnBr$_4$) exhibiting yellowish-green emission peaked at around 550 nm has been designed, synthesized, and fully characterized. Unlike previously reported organic metal halide hybrids with metal halides as emitter, (TPA-P)$_2$ZnBr$_4$ has high Z metal halides acting as X-ray sensitizer and aggregation-induced emission (AIE) organic cations as emitter. As a result, dramatically enhanced X-ray scintillation of TPA-P$^+$ is achieved via sensitization by ZnBr$_4^{2-}$. A light yield of 36,200 Photons/MeV is achieved for this 0D hybrid material, which is significantly higher than that of anthracene (~15,000 Photons/MeV) and comparable to those of inorganic scintillators, while the photoluminescence and radioluminescence decay lifetimes of 3.56 ns and 9.96 ns respectively are similar to those of pure organic scintillators. Moreover, the high light yield to decay time ratio of 3,634 Photons/MeV×ns and low detection limit of 21.3 nGy$_{air}$s^{-1} are among the best values achieved to date for all kinds of scintillation materials. Our work provides a new strategy to achieve molecular sensitization in ionically bonded organic-inorganic hybrid systems and expands the utility and tunability of functional organic molecules in these hybrid systems for useful optoelectronic applications.

11:15 AM *EL20.01.03
Evaluation of Perovskite for MeV Neutron Detection Wyatt Panaccione[1], Zhifang Shi[2], Praneeth Kandlakunta[1], Jinsong Huang[2] and Lei R. Cao[1]; [1]Ohio State Univ, United States; [2]University of North Carolina at Chapel Hill, United States

The detection of thermal neutrons or neutrons with energy in the order of eV is relatively easy because of their high interaction cross-sections with a few conversion elements (e.g., boron, lithium, cadmium of gadolinium, etc). But neutrons are produced in the MeV range in the most commonly used reactions. To take advantage of high cross-section, they have to be slowed down through the neutron-hydrogen scattering process in a bucky moderator. This work explores the direct detection of fast neutrons by neutron-hydrogen scattering reaction in perovskite. We firstly tried the experimental characterization of the electric current response of perovskite solar cells using a MeV fast neutron beam at the Ohio State University Nuclear Research Reactor. We then fabricated the Methyl-hydrazinium Lead Chloride (CH3NH2NH2PbCl3, MHyPbCl3) with a high atomic loading of hydrogens for their transient current response to a time modulated fast neutron beam with 1E7 neutron per cm^2 per second. Additionally, we studied the mechanism of X-ray induced damage in the hybrid halide perovskites where self-healing effect was observed. The threshold electron energies from X-ray interactions to cause the displacement of I- is in a range of 4.6 - 34.6 keV, which is far exceeding its activation energy (0.08 to 0.62 eV).

11:45 AM EL20.01.04
X-Ray Detectors with Ultrahigh Sensitivity Based on High Performance Printed Organic Field Effect Transistors Laura Basiricò[1,2], Ilaria Fratelli[1,2], Andrea Ciavatti[1,2], Adrián Tamayo[3], Carme Martinez-Domingo[3], Paolo Branchini[2], Elisabetta Colantoni[2], Zachary Lamport[4], Stefania De Rosa[2], Luca Tortora[2], Adriano Contillo[5], Raul Santiago[6], Stefan T. Bromley[7], John Anthony[8], Ioannis Kymissis[4] and Beatrice Fraboni[1,2]; [1]University of Bologna, Italy; [2]National institute for nuclear physics, Italy; [3]Campus de la Universitat Autònoma de Barcelona, Spain; [4]Columbia University, United States; [5]Elettra-Sincrotrone Trieste, Italy; [6]Universitat de Barcelona, Spain; [7]Institució Catalana de Recerca i Estudis Avançats, Spain; [8]University of Kentucky, United States

In the last decade organic semiconductors have demonstrated to be excellent candidates for the development of a new class of X-Ray detectors able to fulfil important emerging requirements such as the mechanical flexibility, the possibility to cover large and curved surfaces, low-cost, and low-bias operation. Moreover, they are the only material platform that can offer human tissue equivalence, i.e. due to their chemical composition (i.e. low-Z elements) organic materials have radiation absorption comparable to that of human organs and tissues. This is a highly desirable property for a dosimeter to be employed in the medical field since it avoids complex calibration procedures and the perturbation of the radiation beam when the detector is placed between the radiation source and the patient. In this study we propose a double strategy to achieve ultrahigh sensitivity to X-rays by fully organic direct X-ray detectors. We exploited two different advanced printing techniques to deposit the active layer of the organic X-Ray detectors in a fully controlled way obtaining highly performant Organic Field Effect Transistors (OFETs). This approach allowed us to boost the detecting efficiency by means of both the improvement of the collection/transport properties of the devices and the deep comprehension, identification and control of the active trap states ruling the photoconductive gain mechanism of the thin film-based detectors. We deposited blends of polystyrene (PS) with the organic semiconducting small molecule 1,4,8,11-tetramethyl-6,13-triethylsilylethynyl pentacene (TMTES) by Bar Assisted Meniscus Shearing technique.[1] The molecular structure of this material is similar to TIPS-Pn ((6,13-bis(triisopropylsilylethynyl)-pentacene)), however, the BAMS deposited thin films crystallize in a totally different, and more efficient, crystal packing (i.e., herringbone packing motif). This resulted in OFETs that reached very high mobilities of up to 2.5 cm^{2}V^{-1}s^{-1} and showed a reduced density of interfacial hole traps thanks to vertical segregation of the polystyrene at the semiconductor/dielectric interface and the consequent passivation of defects. In the second case [2] we deposited organic thin films of TIPS-Pn and TIPG-Pn (analogous molecule where the two Si atoms have been substituted with two Ge atoms) by Pneumatic Nozzle Printing. This printing procedure allowed to tune the morphology and packing of the film, to selectively vary key features related to trap states affecting the charge transport and collection and, ultimately, the detecting mechanism. We investigated electrically active traps for minority carriers by Photocurrent Spectroscopy with Optical Quenching. This technique allowed to identify the excitonic peaks which induce the inner amplification mechanism under X-ray exposure. Thanks to the activation of the photoconductive gain effect induced by the simultaneous presence of UV-vis and X-Ray photons, we experimentally assessed for the first time the presence and role of electrical traps for minority carriers responsible for this physical phenomenon. By these strategies, exceptional high sensitivities both for rigid and flexible devices ((4.10 ± 0.05) 10^{10} µC Gy^{-1} cm^{-3} and (9.0 ± 0.4) 10^{7} µC Gy^{-1} cm^{-3} respectively) for X-ray detection are achieved, which are the highest reported so far for direct X-ray detectors based on tissue equivalent full organic active layer, and higher than most perovskite film-based X-ray detectors. As a proof of concept to demonstrate the high potential of these devices, an X-ray image with sub-millimeter pixel size is recorded employing a 4-pixel array. This work highlights the potential exploitation of high performing OFETs for future innovative large-area and highly sensitive X-ray detectors for medical dosimetry and diagnostic applications.
[1] Tamayo et al., Adv. Electron. Mater. 2022, 2200293
[2] Fratelli et al., Adv. Mater. Technol. 2022, 2200769

SESSION EL20.02: Radiation II
Session Chairs: F. Pelayo García de Arquer and Jinsong Huang
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3010

1:30 PM *EL20.02.01
Room Temperature γ-Rays and X-Ray Detection with CsPbBr$_3$ Perovskite Mercouri G. Kanatzidis; Northwestern University, United States

Highly sensitive hard radiation detectors operating at room temperature are in high need for a wide variety of applications. The perovskite semiconductor CsPbBr$_3$ exhibits a high spectral resolution of γ-rays at room temperature. CsPbBr$_3$ is air-stable, non-hygroscopic, and possesses high effective atomic number Z-eff of 65.9. An overview of the research progress on the bulk CsPbBr$_3$ crystals studied so far and detector fabrication and characterization of single crystals will be presented. Highly pure CsPbBr$_3$ single crystals with high quality can be grown using the Bridgman method. CsPbBr$_3$ perovskite's defect tolerance tends to screen electrically activated defects, enabling the carriers' remarkable transport properties. Our CsPbBr$_3$ detector has shown remarkable energy resolving capability under both X and γ rays, particularly in achieving 3.9% (4.8 keV, FWHM) energy resolution for 122 keV ^{57}Co γ-ray with good temporal stability. The hole carrier lifetime in CsPbBr$_3$ detector-grade single crystal was observed to be well over 25 µs. Pixelated devices can resolve ^{137}Cs 662-keV γ-rays with ~1% energy resolution. Results from synchrotron X-ray detection experiments with flux of 10^6 to 10^{12} photons/s/mm^2 at 58.61 keV, operating in current mode, will also be presented.

2:00 PM EL20.02.02
Halide Perovskite@Metal-Organic Frameworks Composites for Highly Stable, Low-Noise High Energy Direct X-ray Detectors Hayden Salway, Elena Avila, Ganbaatar Tumen-Ulzii, Oliver Moseley, Samuel D. Stranks, David Fairen-Jimenez and Miguel Anaya; University of Cambridge, United Kingdom

Halide perovskites one of the most promising materials for next-generation, highly sensitive, low-noise, direct high energy X-ray detectors due to their excellent optoelectronic properties including bandgap tunability, high photoluminescence quantum yields (PLQY), defect tolerance and chemical versatility. However, challenges for the successful commercialization of halide perovskites X-ray detectors remain. For example, processing halide perovskites into thick devices for optimal X-ray attenuation, without introducing defects via pressing, or mixing with polymer membranes represents one set of challenges. Further, to realize highly sensitive, low-noise detectors requires novel material choices to reduce dark currents, minimize current drift and enhance stability.

MOFs are another kind of materials which have started the gather attention as promising x-ray detectors, due to their ease of processing and chemical versatility enabling incorporation of high Z atoms and maximizing attenuation efficiencies.[1] Further, recent advancements in sol-gel MOF processing have enabled us to develop high-density MOF structures through advanced synthesis and densification, resulting in size controllable high-density materials with large attenuation efficiencies for high energy X-rays .[2] Recently, halide perovskite@metal-organic framework (PVKs@MOFs) composites have been successfully synthesized, which enhance perovskite stability and provides opportunities to harness the properties of multiple materials, overcoming the challenges of dark currents and thick film processing for highly stable X-ray detectors. [3]

In this work, we present the first of its kind PVK@MOF direct X-ray detector. Our unique synthesis approach formed halide perovskite nanocrystals via direct conversion from a sol-gel Pb MOF, resulting in a size and shape controllable PVK@MOF composite. This process can be tailored to the required X-ray energies for applications in radiography, CT, and PET scanning. The intrinsically insulating Pb MOF resulted in a composite with high resistivity and significant reduction in dark current. In addition, it maintained high current densities and sensitivity resulting from charge carriers generated upon X-ray excitation of perovskite nanocrystals within the composite. Moreover, reproducible medical imaging requires device resistance to current drift. In this regard, halide perovskites often see large dark current drifts due to strong ion migration effects, thus requiring long pre-biasing before optimally functioning. However, our PVK@MOF composite showed a significant reduction in dark current drift compared to the equivalent standalone perovskite detector, which we attribute to the rigid MOF structure limiting ion migration effects. We further present a full direct X-ray detector material characterisation framework using our PVK@MOF composite, demonstrating the full range of device performances which can be achieved by varying incident properties. The methodology of this work will lay the foundations for further device performance characterisation, removing ambiguity from current performance metrics and significantly advancing the application and commercialisation of halide perovskite X-ray detectors.

References:
[1] Perego, J., Villa, I., Pedrini, A. et al. Composite fast scintillators based on high-Z fluorescent metal–organic framework nanocrystals. Nat. Photonics 15, 393–400 (2021).
[2] Tian, T., Zeng, Z., …, Fairen, D. A sol–gel monolithic metal–organic framework with enhanced methane uptake. Nat. Mater. 17, 174–179 (2018).
[3] Avila, E., Salway, H., …, Stranks, S.D., Anaya, M., Fairen-Jimenez, D. Metal-organic framework/halide perovskite composites for stable x-ray scintillators. [Submitted]

2:15 PM *EL20.02.03
Quasi-2D Perovskite Photo-Diode for X-Ray Sensing Wanyi Nie; Los Alamos National Laboratory, United States

Polycrystalline perovskite film-based X-ray detector is an appealing technology for assembling large scale imager by printing methods. However, thick crystalline layer without trap and solvent residual is challenging to fabricate. First, I will introduce the solution method for the thick perovskite layer fabrication suitable for X-ray sensing. By introducing n-butylamine iodide into methylammonium lead iodide precursor and coating at elevated temperatures, compact and crystalline layers with exceptional uniformity are obtained on both rigid and flexible substrates. Photodiodes built with the quasi-2D layers exhibit low dark current and stable operation as well as a high X-ray sensing performance. Next, I will present our recent achievements in stabilizing the 2D perovskite photo-diode under electrical field stress. We found that the moisture in the environment can trigger voltage induced device failure. To circumvent this problem, we incorporated a hydrophobic interface layer to stabilize the device. As a result, the detector can stand for high electrical field stress that deliver high X-ray sensing efficiencies.

2:45 PM EL20.02.04
Thickness-Controlled Large Area (over 2500 cm^2) Perovskite Single Crystal for X-Ray Imaging Applications Youngseung Choi[1], Min Kyu Kim[1], Kang Heo[2], Dooho Kim[2] and Byungha Shin[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Vieworks, Korea (the Republic of)

In recent years, metal halide perovskite (MHP) has been actively studied in the fields of solar cells, light emitting diodes and X-ray detectors due to its excellent optical properties. In particular, large diffusion length, high resistivity, high attenuation coefficients and tunable band gap make MHP as an attractive candidate as a photon-absorber for direct x-ray detector application. Furthermore, MHP in the form of single crystal is attracting a lot of attention due to its lower defect density and higher mobility-lifetime product values than MHP thin films.

However, there still exist several issues to be addressed for MHP single crystal to be incorporated into commercial X-ray detectors. The primary issue is the synthesis of large-area single crystals while keeping its thickness on the order of mm—a thicker absorber will reduce charge collection efficiency and a thinner absorber causes insufficient X-ray absorption. In a conventional solution method of growing MHP single crystal, where a single crystal grows in free-standing configuration, the growth along the lateral dimensions is accompanied by the increase of the thickness. In order to utilize a free-standing single crystal for x-ray imaging, the crystal must be sliced or grinded into a smaller thickness, during which there is a high risk of crack formation or fracture due to highly brittle nature of MHP single crystal. In addition, a considerable amount of the material is wasted.

In this study, we designed a novel growth apparatus that allows us to grow MHP single crystals as large as 50 mm X 50 mm while limiting the thickness to 1 mm with no need for post-processing to reduce the thickness to apply for X-ray detectors. We fabricated X-ray detectors with our large-scale and thin single crystal and they exhibited an excellent sensitivity of 3.0x104 μC Gyair−1 cm−2. Thin film transistor panel integrated X-ray detector was also fabricated for large-scale imaging. The details of the synthesis of MHP single crystals as well as device characterizations will be discussed.

3:00 PM BREAK

SESSION EL20.03: Photomultiplication Photodetectors
Session Chairs: Rene Janssen and Vincenzo Pecunia
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3010

3:30 PM *EL20.03.01
Designs for Upconversion and Photomultiplication in Organic Shortwave Infrared Detectors Tse Nga Ng; University of California, San Diego, United States

The shortwave infrared spectral region is particularly powerful for a variety of applications including environmental monitoring and medical diagnosis, enabling greater penetration depth and improved resolution in comparison to visible light. Upconversion imagers that combine photosensing and display in a compact structure are attractive since they avoid the costly and complex process of pixilation. This talk will present the designs of polymeric upconversion imagers that combine photo-sensing and display in a compact structure, to enable visualization to 1300 nm. The photoresponse exhibited a high external quantum efficiency of 35% at a low bias of ≤ 3 V with –3 dB bandwidth of 10 kHz. The large active area of 2 cm^2 enabled demonstrations such as object inspection, imaging through smog, and concurrent recording of blood vessel location and blood flow pulses. The organic photodetectors are further improved by incorporating a new heterojunction interlayer to trigger trap-assisted photomultiplication. The interlayer served to suppress the dark current and enhance the photoresponse, leading to a detectivity of 10^10 Jones at -1.5 V and improves the contrast of an upconversion imager by 2x.

4:00 PM EL20.03.02
Photomultiplication Organic Photodetectors with High and Bias-Independent Specific Detectivity Shen Xing, Jonas Kublitski, Christian Hänisch, Louis C. Winkler, Hans Kleemann, Johannes Benduhn and Karl Leo; TU Dresden, Germany

Highly responsive organic photodetectors are of interest for imaging, health, and security monitoring applications. Photomultiplication organic photodetectors (PM-OPDs) are an ideal option due to the excellent sensitivity given by their internal amplification mechanism. However, for most PM-OPDs, the specific detectivity is likely to be sacrificed under reverse bias since a large operation voltage is usually required to obtain high sensitivity, but is usually accompanied by high shot noise. Here, we propose a fully vacuum-processed PM-OPD based on the low donor BDP-OMe:C_{60} material system. With the trap-induced interfacial bending of energy levels, the electrons can be efficiently injected via tunneling under only -1 V, leading to an external quantum efficiency of over 100% and a superior specific detectivity of $\sim 10^{13}$ Jones. More importantly, this high detectivity is almost independent of the increasing reverse voltage up to -10 V in the near-infrared spectral region. The bias-independent specific detectivity, high responsivity, and fast response speed prove the great potential of PM-OPDs.

4:15 PM *EL20.03.03
Molecular Switch-Embedded Organic Photodiode for Active Matrix Image Sensor Dae Sung Chung; POSTECH, Korea (the Republic of)

We suggest a strategy to artificially widen the linear dynamic range (LDR) of an organic photodiode (OPD) by introducing a light-intensity-dependent transition of its operation mode, such that a low saturation photocurrent can be overcome by additional operation mechanism. The active layer of OPD is doped with a strategically designed and synthesized molecular switch, which shows typical OPD performances with an EQE < 100% under low-intensity light illumination and photomultiplication behaviors with an EQE > 100% under high-intensity light illumination, resulting in an artificially extended LDR up to 225 dB. Such unique and reversible transition of the operation mode by light intensity self-recognition of molecular-switch-embedded OPDs can be explained by charge trapping/detrapping behavior of closed/open isomers of the molecular switch as well as the unbalanced quantum yield of the photocyclization/photocycloreversion of the molecular switch. To prove the suggested operation mechanism, various molecular switches with various functional groups are studied in conjunction with various photophysical analyses.
Regarding the suggested mechanism, we show that the fluorinated benzene group in the molecular switch is responsible for the formation of interfacial band bending at the interface between the semiconductor and itself, resulting in exciton quenching and electron trapping. In general, such unprecedented exciton quenching and electron trapping may degrade the performance of organic electrons, but in certain applications, these phenomena can be positively utilized. An example suitable for this application is a photomultiplication-type organic photodiode (PM-OPD). The operating mechanism of PM-OPD can be divided into two stages. First, photogenerated excitons are separated at the donor-receptor interface, electrons are trapped by spatially localized trap centers, and remaining holes are transited to the collecting electrode. Second, trapped electrons near the anode interface induce band bending, resulting in hole injection to generate photomultiplication. In other words, molecular switches embedded in OPD become such trapping centers under high-intensity light illumination and regains its original neutral properties under low- intensity light illumination.
After carefully optimizing dynamics of the light-intensity-dependent transition of operation mode of the suggested molecular-switch-embedded OPDs, these unique OPDs are integrated onto CMOS chip to demonstrate organic image sensors with superior sensitivity against strong light illumination.

SESSION EL20.04: Intrinsic Dark Current Limits

Session Chairs: Ardalan Armin and Nicola Gasparini
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3010

10:15 AM *EL20.04.01
New Device Architectures and Performance Limiting Factors of Organic Near-Infrared Detectors Koen Vandewal; Hasselt University, Belgium

Organic photodetectors (OPDs) with a performance comparable to that of conventional inorganic ones have been demonstrated for the visible regime. However, near-infrared (NIR) photodetection has proven to be challenging and, to date, the true potential of organic semiconductors in this spectral range (800–2500 nm) remains largely unexplored. In this talk, I will introduce new device concepts for organic NIR detectors, based on resonant optical cavities and doped photo-active layers. Design rules and optimization strategies will be discussed, yielding wavelength selective devices (20 nm resolution) with a tunability of the detection wavelength over several hundreds of nanometers, allowing the printing of miniature NIR spectrometers. In a second part of the talk, we explore the performance limitations of organic NIR detectors: A relation between open-circuit voltage, dark current, and noise current is demonstrated for OPDs with detection wavelengths beyond 1100 nm. Based on these findings we estimate an upper limit of achievable specific detectivity values for organic photodiodes as a function of their longest NIR detection wavelength.

10:45 AM EL20.04.02
On the Role of Mid-Gap Trap States in Organic Photodetectors Stefan Zeiske[1], Oskar Sandberg[1], Nasim Zarrabi[1], Christina Kaiser[1], Sam Gielen[2], Wouter Maes[3], Koen Vandewal[2], Paul Meredith[1] and Ardalan Armin[1]; [1]Swansea University, United Kingdom; [2]Hasselt University, Belgium; [3]IMEC, Associated Lab IMOMEC, Belgium

Photodetectors derived from organic, semi-crystalline and amorphous semiconductors receive significant interest in the optoelectronic research community, industry, and consumer electronics. Their UV-to-NIR tuneable and narrow spectral responses, detectivities comparable with silicon and other crystalline semiconductors, and low embodied energy manufacturing with the potential of flexible application form factors offer great potential in next generation light sensing and imaging applications, such as wearable and building integrated electronics, or the internet of things. In any photodetector, the dark current is a critical parameter limiting the sensitivity at low light intensity and thus, defining the maximum achievable signal-to-noise. Organic photodetectors, in particular, are characterized by intrinsically high dark currents orders of magnitude higher than expected for thermally excited band-to-band transitions, the origins of which are still subject of current debate. Here, we find the dark current in organic semiconductor photodetectors to be universally mediated and thus limited by mid-gap trap states. We derive a diode equation based on Shockley-Read-Hall statistics and determine a revised upper limit for the specific detectivity of organic photodetectors. Finally, we present a method to overcome the limitations of those mid-gap trap states. Our results deliver new insight on the origin of performance- and sensitivity-limiting noise in organic light-harvesting applications, such as photodiodes and detectors.

11:00 AM EL20.04.03
Tuning Perovskite Composition for Low Dark Current and High Specific Detectivity Photodetectors Francesco Furlan, Davide Nodari, Matthew J. Fuchter and Nicola Gasparini; Imperial College London, United Kingdom

Organo-metal halide perovskites have gained attention for their remarkable optoelectronic properties, which made them an ideal material for photodetectors (PDs). In particular, modern PDs require to be cost-effective, self-powered, highly sensitive and flexible, all conditions that can be fulfilled by using a perovskite-based active layer.
The route to obtain highly sensitive sensors requires minimizing dark current (J_d) values, which limits the noise (i_n) in devices and maximizes light conversion. To date, few methods exist to reduce the dark current in perovskite PDs. They are based on the use of charge-blocking layers to minimize charge injection[1]. Other strategies are related to inclusion of additives or controlling film crystallization[2] to minimize backward charge injection at the electrodes. However, there is a deficit of efforts focused on understanding the role of perovskite composition and its correlation to device J_d.
In recent years, compositional engineering has played a fundamental role in developing perovskite solar cells, enabling higher device efficiencies, an adjustment of film defect densities and longer stabilities[3]. In this work[4], we study the effect of tuning the perovskite composition and report the performance of PDs fabricated with these active layers. We obtained ultra-low J_d values of 1.3×10^{-9} A cm^{-2} at –0.5 V with specific detectivity approaching 10^{13} Jones. Moreover, we observe for the first time a linear relationship between the J_d of devices and their V_{oc} over the 0-15 % Br range.
With a combination of optoelectronic measurements, transient analyses, impedance spectroscopy and morphological investigations, we attributed the low J_d of the of the 15% Br containing devices to the reduction of trap states, a better charge extraction of photogenerated carriers and an improvement in photoactive layer morphology and crystallinity.
Therefore, we demonstrate how compositional engineering of the active layer can be an alternative approach to conventional transport layer optimization to improve photodetector performances.

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11:15 AM *EL20.04.04
Understanding and Reducing Dark Currents in Perovskite Photodetectors Rene A. Janssen; Eindhoven Univeristy of Technology, Netherlands

Perovskite semiconductors offer the possibility of spectral sensitivity from the visible to the near infrared and can be used in future photodetection applications like image sensing,[1] optical communication, environmental and health monitoring, or chemical and biological detection. Perovskite photodiodes, however, often suffer from relatively high dark current densities under reverse bias. Among the common strategies to reduce dark current density, the inclusion of charge-blocking layers between the electrodes and the perovskite layer has become popular. While these blocking layers are successful in increasing the energy barrier for charge injection, the lower limits of dark current density reached experimentally remain typically orders of magnitude higher than the expected intrinsic bulk thermal-generated dark current density. By determining the activation energy of the dark current in optimized perovskite photodiodes with different bandgaps and employing a series of electron-blocking layers, we find that the activation energy corresponds to the energy offset between the highest occupied molecular orbital of the electron blocking layer and the conduction band minimum of the perovskite.[2] Increasing this energy offset by using an appropriate blocking layer, a perovskite photodiode was fabricated that has a wavelength sensitivity up to 1050 nm, combined with an ultralow dark current density of 5×10^{-8} mA cm^{-2} and noise current of 2×10^{-14} A Hz$^{-1/2}$.[2]
To further increase performance we employ low-dimensional perovskites. Perovskite thin films with a vertical gradient in dimensionality result in graded electronic bandgap structures that are ideal for photodiode applications. Positioning low-dimensional, vertically-oriented perovskite phases at the interface with the electron blocking layer further increases the activation energy for thermal charge generation and thereby effectively lowers the dark current density to a record-low value of 5×10^{-9} mA cm^{-2} without compromising responsivity, resulting in a noise-current-based specific detectivity exceeding 7×10^{12} Jones at 600 nm.[3] These multidimensional perovskite photodiodes show promising air stability and a dynamic range over ten orders of magnitude, and thus represent a new generation of high-performance low-cost photodiodes.[3]
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11:45 AM EL20.04.05
Chemical Fundamentals Defining The Intrinsic Detectivity Limits of Near-Infrared Organic Photodetectors Sam Gielen[1,2], Jochen Vanderspikken[1,2], Paul Meredith[3], Koen Vandewal[1,2], Ardalan Armin[3] and Wouter Maes[1,2]; [1]Hasselt University, Belgium; [2]imec, Belgium; [3]Swansea University, United Kingdom

Organic photodetectors (OPDs) with a performance comparable to that of the conventional inorganic ones have recently been demonstrated for the visible regime.[1] However, high performance near-infrared organic photodiodes are more challenging, as non-radiative recombination losses limit the specific detectivity (D^*), as well as the open-circuit voltage.[2] Besides, thermally excited transitions from mid-gap trap states further limit the dark current. Taking this into account, it can be concluded that OPDs have the potential to be a useful technology for wavelengths up to 2 μm, given that high external quantum efficiencies can be maintained at these low photon energies. To further elaborate on the fundamentals defining these limitations and investigate the (chemical) origin of mid-gap trap states, a next-generation of 'defect-free' organic semiconductors is synthesized. This allows to investigate the influence of specific material imperfections (end-capping, homocoupling defects, and metal impurities) on the material properties and device performance. In this contribution, we will give an overview of the synthetic approaches applied to produce the high performance near-infrared organic semiconductors, and show how defects and impurities have an impact on their intrinsic limits.

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SESSION EL20.05: Nano Crystals Photodetectors

Session Chairs: F. Pelayo García de Arquer and Jinsong Huang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3010

2:00 PM *EL20.05.01
Colloidal Quantum Dot SWIR Photosensors Edward H. Sargent; University of Toronto, Canada

I will update on the use of InAs colloidal quantum dots in achieving NIR and SWIR photon detectors.

2:30 PM EL20.05.02
Highly Responsive 2D/2D TMDC/Perovskite Hetero-Photodetectors through Photo-Gating Leon Spee[1], Julius Konietzka[1], Annika Grundmann[2], Michael Heuken[2,3], Holger Kalisch[2], Andrei Vescan[2] and Franziska E. Muckel[1]; [1]University Duisburg-Essen, Germany; [2]Compound Semiconductor Technology, RWTH Aachen University, Germany; [3]Aixtron SE, Germany

Photoconducting photodetectors convert light to current through light absorption in a conducting channel, which changes resistivity or conductivity temporally. This kind of light detection is needed in a wide field of different applications like optical communication, optical sensing in healthcare and different lifestyle applications. For some applications special device attributes like e.g. flexibility or minimized weight and volume are needed. One highly promising material class for the realization of lightweight flexible photodetectors are 2D materials, especially semiconducting transition metal dichalcogenides (TMDCs). They offer high mechanical flexibility combined with large in plane conductivities and low intrinsic carrier concentrations, enabling low dark currents. However, due to their intrinsically limited light absorption, high responsivities and sensitivities are hard to achieve.
A great way to increase those measures in a photoconductive device is introducing a gain mechanism. For a gain the minority charge carriers are usually trapped, while the other type of charge carriers circle through the channel multiple times, generating multiple carriers by a single incident photon. In addition, in 2D materials, the trapped charges can act as localized floating gate and strongly modulate the conductivity.
Here we propose a combination of a TMDC and microscopically structured 2D perovskite in a heterostructure to achieve a high-responsivity photoconductor exhibiting a gain mechanism. 2D perovskites crystalize as inorganic perovskite layers which are intrinsically separated by insulating intercalated organic cations, forming natural grown multiple quantum wells. As channel material we use MOCVD grown MoS_2 monolayer, in which the MoS_2 layer completely covers the substrate. A liquid phase prepared $(BA)_2PbI_4$ layer on top of MoS_2 is intended to form trap states for minority carriers (holes) in order to achieve a gating mechanism. Electron transfer is blocked due to the organic cations acting as electron blocking layer [1]. To prevent the transferred holes from reaching the contacts, the $(BA)_2PbI_4$ is realized as a non-continuous layer. The optical quality of both material classes is preserved in the heterostructure architecture. We investigated the transfer mechanism by conducting photocurrent spectroscopy on devices with and without $(BA)_2PbI_4$ layer on top of MoS_2 and we demonstrate an increased responsivity in the heterostructure compared to the monolayer MoS_2, which we attribute to photo-gaiting through unidirectional charge carrier funnelling. We show that with an optimized device architecture responsivities up to 20 A/W are possible, which corresponds to a gain of 38.

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2:45 PM BREAK

SESSION EL20.06: Wavelength Selective Photodetectors

Session Chairs: Ardalan Armin and Nicola Gasparini
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3010

3:30 PM *EL20.06.01
Nanostructured and Hybrid Materials Enabled Photodetection Technologies for Biomedical Applications Guodong Zhou[1], Yuanzhe Li[1], Chuan Liu[2], Shih-Chi Chen[1] and Ni Zhao[1]; [1]Chinese University of Hong Kong, Hong Kong; [2]Sun Yat-sen University, China

Optical sensors for biomedical applications typically have to operate under very weak light intensity due to strong scattering of photons by tissues of biological objects. To optimize the sensing performance, the photodetector units of the optical sensors should possess high detectivity and mechanical flexibility, thus allowing for efficient collection of photons over curved skin/tissue surfaces and with high signal-to-noise ratio. In this talk, I will introduce our recent efforts in developing photodetector structures with self-amplification mechanisms, which are particularly suitable for weak light biomedical applications. I will first talk about organic bulk heterojunction (BHJ) phototransistors with a tri-layer gate dielectric design to realize high fabrication reproducibility and excellent light bias stability. Such devices enabled us to demonstrate, for the first time, portable functional near-infrared spectroscopy (fNIRS) for brain monitoring. In the second part, I will extend the discussion to the comparison between polymer/fullerene and polymer/non-fullerene BHJ systems and analyze how the recent material development in the organic photovoltaic community can be leveraged to enhance the performance of organic photodetectors. Finally, I will focus on the commonly seen gain – bandwidth trade-off problem of photodetectors and introduce a monolithically integrated photovoltaic transistor (PVT) design to solve this dilemma. The PVT exploiting a lead halide perovskite as the photoactive layer achieved a record high gain – bandwidth product of ~ 10^{11}. The unique advantage of such devices for fNIRS and other weak light detection applications will be discussed.

4:00 PM EL20.06.02
A Tetrathienopyrrole-Based Ladder-Type Donor Polymer for Wavelength-Selective Organic Near-Infrared Cavity Detectors. Kaat Valkeneers[1,2], Quan Liu[1,2], Jochen Vanderspikken[1,2], Sander Smeets[1,2], Koen Vandewal[1,2] and Wouter Maes[1,2]; [1]Hasselt University, Belgium; [2]IMO IMOMEC, Belgium

Incorporation of compact spectroscopic near-infrared (NIR) light detectors into various wearable and handheld devices opens up various new applications, such as on-the-spot medical diagnostics. To extend beyond the detection window of silicon, i.e., past 1000 nm, organic semiconductors are highly attractive because of their tunable absorption. In particular, organic NIR wavelength-selective detectors have been realized by incorporating donor:acceptor thin films, exhibiting weak intermolecular charge-transfer (CT) absorption, into an optical microcavity architecture. In this work, a new ladder-type donor polymer, based on an extended dithienopyrrole unit, is investigated in blends with PC61BM as the acceptor. It is shown that extending the rigid backbone enhances the CT absorption and extends the detection range further into the NIR. This results in a full-width-at-half-maximum of 32-40 nm at wavelengths between 920 and 1450 nm, yielding detectivities in the range of 1.07 × 10^12 to 1.82 × 10^10 Jones, thereby outperforming the state-of-the-art PBTTT-based devices, both in terms of absorption range as well as efficiency.

4:15 PM *EL20.06.04
Defect Healing and Defect Metrology of WSe2 by Gate-Modulated Photoluminescence Doron Naveh; Bar-Ilan University, Israel

Defects in semiconductors have been at the focus of advanced materials research in the past century. Still, it is one of the most vibrant topics in materials research and particularly two-dimensional (2D) semiconductors. Spectroscopy and particularly photoluminescence is one of the main tools for inspecting 2D semiconductors, and in this work we have modulated the spectral measurements with a field effect potential in order to enhance the charge trapping and detrapping from point defects.
By performing gate modulated spectroscopy we determined a lower bound for the intrinsic defect density of CVD grown (and exfoliated WSe_2 samples. We demonstrated that a thin hBN buffer between the device and substrate eliminates hysteresis associated with injected holes.
Additionally, we performed a chemical healing process which replaces the oxygen defects with sulfur via adsorption of thiol molecules in solution and trimming of the carbon chains using rapid thermal treatment. We confirmed the efficiency of process in eliminating vacancy defects by XPS, cryogenic photoluminescence and by gate-modulated photoluminescence.
Lastly, we showed that the thermal detrapping process can be described as an activated reaction with an energy barrier of, which is an estimate for the defect states' electronic binding energy.

SESSION EL20.07: Poster Session: Photo and Radiation Detection with Organic, Perovskite and Nano-Crystalline Semiconductors
Session Chairs: Ardalan Armin, F. Pelayo García de Arquer, Nicola Gasparini and Jinsong Huang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL20.07.01
Boosting the Performance and Stability of All-Polymer Photomultiplication-Type Organic Photodiode: A Synthetic Approach Sangjun Lee[1], Gyeong Seok Lee[2], Mingyun Kang[1], Yeon Hee Ha[2], Yun-Hi Kim[2] and Dae Sung Chung[1]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Gyeongsang National University, Korea (the Republic of)

We demonstrate how achieving near-ideal spatial isolation of the polymer acceptor through a synthetic method can greatly improve not only the EQE but also the operational stability of an all-polymer photomultiplication-type organic photodiode (PM-OPD). Due to their extraordinarily high external quantum efficiency (EQE, often higher than 10,000%), photomultiplication-type organic photodiodes (PM-OPDs) have recently attracted a lot of attention and can be used as efficient self-amplifying photodiodes for the detection of weak light intensity. The trap-assisted photomultiplication mechanism in the PM-OPD is artificially activated, which sets it apart from traditional photovoltaic devices. The photoactive layer in a typical PM-OPD structure consists of a donor:acceptor (100:1, w:w) ratio to produce spatially segregated acceptor domains. Next, holes are gathered along the percolation pathway following the separation of photogenerated excitons at the donor/acceptor interface, and electrons are captured by the localized acceptor. Here, the Schottky barrier thins at the Al contact due to the trapped electrons, enabling hole injection through tunneling under reverse bias. Additional hole injection is necessary for current continuity; this is triggered by the narrowing of the Schottky barrier once a photogenerated hole is gathered by the counter electrode while the electron is still trapped. In order for PM-OPD to obtain a high EQE, "efficient electron trapping" is therefore a crucial requirement. In terms of effective electron trapping in PM-OPD, poly(3-hexylthiophene) (P3HT) as a donor and [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) as an acceptor have so far proven to be the most effective active layer combination. We hypothesize that this is mostly because the donor polymer semiconductors have better spatial distribution and localization of tiny molecule acceptors. We propose to address the simple phase separation of active layers with small molecular acceptors mixed with polymer donors during PM-OPD operation despite their high molecular diffusivity and the high operating voltage of a typical PM-OPD. To obtain not only a high EQE but also a high operational stability of PM-OPD, all-polymer bulk heterojunction (BHJ) should be researched in this regard, much like the organic photovoltaic field. Here, a series of naphthalenediimide (NDI)-based copolymers with variously alkylated benzenes are used in a synthetic method to examine the impacts of a polymer acceptor structure on PM-OPD performance. PNDI-Ph, PNDI-Tol, and PNDI-Xy were used as the polymer acceptors to create high-performance all-polymer PM-OPDs. PNDIs were subjected to systematic analyses using UV-vis absorption spectroscopy, density functional theory (DFT) calculations, and two-dimensional grazing-incidence X-ray diffraction (2D-GIXD). These analyses showed that structural features influence not only their optical, electrochemical, and microstructural properties but also their miscibility with donor polymers, and ultimately, the performance of the constructed all-polymer PM-OPD devices. This was demonstrated by effective Schottky barrier height measurement and drift-diffusion simulation. We showed that the crucial factor in the performance of an all-polymer PM-OPD device is spatial isolation of the acceptor domain inside the donor matrix, not high crystallinity or favorable electron transport characteristics. This led to the realization of an optimized PNDI-Xy based PM-OPD, which is greater than any previous all-polymer PM-OPD disclosed, with a high EQE of 770,000% and a high specific detectivity of 3.06 1013 Jones. We also discuss the improved operational stability of all-polymer PM-OPD devices against traditional small-molecule acceptor-based PM-OPD devices.

5:00 PM EL20.07.02
Imaging Carrier Redistribution in MoS_2 Photodetectors with Kelvin Probe Force Microscopy Woongbin Yim[1], Van Tu Nguyen[2] and Ji-Yong Park[1]; [1]Ajou University, Korea (the Republic of); [2]Vietnam Academy of Science and Technology, Viet Nam

The redistribution of charge carriers in monolayer MoS_2 photodetectors upon light illumination is investigated by surface photovoltaic measurements with

Kelvin probe force microscopy (KPFM). The surface potential changes with light illumination are related to the generation, diffusion, and recombination of photo-excited carriers in the photodetectors. It is found that photogenerated holes are trapped at the interface between MoS2 and the substrate, which is responsible for the device's photogating response. The photoresponse mechanism is further elucidated by temporal and spatial measurements of surface potential changes. The temporal response is consistent with the photogating mechanism as a major photoresponse mechanism in MoS2 photodetectors. The intensity-dependent measurements reveal the spatial distribution of defects in the devices. The result shows that KPFM is sensitive enough to probe in-plane as well as vertical charge carrier distribution in atomically thin materials.

5:00 PM EL20.07.04
High Responsivity Organic Phototransistors with Wide Absorption Spectrum for Underwater Optical Wireless Communication Lee Jeongmin and Kang-jun Baeg; Pukyong National University, Korea (the Republic of)

The technology of underwater communications can greatly enhance human's ability to study, monitor, and explore the ocean, as weall as to realize smart aqua farm, defense systems, and drone. Optical communication has the advantage of being able to communicate much faster than acoustic communication mainly used for underwater wireless communication and not being greatly affected by various noises. Therefore, optical communication is selected as an essential technology for underwater wireless communication. However, the unique characteristics under the surface of the sea present grand challenges to the development of wireless communication and networking system, including a harsh enviroment,severe attenuation, and multipath dispersion, and so on. Therefore, the photodetector must show high sensitivity even with weak light, and must be able to absorb light in a wide range. In this study, we aimed to manufacture a high-sensitivity organic phototransistor that showed high performance and high responsivity. Bulk hetero-junction organic phototransistors(OPTs) are fabricated from the profer combination of composite active layers consist of P-type electron donor organic semiconductor and an N-type non-fullerene electron acceptor. The bulk hetero-junction structure was used to maximize the separation efficiency of electrons and holes generated at the interfaces between the donor and the acceptor, indicating higher light response with light irradiation. This shows much higher excition dissociation efficiency than the layer-by-layer structure of the two materials. The bulk hetero-junction structure of the non-fullerene acceptor and the wide band-gap polymer material was well formed through AFM image by adjusting the donor and acceptor ratio. In addition, it was confirmed that the electrical characteristics of the Top-gate Bottom-contact TFT device showed high responsivity(>1A/W) even very weak light of 10μW(wavelength : 450nm~532nm) irradiation using a monochromator. The high sensitivity to light and the wide range of light absorption regions of the donor material showed high responsivity throughout the visible light region. It is expected that this high performance OPTs devices can be widely used like high-speed underwater optical communication fields such as underwater robots and drones, and is also expected to be used such as the marine defense industry and wide-area underwater communication network.

5:00 PM EL20.07.05
Dark Current Prevention and Fast Response of Efficient Injection Barrier Formation in Organic Photodetectors Woongsik Jang[1], Keum Hwan Park[2] and Dong Hwan Wang[1]; [1]Chung-Ang Univ, Korea (the Republic of); [2]Korea Electronics Technology Institute, Korea (the Republic of)

Complementary metal-oxide semiconductors (CMOS) image sensors include of photodetectors in pixel units. Organic photodetectors have in-built advantages in terms of chemically tailorable optical bandgap energy, lightweight components, solution and room temperature processable process via a specific molecular design. Specially, since the organic sensitive layers show excellent mechanical properties, curved and flexible design of photodetector is implemented. Despite many advantages of organic photodetectors, the dark current and noise current can induce degradation of detector performance. However, the source of dark current is unclear which of various contributions, such as electron flow through the junction, shunt leakage, thermionic emission, and tunnelling, are dominant.

In this research, we investigated source of dark current in organic photodetector structure consisting of photosensitive layers, interlayers, and electrodes. First, we introduce a non-fullerene acceptor to photodetector structure by comparing with a fullerene acceptor. The non-fullerene acceptor, eh-IDTBR leads to a high detectivity (1.61×10^{13} cm $Hz^{1/2}$/W) and a faster response time (2.7 μs) than those of fullerene acceptor ($PC_{71}BM$)-based photodetector. The eh-IDTBR can form higher injection barrier related with the excellent dark current suppression. In addition, the photodetector with eh-IDTBR shows excellent stability than the device with fullerene under continuous reverse bias and thermal stress.[1,2] Second, we apply carbon nanotubes as transparent anodic electrode. The carbon nanotubes reveal notable mechanical, optical, and electronic properties, which can realize curved and flexible organic photodetector structure with nearly 100% omnidirectional detection. The carbon nanotube electrode leads to a high detectivity of 2.07×10^{14} cm $Hz^{1/2}$/W, which is 100 times higher than that of device with the indium–tin oxide. The carbon nanotube electrode suppresses dark current to 9.62×10^{-13} A/cm^2 owing to its deep work function and high electron injection barrier. The flexible organic photodetectors are fabricated with the carbon nanotube electrode and operate stably after a bending test of 500 cycles.[2] Consequently, it is demonstrated the implementation of curved and flexible design by introducing the non-fullerene acceptor and the carbon nanotubes. This work sets a milestone in investigation of dark current and photo response for high-performance organic photodetectors.

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5:00 PM EL20.07.07
Photomultiplication Type Organic Photodetectors with Fast Response Speed by Introducing $CsPbI_3$ Perovskite Quantum Dot Interlayer Minyoung Jeong, Se Gyo Han and Kilwon Cho; Pohang University of Science and Technology, Korea (the Republic of)

Organic photodetectors (OPDs) are promising optical sensor that detects color and brightness by converting light energy into electrical energy. Recently, many researches on photomultiplication (PM) type OPDs have been studied, which have an external quantum efficiency (EQE) over 100%, so that even weak light can be detected. Most of the reported PM type OPDs are operated by a trap-assisted charge carrier tunneling injection mechanism, which require a large external voltage and consequently have relatively slow response time. Here, we fabricated PM type OPDs with fast response and low operating voltages enabled by exploiting the ionic motion of $CsPbI_3$ perovskite quantum dots (QDs). A $CsPbI_3$ QD monolayer is inserted as a PM inducing layer on the photoactive layer composed of PM6:Y6 bulk heterojunction. Our PM type OPD has an EQE over 2000 % and 2.8 μs response time (f_{-3dB} = 125 kHz) at the 3 V, and yields a large EQE-bandwidth product of Hz. It also shows over the 10^{12} Jones of specific detectivity which value is comparable to the specific detectivity of commercial Si photodiode.

5:00 PM EL20.07.08
Tunable Photoluminescence from the Stoichiometry of $AgInS_2$ Nanoparticles with 2D WSe_2/h-BN Hybrid Photodetector Jae-Hyeon Ahn, Somi Lee, Min-Hye Jeong, Derrick Allan Taylor and Jong-Soo Lee; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

The ternary I–III–VI nanoparticles, such as $AgInS_2$, $CuIn_S$, and $CuInS_2$, have been reported the future materials for optoelectronic devices. As one of these nanoparticles, environmentally benign silver indium sulfide nanoparticles (AIS NPs) have a significant absorption coefficient and strong photoluminescence quantum yield (PLQY) with a direct band gap. AIS NPs were synthesized by heating an Ag/In/S solution from 150 °C to 190 °C with various ratios to provide highly tunable photoluminescence (PL). The growth of crystal structure even at low temperatures (~80 °C) and the increased cation exchange of silver by indium at higher temperatures strongly influence the optical properties of the AIS NPs. The correlation between optical properties and synthesis parameters provided insights into the growth and stability of ternary NPs. Attempts to prepare stoichiometric and non-stoichiometric AIS NPs resulted in the tunable absorption and PL behavior as the hot-injection reaction product indicating that cation exchanges with Ag and In ions even when not directly incorporated in the initial reaction mixture. Control of the optical properties of these AIS NPs makes them potentially useful for applications in the photoelectric field, particularly in environmentally friendly electronics and wearable devices. In this study, we demonstrate that the photogenerated carriers formed from AIS NPs layers migrate to the WSe_2 layer and not only improve the photodetector performance but also enhance the photodoping effect of the WSe_2 layer with an ambipolar characteristic by holes injected from n-type AIS NPs. The results explain that the AIS NPs appeared to have high photosensitivity and stability under illumination. The high photosensitivity and stability of the hybrid photodetector indicate potential optoelectronic application.

5:00 PM EL20.07.10
Ab Initio Calculations of the Dielectric Function of $Eu_5In_2Sb_6$ for Light Dark Matter Detection Elizabeth Peterson, Priscila Rosa, Sean M. Thomas, Filip Ronning, Daniele Spier Moreira Alves, Christopher Lane and Jian-Xin Zhu; Los Alamos National Laboratory, United States

More than just answering an elusive question in fundamental physics, successful dark matter (DM) detection capabilities will have wide-ranging significance in the field of rare event detection, which makes this an exciting area of research for developing high-sensitivity detectors. Quantum materials with narrow meV-scale band gaps have recently emerged as promising targets for the detection of light DM in the largely unexplored mass range below MeV. The scattering and absorption rates of light DM with electrons in solid-state materials can be calculated with knowledge of the loss function, or the imaginary part of the inverse complex dielectric function, which in turn would enable prediction of the projected reach of a solid-state detector. To accomplish this from first-principles, it is critical to have accurate energy eigenvalues and the ability to calculate the dielectric function for finite momentum transfer q. Unlike visible light, DM may impart significant momentum transfer in the scattering process.

$Eu_5In_2Sb_6$, a narrow band gap material with complex antiferromagnetic ordering and potentially non-trivial band topology, is currently under investigation for DM detection, but many questions about its electronic structure remain open. Here, we present density functional theory based first-principles calculations of the electronic structure and complex dielectric function of $Eu_5In_2Sb_6$, which address the effects of magnetic ordering, spin-orbit coupling, and GW self-energy corrections. We will discuss the challenges of accurately calculating the electronic structure and dielectric function of narrow band gap quantum materials, such as $Eu_5In_2Sb_6$, and the implications this has for accurate prediction of the projected reach of light DM scattering and absorption.

Funding support: This work was supported by the U.S. DOE NNSA under Contract No. 89233218CNA000001. It was supported by the LANL LDRD Program, and in part by the Center for Integrated Nanotechnologies, a DOE BES user facility, in partnership with the LANL Institutional Computing Program for computational resources. Additional computations were performed at the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility located at Lawrence Berkeley National Laboratory, operated under Contract No. DE-AC02-05CH11231 using NERSC award ERCAP0020494.

5:00 PM EL20.07.11
A Novel Inkjet Printing Methodology to Form LiPCDA Radiochromic Films Paria Naderi[1], Rohith Kaiyum[1,2], Christopher W. Schruder[1], David F. Lewis[3], Ozzy Mermut[1], Alexandra Rink[2,4,4] and Gerd Grau[1]; [1]York University, Canada; [2]TECHNA, University Health Network, Canada; [3]RC Film Consulting, United States; [4]University of Toronto, Canada

Background & Objective:
In vivo dosimetry of the delivered radiation in cancer treatment is of utmost importance to ensure quality of care. Radiotherapy inaccuracies occur due to different factors such as organ motion, treatment setup errors, and complex energy delivery mechanisms. Radiochromic materials based on diacetylene monomers are good sensors for dose measurements, with several. advantages over the other dosimeters. Their effective atomic composition is close to that of water, making them suitable for in vivo radiotherapy measurements, and they can be engineered in a range of sensor area sizes and sensitivities. In radiochromic films, the monomers polymerize upon exposure to radiation. 10, 12-pentacosadiynoic acid (PCDA) is a common exemplar owing to its color transition upon polymerization. The films are initially colorless and spectral peaks in the red region of the visible region of the absorbance spectrum confirm the color change corresponding to the dose. The chromatic properties arise from highly conjugated (double-bond and triple-bond) backbones. With the substitution of lithium for hydrogen in the carboxylate group of the monomer, the sensitivity is markedly increased so that doses as low as 0.01 Gy are detectable. Both the sensitivity and morphology of the crystals are dependent on factors such as hydration, temperature, and Li^+ to PCDA molar ratio, with the most sensitive LiPCDA crystal in occurring in hydrated hair-like form.
Construction of commercial radiochromic films has been optimized for handling and use in two-dimensional dose measurements. However, using these materials for fibre-based *in vivo* dosimetry requires alternative deposition methods. Inkjet printing can enable fabricating compact sensor devices and may give more control over film thickness, which would help control the sensitivity of the deposited film. However, printing the most sensitive form of LiPCDA poses challenges due to the large size of the crystals (up to 20 µm in length), and viscosity of the gelatin. The objective of this work is to create LiPCDA crystals using ink-jet printing and separate components.
Materials & Methods:
LiPCDA was inkjet-printed onto a controlled area by separating the solution components: TEA.PCDA, LiCl, and gelatin.. Gelatin works as a binder while allowing lithium atoms to diffuse slowly into the tetraethyl ammonium/PCDA (TEA.PCDA) structure and form LiPCDA monomers, which is critical for proper crystal formation. A wet blade-coated bed of LiCl in gelatin was created. TEA.PCDA was inkjet-printed on the LiCl/gelatin bed using a custom-built inkjet printer and a 100-µm piezoelectric Microfab nozzle. The process was repeated while varying the molar ratio of Li^+ to PCDA. Dry films were then exposed to ionizing radiation using a UV lamp and were characterized by scanning electron microscopy (SEM) and UV-visible microscopy.
Results:

We could consistently form LiPCDA crystals using the above technique. At lower Li^+ to PCDA molar ratios the resulting form is hair-like composed of structures with a very high aspect ratio, and the absorption spectrum has a peak at ~ 630 nm. At higher ratios, the form is plate-like, and the absorption peak is at ~670 nm.

Conclusion:

With this inkjet printing methodology, LiPCDA radiochromic films are deposited while their morphology and absorption peaks are regulated by adding a precise amount of its components. The exact ratio of Li^+ to PCDA can be varied, resulting in films with two distinct forms and absorption peaks upon UV irradiation. This approach can later be applied to printing on the end of a thin fibre sensor.

5:00 PM EL20.07.12

Visible-Light-Driven Photocathodes Based on Mn-doped Colloidal Quantum Dots Ho Jin[1,2], Heeyoung Jung[1,2], Clement Livache[1] and Victor I. Klimov[1]; [1]Los Alamos National Laboratory, United States; [2]The University of New Mexico, United States

A typical photocathode is based on a photoelectric effect. It describes the ejection of electrons from the surface of a material when the photon energy is greater than the electron 'binding energy'.[1] Therefore, the quantum efficiency (QE) of a photocathode directly depends on the offset between the photon energy and the electron binding energy. For example, GaN photocathodes can reach QE = 70% at 10 eV, but their efficiency drops below 10^{-6} at 2 eV. There is considerable need for photocathodes that can be driven by low-energy photons.

A possible pathway to achieve photoemission with visible and even infrared photons is 'Auger ionization'. In this process, the energy released during electron-hole recombination is transferred to an 'acceptor' electron which thus is excited to a higher-energy state. However, for standard 'direct' Coulomb interactions, the efficiency of this process is low as the uphill Auger transitions are much slower than downhill transitions due to phonon-assisted cooling.[2] Recently, it was shown that the rate of uphill Auger-type energy transfer could be dramatically enhanced using spin-exchange interactions in Mn-doped colloidal quantum dots (CQDs).[3,4]

In the present study, we exploit this enhancement to demonstrate high-efficiency photocathodes driven by visible light. To prepare photocathodes, we deposit Mn-doped CQDs on top of a metal substrate with a thin insulating interlayer. The photocathode is placed into a home-made vacuum chamber and is biased with high voltage. To initiate photoemission, we illuminate the CQD film with 2.4 eV laser pulses. The ejected electrons are detected as a photocurrent which is measured as a function of incident laser power. We observe that the photoemission yield strongly depends on a Fermi-level of the metal substrates and the properties of the insulating layer. We find that both factors affect QEs primarily via the efficiency of re-neutralization of the CQDs following electron ejection. Without re-neutralization, the dot remains in the positively charged state which impedes photoemission due to electron-hole Coulombic attraction. After optimizing the photocathodes, we achieve ~0.2% internal photoemission QE with 2.4-eV visible-light excitation. This is about two orders of magnitude higher than for the undoped CQD films and ca. four orders of magnitude higher than for standard Cu photocathodes. The photocathodes show excellent stability for several hours of continuous operation.

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5:00 PM EL20.07.13

Study of the Efficacy of a Perovskite Sensor-Based Non-Invasive Glucose Monitoring System Using Infrared Light Intensity Correlations�Towards the Development of Measurement Metrics Using Data Analytics David Ryman[1], Edgar Perez-Lopez[2], Saquib Ahmed[3,3] and Sankha Banerjee[1,4]; [1]California State University, Fresno, United States; [2]University of California, Merced, United States; [3]Buffalo State College, United States; [4]University of California, Davis, United States

The current work involves the use of perovskite oxide and halide interfaces toward the development of a non-invasive glucose monitoring device. A proof-of-concept glucose monitoring sensor circuit was embedded in an active polymer matrix with the goal of producing a correlation between the signal detected by a photodiode and a pulsed laser module using near-infrared light. Multiple modalities of the interaction are used for the detection of glucose concentrations in the control solution. The work involves the characterization of material electrical property characterization including the correlations between the heat generation in the LED/laser module, issues related to the dispersed nature of LEDs, precision of the perovskite photodiode module, alignment between the photodiode module and LED, and data from the continuous LED signal as compared to the pulsed laser signal. Correlations between these independent variables including the output voltage and the glucose concentrations are developed using machine learning methods. The active properties of the polymer matrix are also characterized using electrical impedance spectroscopy.

5:00 PM EL20.07.14

Improved Quality of Perovskite Materials Grown in Space and a Sustainable Business Model for Them Patrick Flowers and Jennifer Ruliffson; Redwire, United States

The push to privatize and commercialize space is gaining momentum in recent years. Indeed, a number of corporations now exist in the space sector who primarily focus on developing commercial products in space for terrestrial use. These space-enabled products take advantage of certain aspects of the space environment, like the lack of gravity, to manufacture higher quality products than could be made terrestrially. A great deal of research is currently underway, using platforms like the International Space Station, to identify viable space-enabled products.

Perovskite radiation detectors are one such class of materials that stand to benefit from space-based manufacturing. While their theoretical performance is quite promising, issues have persisted in real-world testing. Device performance suffers from the presence of dark currents several orders of magnitude higher than expected. This behavior is typically attributed to high defect density in the photosensitive perovskite material. Therefore, the quality of these perovskite materials is the performance limiting factor in radiation detector devices. It is expected that suppression of buoyancy effects during the growth process will significantly increase crystal quality.

One of the biggest challenges to successfully commercializing products manufactured in space is transportation costs. The cost per kilogram to launch materials to space and return them to earth is quite high. The sale price of commercially viable products made in space must be able to absorb these costs. This typically means that space-made products are much more expensive than their terrestrially produced counterparts. It can be difficult to convince consumers that the higher quality of space-made products justifies their higher costs.

Redwire, a leader in space enabled materials, addresses these challenges in a novel way. Redwire is the owner/operator of the Industrial Crystallization Facility (ICF), a payload designed for crystal growth experiments onboard the International Space Station. In this presentation, Redwire discusses the capabilities of ICF, and introduces a new paradigm for commercialization of crystalline space-enabled materials wherein launch costs are drastically diluted. High quality seeds are manufactured in ICF and sold to manufacturers on earth for use in bulk crystal growth processes. The properties of the final bulk crystals are enhanced through the use of high-quality seeds, and the launch cost per kilogram of product produced is diluted by propagating these seeds into bulk crystals on earth. The result is a competitive space-enabled product. This business strategy will be discussed in detail and supported by specific material examples, including perovskites.

5:00 PM EL20.07.15

Suppressing Leakage Current by Interfacial Engineering for Highly Sensitive, Broadband, Self Powered FACsPbI3 Perovskite Photo Detectors

Bhupesh Bhardwaj[1,2], Urvashi Bothra[1], Shivam Singh[1], Sanjay Krishna[2] and Dinesh Kabra[1]; [1]Indian Institute of Technology Bombay, India; [2]The Ohio State University, United States

Photodetectors has important parameters like; leakage current, specific detectivity(D*), linear dynamic range (LDR) and noise equivalent power (NEP) referred as Figure of merit (FOM). Leakage current is considered as one of the most important among them as it plays an important role in determining other FOMs. This study shows the effect of active layer thickness and different interfacial layers in suppression of leakage current which ultimately effects the overall perovskite photodetector (PPDs) performance. Highly sensitive (D* = 10^13 Jones) PPDs fabricated using device structure of ITO/PEDOT: PSS/FACsPbI3 (Eg =1.51 eV; d nm)/ETL/BCP/Ag with noise current < 1 pAHz^-1/2. These PPDs have broadband response from near-ultraviolet to NIR region (300nm-850nm). The performance of the PPDs enhanced for optimal thickness of active layer of d = 600 nm and ETL PC60BM layer thickness of 50 nm. The leakage current of the PPD is further suppressed by replacing ETL PC60BM (in=0.51pAHz^-½) layer by PC70BM (in=0.27pAHz^½) layer. This further improved values of other figure of merits for PPDs. Comparison with published reports on PPDs suggest FACsPbI3 based these PPDs performs significantly better than most of perovskite-based photodetectors reported so far for given spectral range.

5:00 PM EL20.10.01

Vertical 3-Terminal Photonic Sensors Based on Organic Permeable Base Transistor Su-Hyeon Lee[1,2] and Kyung-Geun Lim[1]; [1]Korea Institute of Standards and Science, Korea (the Republic of); [2]Hanyang University, Korea (the Republic of)

Keyword : vertical organic photo transistor, permeable base electrode, pinholes, anodizing

Vertical organic 3-terminal photonic transistors (VOPTs) operate with low dark current, short response time, and a large amplifying current of photonic carrier. The novel VOPT architecture based on vertical organic permeable transistors (OPBTs) vertically forms conducting channel in the nanometer scale by using permeable base electrode, thus can achieve a large amplifying current and a record-breaking switching speed. VOPTs based on OPBT are also suitable for flexible convergence device using organic semiconductors and optoelectronic materials. In this study, We facilitates permeability of OPBTs and achieved advanced VOPTs. The permeable base electrode pinhole morphologies such as density or size were controlled by the electrodes thickness and deposition rate speed. The surface treatment on organic semiconductor layer reduces the interface energy to control the pinhole formation in permeable base electrode. Vertical transistor with permeable base electrode achieves low dark current, high current density and high switching speed. As a result, the response time and detectivity are significantly improved in VOPTs based on OPBT compared to the organic 2-terminal photodiode or the organic phototransistor with lateral channel.

SESSION EL20.08: Next Generation Organic Photodetectors
Session Chairs: Ardalan Armin and Nicola Gasparini
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3010

10:30 AM *EL20.08.01

Organic Small Molecule Based Emerging Applications in Opto Electronic Kyung-Bae Park[1], Sungyoung Yun[1], Younhee Lim[1], Chul-Joon Heo[1], Jeong-Il Park[1], Hiromasa Shibuya[1], Jeoungin Yi[1], Daiki Minami[2], Taejin Choi[1], Hyeong-Ju Kim[1], Feifei Fang[1], Jisoo Shin[1], Hyerim Hong[1], Juhyung Lim[1], Hwijoung Seo[1] and Byoungki Choi[1]; [1]Samsung Electronics, Korea (the Republic of); [2]Samsung Electronics, Co. Ltd., Korea (the Republic of)

Organic conjugated small molecules are freely band gap tuning, low molecular weight to be available thermally deposited allowing semiconductor process, which have served as an important material for electronic devices today. Wavelength selectivity among absorption properties allowed for expansion with organic light sensors. Image sensor companies have showed sensor demonstrations to replace Si-CIS (CMOS Image Sensor), which accounts for most of the global image sensor market, with organic CIS.[1-3] In particular, unlike inorganic materials, organic material have absorption characteristic of selective wavelength, therefore stacked image sensor can be fabricated with especially green selective organic material. The stacked image sensor with green colour absorbed organic semiconductor material have the advantage of increasing sensing area and increasing sensitivity. In addition, it has the advantage of increasing the number of effective pixels compared to the same pixel size, becoming increased the resolution of the image sensor.[4]

Sensors applied with organic materials are expanding not only to image sensors for cameras but also to bio-recognition sensors in display of mobile. Currently, MUT (Micromechanic Ultrasonic Transducer) and optical Si CIS are used as the authorized finger-print sensors in the form of chips underneath the OLED display. If organic light sensors are applied as bio-recognition sensors, certain sensing areas about the size of existing chips (1cm~2cm) can be expanded to all areas of the display. As a result, multi-fingerprint and palm recognition can be possible, which can enhance security functions.[5,6]

Although it is an early development stage in the field of beyond 6G optical wireless communication, Organic photodetectors, such as organic photodiodes (OPD)and organic photovoltaics (OPV), can be manufactured with a large detection area and a high optical gain. Additionally, these can be operated without an external bias voltage, extending their application range. The optional external bias voltage results in increased efficiency and response time. he present work introduces a high-bandwidth OPD device with a bandwidth of 1.4 MHz, which is nearly a factor of ten faster than the fastest previously reported. Additionally, much faster data rates are demonstrated through the convergence of a preequalization and machine learning (ML)-based digital signal processing technique (DSP). The data transfer rates achieved are 30 Mbps (zero bias) and 150 Mbps (−4 V bias).[7]

In order to contribute the expectations of these diverse electronic devices, organic absorbent molecules would become an important material for information and communication electronic devices in the future due to their high absorption wavelength selectivity and specific characteristic of circular dichroism compared to conventional inorganic materials.

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11:00 AM EL20.08.02
Realizing Photostable Detection in Organic Photodiodes with ZnO Electron Transport Layer Theodorus Jonathan Wijaya, Tomoyuki Yokota, Sunghoon Lee, Ryo Okano, Masaki Kobayashi and Takao Someya; The University of Tokyo, Japan

Organic photodiodes (OPDs) have demonstrated distinctive mechanical properties, such as flexibility and stretchability, which allow their implementation as skin-conforming photodetectors. These photodetectors provide highly reliable measurements of the pulse rate and vein images.[1] This reliability owes to the high specific detectivity (10^{11} – 10^{13} Jones) of the recent OPDs. Achieving this high detectivity has been facilitated by the suppression of dark current via the insertion of an electron transport layer (ETL). ZnO is widely used as an ETL, and the OPDs using ZnO ETL also exhibited mechanical and air storage stability of dark current characteristics, thereby enabling their usage as ultra-flexible photodetectors for continuous measurement of bio-signals.[2] However, dark current in OPDs using ZnO ETL increases by several orders of magnitude after light irradiation, thereby notably reducing its specific detectivity.[3] Sol-gel ZnO ETL is widely fabricated with a post-annealing at a maximum of 180 ^{o}C, whereas ZnO ETL requires a minimum temperature of 280 ^{o}C to fully synthesize from its precursor solution. The defective formation of ZnO ETL is considered to cause the photoinduced increase of dark current in the OPDs. Additionally, the effects of the annealing temperature of the ZnO ETL on the photostability of the OPDs have not been thoroughly studied.
In this work, we examined the effects of the annealing temperature of the ZnO ETL on the photostability of the OPDs. We employed the inverted OPD structure of “glass/ITO (70 nm)/ZnO (30 nm)/P3HT:$PC_{61}BM$ (250 nm)/MoO_x (10 nm)/Ag (100 nm)” where the ZnO ETL was synthesized as a sol-gel from the zinc acetate dehydrate precursor and fabricated using standard spin-coating followed by post-coating annealing. We increased the commonly adopted annealing temperature of the ZnO ETL from 180 to 350 ^{o}C and confirmed that the external quantum efficiency (EQE) of the devices was not affected. By this high-temperature annealing, we reduced the increase of dark current after light irradiation by 51 times, thereby suppressing the increase to approximately 2.0 times the original value. Specifically, the dark current density at –2 V in OPDs with ZnO ETL annealed at 180 ^{o}C increased by 100 times from the initial value of $(6.2 \pm 0.21) \times 10^{-8}$ A cm^{-2} to $(6.2 \pm 0.15) \times 10^{-6}$ A cm^{-2} after irradiation. On the contrary, those with ZnO ETL annealed at 350 ^{o}C increased by only 2.0 times from the initial value of $(1.9 \pm 0.19) \times 10^{-6}$ A cm^{-2} to $(3.9 \pm 0.39) \times 10^{-6}$ A cm^{-2}. By suppressing this increase in dark current, the stability of the specific detectivity of the OPDs based on the shot noise was improved by 7.1 times. Specifically, the OPDs with ZnO ETL annealed at 180 ^{o}C showed an initial specific detectivity of 2.8×10^{12} Jones but deteriorate to 2.8×10^{11} Jones after light irradiation, thereby only exhibiting 10 % retention. On the other hand, the OPDs with ZnO ETL annealed at 350 ^{o}C showed an initial detectivity of 5.9×10^{11} Jones and held the detectivity to a sufficiently high value of 4.1×10^{11} Jones, thus showing a 70 % retention. Additionally, we demonstrated that UV is the cause of this photo-instability by showing that the increase in dark current after irradiation with wavelengths longer than 380 nm was lower than and at most 17.6 % of those observed after sub-370-nm irradiations. Furthermore, A better quality of the ZnO ETL was identified to be crucial to improve the photostability of OPDs using ZnO ETL, as confirmed through XPS and XRD measurements. These results underscore the importance of choosing a defect-free ETL synthesis or material to realize next-generation photostable OPDs.

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11:15 AM *EL20.08.03
Organic Photovoltaics for Simultaneous Harvesting of Power and Data in Optical Wireless Communications Iman Tavakkolnia[1], Lethy K. Jagadamma[2], Rui Bian[3], Pavlos P. Manousiadis[2], Stefan Videv[1], Graham A. Turnbull[2], Harald Haas[1] and Ifor Samuel[2]; [1]University of Strathclyde, United Kingdom; [2]University of St. Andrews, United Kingdom; [3]pureLiFi, United Kingdom

The rapid growth of internet-connected devices presents two important challenges. The first is how will they all communicate? The second is how will they be powered? Optical communications can contribute to the solution, particularly in the form of “Li-Fi” in which indoor lighting is modulated to transmit information and supplement Wi-Fi. Organic semiconductors have been shown to be useful as both transmitters and receivers for Li-Fi. In this talk we will show how organic photovoltaics can be used as receivers that simultaneously receive data and generate power. Furthermore by using small arrays useful data rates of up to 363 megabits/second have been achieved.

SESSION EL20.09: Hybrid Photodetectors
Session Chairs: F. Pelayo García de Arquer and Jinsong Huang
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3010

1:30 PM *EL20.09.01
Photoconducting Devices with Specific Attributes based on 2D Metal-Halide Perovskites Franziska E. Muckel; University Duisburg-Essen, Germany

Flexible optoelectronic devices offer possibilities for a wide range of novel applications. Especially flexible photodetectors enable functionalities like optical communication or optical sensing for healthcare, lifestyle applications or optical cross-linking systems in the “Internet of Things”. These diverse applications areas result in a variety of required device attributes. One device architecture which is noncomplex, easy-to-fabricate and allows facile tuning of the device functionalities are photoconducting devices. Herein the conductivity of a semiconducting channel is mediated through illumination. By engineering the optical properties as well as the structure of the semiconductor, the functionality of the photodetectors can be altered to meet requirements for specific applications, e.g., defined color ranges, high sensitivities or low noise signals.
Promising materials for flexible photoconducting devices are two dimensional (2D) metal-halide perovskites, which can be fabricated at room temperature out of solution and crystalize as naturally grown multi quantum wells in the form of inorganic semiconducting layers separated by bilayers of electrically insulating organic cations. 2D perovskites exhibit mechanical flexibility combined with the optical and electronic properties of a 2D system.
Here we show, that the excitonic absorption feature of 2D perovskite $(BA)_2PbI_4$ can be utilized to realize filter-free narrow-bandgap photodetectors. We report the fabrication of a lateral, wavelength selective photodetector based on n=1 $(BA)_2PbI_4$, exhibiting a well defined peak in the photocurrent spectrum at 520 nm, which can be related to the excitonic absorption. We achieve colour-selective light detection with a responsivity of 0.750 mA/W and a specific detectivity up to 4.7×10^{10} J. On-Off ratios are larger than 10^4.

Aiming for high-responsive device, we combine a non-continued layer of $(BA)_2PbI_4$ 2D perovskite with a transition metal dichalcogenide as conducting channel to achieve a 2D/2D hetero-photodetector with a gain mechanism. In this architecture, the two-dimensional $(BA)_2PbI_4$ layer traps the minority charge carriers (holes), enabling the electrons to circulate through the transition metal dichalcogenide channel multiple times. Using optimized channel length, we achieve responsivities of up to 20 A/W, which corresponds to a gain of 38.

2:00 PM EL20.09.02

Multidimensional Perovskites for High Detectivity Photodiodes Alessandro Caiazzo[1], Riccardo Ollearo[1], Junyu Li[1], Marco Fattori[1], Albert van Breemen[2], Martijn M. Wienk[1], Gerwin Gelinck[1] and Rene A. Janssen[1]; [1]TU Eindhoven, Netherlands; [2]Holst Centre, Netherlands

Low-dimensional perovskites attract increasing interest due to tunable optoelectronic properties and high stability. In our work, we show that perovskite thin films with a vertical gradient in dimensionality result in graded electronic bandgap structures that are ideal for photodiode applications. Positioning low-dimensional, vertically-oriented perovskite phases at the interface with the electron blocking layer increases the activation energy for thermal charge generation and thereby effectively lowers the dark current density to a record-low value of 5×10^{-9} mA cm^{-2} without compromising responsivity, resulting in a noise-current-based specific detectivity exceeding 7×10^{12} Jones at 600 nm. These multidimensional perovskite photodiodes show promising air stability and a dynamic range over ten orders of magnitude, and thus represent a new generation of high-performance low-cost photodiodes.

2:15 PM EL20.09.03

Near Infrared Photomuliplication-Mode Perovskite Photodetectors with Various Organic Passive Electron transport Layers Seyeong Song; Ulsan National Institute of Science and Technology, Korea (the Republic of)

The pace of advancement and increasing stability and perfomances have provided the possibility for perovskite materials to be commercialized in a variety of applications, including solar cells(PVs), light emitting diodes(LEDs) and photodetectors(PDs). As a next-generation semicondutor, advantages of perovskite-based applications are light-weight, solution-processible, tunable bandgap and easy device fabrication.

Two-terminal perovskite photodetectors (PePDs) with p-i-n structure generally have configuration of transparent conducting oxide /hole transport layer/Perovskite/passive-electron transport layer/electrode, wherein the passive electron transport film is mostly organic semiconductors such as C60 and PCBM. The p-i-n structural PePDs are challenging due to several issues. First, photodetectors work in applied negative bias. However, perovskite optoelectronics are quite unstable at strong reverse bias, since the halide migration can occur into organic layers and work as a p-type dopant in the organic layer, leading to accelerate perovskite separation and the device degradation. Secondly, perovskite and the device are significantly affected by following passive-electron transport layers (P-ETLs) and their technical processing methods. To obtain the high quality of perovskite grains and high performance of the device, efficient energy level alignment and interfacial compact between the perovskite layer and organic P-ETL are required.

We investigate NIR perovskite photodetectors by introducing Tin (Sn) with lead (Pb) halide perovskite, which can detect by 1000 nm. We fabricated p-i-n architecture photomultiplication (PM) mode photodetectors devices and compared device performance of different four type organic P-ETLs including C60, PCBM, non-fullerene acceptor (NFA) and Donor polymer:NFA bulk heterojunction (BHJ) blend films to figure out the photomultiplication phenomenon from breakdown of diode at weak reverse voltage. Since the non-fullerene organic material has interesting molecular stacking changes with and without a chloronaphthalene (CN) processing additive, PePDs based on NFA P-ETL with CN also studied in this work. Furthermore, our NIR PM-mode PePDs were fabricated on flexible substrates and applied to photoplethysmogram (PPG) medical monitoring device application. We believe that these comparison of PePDs performance for passive electron transporting organic layers as well as utilizing the photomultiplication present high potential and possibility in the future sensors industrial market.

2:30 PM *EL20.09.04

Develop Photodetection Toolbox for Ultraviolet Photodetectors Qiuming Yu; Cornell University, United States

Photodetectors have a wide variety of applications in modern technology, and new ones are constantly arising. Therefore, it is highly desirable to be able to design devices quickly and cheaply**.** Traditional design process starts with making decisions and optimizing them to meet application needs. Inverse design offers promising approach for expediting design by starting with application criteria**.** Either way, the toolbox must be thoroughly understood and generalizable to different materials, spectral ranges, and devices**.** In this talk, I will cover our recent work on the development of photodetection toolbox to achieve sensitive, low driving-force, narrowband UV photodetectors. Our UV photodetectors are based on the photodiode structure. To enhance the photodetection sensitivity or to increase the specific detectivity of UV photodetectors, we vary the ratio of p-type conjugated polymer to n-type fullerene electron acceptor and control the photoactive layer morphology to achieve electron-trapping induced band bending and charge injection, and hence inducing the photomultiplication effect to gain the external quantum efficiency much higher than unit. Similar strategy can be applied to the polymer-ZnO nanoparticle nanocomposite system to utilize trapped electrons in ZnO nanoparticles to realize the photomultiplication effect. Additionally, by controlling and utilizing charge generation, separation and transport in the hole-only photodiode devices, we can achieve narrowband, photomultiplication, low-driving force UV photodetectors. Another strategy to achieve the narrowband photodetection is through the charge-collection narrowing by on purpose increase the thickness of the active layer to allow the selective detection of photons at the long-wavelength absorption edge. Considering the function of manipulating light absorption and confining electromagnetic energy into the nanoscale volume, we integrate aluminum plasmonic nanostructures into the photodiode to manipulate the UV photodetection. We can ether place the aluminum nanohole arrays on top of a glass substrate to replace the ITO layer as a transparent electrode or embed aluminum nano-hemisphere arrays into the top aluminum electrode to achieve the bias-dependent photoresponses and enhanced photosensitivity. All these developments are aided by the finite-difference time domain (FDTD) simulations, transfer matrix method (TMM) optical calculations, and experimental studies to understand the charge generation, separation, transport, and recombination in the devices. Our work highlights the importance to correlate the device internal physical processes to the design inputs and the sensing capabilities in order to achieve the desired photodetection.

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SESSION EL21.01: Topological and Quantum Materials
Session Chairs: Iuliana Radu and Subhash Shinde
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3011

10:30 AM *EL21.01.01
Topological Thin Films for Electron and Quantum Device Applications Susanne Stemmer, Arman Rashidi, Alexander Lygo, Simon Munyan, Binghao Guo and Robert Kealhofer; University of California, Santa Barbara, United States

Over the past decade, the unique properties of topological quantum matter have generated huge excitement in the materials physics community. At the same time, solid state electronic devices are increasingly limited by current generations of electronic materials. New materials are also needed for enabling quantum information technologies. In this talk, we will discuss progress in heterostructure fabrication and measurements of high-quality thin films of topological semimetals, such as cadmium arsenide. We show that these thin films are highly tunable and describe measurements that can identify different topological states and their unique electronic properties. We also discuss their potential applications in electronic and quantum devices and show results, including from field effect transistors, hot electron transistors, and superconducting hybrid devices.

11:00 AM *EL21.01.02
Opportunities of Topological Semimetals as Novel Material for Computing. Experimental Transport Studies and Device Implementations Heinz Schmid[1], Alan Molinari[1], Federico Balduini[1], Lorenzo Rocchino[1], Igor Kladaric[1], Marilyne Sousa[1], Holt P. Bui[2], Marco Hopstaken[2], Christian Lavoie[2], Rafal Wawrzynczak[3], Marcus Schmidt[3], Claudia Felser[3], Vicky Suess[3], Mathieu Luisier[4], Selma Franca[5], Sergueï Tchoumakov[5], Simone Fratini[5], Johannes Gooth[3], Adolfo Grushin[5], Cezar Zota[1] and Bernd Gotsmann[1]; [1]IBM Research, Europe, Switzerland; [2]IBM Research, US, United States; [3]Max Planck Institute for Chemical Physics of Solids, Germany; [4]ETH Zürich, Switzerland; [5]Institute Neel, France

Topological materials have attracted strong interest in recent years due to their exotic transport properties set by non-trivial band structures. These materials were shown to exhibit exceptional properties such as high electron mobilities and large magnetoresistance, for example. Among the many identified semimetal compounds, we will focus on our recent work involving the two semimetals NbP and CoSi to highlight promising applications. NbP was selected due to the high magnetoresistance and demonstrated to modulate a current in a transistor configuration with very high efficiency. The chiral semimetal cobalt monosilicide (CoSi) has been identified as a prototype for topological materials exhibiting extremely long Fermi arc surface states. However, CoxSi1-x is stable at various stoichiometries and defect densities, the effect of which on topological and normal magnetotransport is little explored. We show a study of CoSi samples ranging from single crystals, via textured polycrystalline films to amorphous thin films grown using molecular beam epitaxy. Exhaustive structural characterization (STEM, AFM, XRD) and chemical analysis (XPS, SIMS, EDS, RBS) enable a detailed correlation to transport as a function of magnetic field, temperature and dimension. This enables us to relate anomalous Hall effects, quantum anomalies in longitudinal and transverse magnetoresistance, quantum oscillations, as well as unconventional size-scaling of conductivity down to the nm-range to structure and composition. As expected from the band structure, transport in CoSi is remarkable in many aspects.

11:30 AM EL21.01.03
Unconventional Resistivity Scaling in Topological Semimetal CoSi Hsin Lin[1], Shang-Wei Lien[2], Ion Garate[3], Utkarsh Bajpai[4], Cheng-Yi Huang[5], Chuang-Han Hsu[1], Yi-Hsin Tu[2], Nicholas Lanzillo[4], Arun Bansil[5], Tay-Rong Chang[2], Gengchiau Liang[6] and Ching-Tzu Chen[7]; [1]Academia Sinica, Taiwan; [2]National Cheng Kung University, Taiwan; [3]Université de Sherbrooke, Canada; [4]IBM Research, United States; [5]Northeastern University, United States; [6]National University of Singapore, Singapore; [7]IBM T.J. Watson Research Center, United States

Nontrivial band topologies in semimetals lead to robust surface states that can contribute dominantly to the total conduction. This may result in reduced resistivity with decreasing feature size contrary to conventional metals, which may highly impact the semiconductor industry. Here we study the resistivity scaling of a representative topological semimetal CoSi using realistic band structures and Green's function methods. We show that there exists a critical thickness d_c dividing different scaling trends. Above d_c, when the defect density is low such that surface conduction dominates, resistivity reduces with decreasing thickness; when the defect density is high such that bulk conduction dominates, resistivity increases as in conventional metals. Below d_c, the persistent remnants of the surface states give rise to decreasing resistivity down to the ultrathin limit, unlike in topological insulators. The observed CoSi scaling can apply to broad classes of topological semimetals, providing guidelines for materials screening and engineering. Our study shows that topological semimetals bear the potential of overcoming the resistivity scaling challenges in back-end-of-line interconnect applications.

11:45 AM EL21.01.04

Exploring Topological Semimetals for Highly Scaled Interconnects Beyond Copper Ching-Tzu Chen[1], Christian Lavoie[1], Nicholas Lanzillo[1], Utkarsh Bajpai[1], Oki Gunawan[1], Asir Intisar Khan[1,2], John Bruley[1], Guy Cohen[1], Vesna Stanic[1], Hsin Lin[3], Ion Garate[4], Gengchiau Liang[5], Shang-Wei Lien[6], Yi-Hsin Tu[5,6], Sushant Kumar[7], Ravishankar Sundararaman[7], Peter Kerns[1], Teodor Todorov[1], Nathan Marchack[1], Jean Jordan-Sweet[1], Cheng-Yi Huang[8], Arun Bansil[6] and Tay-Rong Chang[6]; [1]IBM T.J. Watson Research Ctr, United States; [2]Stanford University, United States; [3]Academia Sinica, Taiwan; [4]Université de Sherbrooke, Canada; [5]National University of Singapore, Singapore; [6]National Cheng Kung University, Taiwan; [7]Rensselaer Polytechnic Institute, United States; [8]Northeastern University, United States

Due to surface and disorder scattering, resistivity of metal wires keeps increasing with shrinking dimensions, which severely impacts the performance of highly scaled integrated circuits. Here we explore a new class of materials – topological semimetals – as an alternative solution. We demonstrate that, via conduction of the protected surface electronic states, resistivity in topological semimetals reduces with decreasing feature size down to ~ nm scale, even in the presence of defects and grain-boundary scattering. This novel scaling behavior sharply contrasts that of conventional metals, such as Cu, and topological insulators. In this talk, we will first present first-principles-based electrical transport calculations of a Si-CMOS compatible topological semimetal CoSi and a prototypical Weyl semimetal NbAs. We will then report experimental evidence for surface-dominated transport in CoSi thin films, showing resistivity below that of the bulk single-crystals. Our proof-of-principle study demonstrates the potential of topological semimetal as beyond Cu interconnect materials.

SESSION EL21.02: Semiconducting Oxide and Memory Materials
Session Chairs: Asif Khan and Hui Jae Yoo
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3011

1:30 PM *EL21.02.01
First Fire-free Selectors Based on Te in an Insulating SiO_x Matrix Isha Datye, Sam Vaziri, Elia Ambrosi, Cheng-Hsien Wu, Jeremy Guy, H.S. Philip Wong and Xinyu Bao; TSMC, United States

Low voltage and off-current selectors are necessary for low power operation of high density one selector-one resistor (1S1R) arrays for 3D-compatible embedded memory. Chalcogenide-based materials are promising for selectors because they have low off-current, high on-current, good endurance, and decent thermal stability [1-2]. However, they typically require a one-time high voltage pulse or "first fire" operation larger than the threshold voltage, which is incompatible with low voltage memory requirements [1-2]. In addition, these selectors often suffer from threshold voltage drift, leading to a narrower memory window [1,3-4].
In this work, we show that selectors based on SiO_xTe_y, a simple and stable material system, are very promising due to their low voltage and off-current, as well as fast switching speed and good endurance [5]. We present selectors with threshold voltage (V_{th}) down to ~1.2 V and off-current of ~3 nA at 0.5 V. By modifying the tellurium to oxygen atomic ratio and film thickness with different deposition conditions, we show tunable first fire voltage (V_{FF}) and V_{th} and also achieve first fire-free selectors ($V_{FF} = V_{th}$). We investigate the switching mechanism of these devices by studying their dependence on bottom electrode size and temperature. We also measure V_{th} drift and find the drift slope to be lower than many values reported in literature for other chalcogenide-based materials.
After one year stored in air, the threshold voltage and leakage current of the uncapped selectors remains fairly stable, indicating good long-term stability. These selectors also have decent thermal stability and exhibit a novel recovery mechanism after annealing. Finally, we demonstrate fast switching speed (~3 ns) and good endurance (>10^{11} cycles), making these selectors very promising for integration with nonvolatile memory.

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2:00 PM EL21.02.02
V_3O_5 as a Functional Oxide for Metal-Oxide-Metal Relaxation Oscillators Sujan K. Das[1], Sanjoy Nandi[1], Camilo V. Marquez[2], Armando Rua[2], Mutsunori Uenuma[3], Etienne Puyoo[4], David Albertini[4], Nicolas Baboux[4], Teng Lu[1], Yun Liu[1], Shimul K. Nath[1], Thomas Ratcliff[1], Tobias Haeger[5], Thomas Riedl[5], Ralf Heiderhoff[5] and Robert G. Elliman[1]; [1]Australian National University, Australia; [2]University of Puerto Rico, Puerto Rico; [3]Nara Institute of Science and Technology (NAIST), Japan; [4]Université Lyon, France; [5]University of Wuppertal, Germany

Oscillatory neural networks (ONN) provide a powerful platform for analogue computation and are of increasing interest as accelerators in artificial intelligence hardware, where they provide an energy efficient means of undertaking simple repetitive functions such as calculating dot products, convolutions, applying nonlinearities, and recognising or matching simple patterns. However, it is generally recognised that oscillator-arrays based on conventional CMOS circuits are too large and energy consuming to enable integration into the dense, low-power arrays required for solving complex, real-world problems. This has motivated the development of a broad range of alternative nanoscale oscillators based on phase-change materials, spintronics (i.e. spin-torque and spin-Hall oscillators), Nano-Electro-Mechanical systems (NEMS), superconducting devices (e.g. Josephson junctions), and negative-resistance oscillators. Among these contenders, relaxation oscillators based on negative differential resistance (NDR) in metal-oxide-metal (MOM) devices are of particular interest due to their simple structure, scalability and energy efficiency.

Devices based on VO_2 have been shown to exhibit reliable, energy-efficient operation due to the abrupt conductivity change resulting from its low-temperature (i.e. T_c= 340 K) insulator-metal transition (IMT). However, this temperature is too low for applications requiring large scale integration. A possible alternative is V_3O_5, a Magneli phase of vanadium-oxide, that undergoes an IMT at a temperature of ~420 K.

This study examines the structural, electrical and thermal properties of sputter deposited V_3O_5 films and their application as relaxation oscillators for neuromorphic computing applications. The former includes temperature dependent measurements of the electrical conductivity, thermal conductivity and lattice structure, while the latter are based on lateral (in-plane) metal-oxide-metal device structures. These devices are shown to exhibit electroforming-free volatile threshold switching and negative differential resistance (NDR) with stable (<3% variation) cycle-to-cycle operation. The physical mechanisms underpinning these characteristics are investigated using a combination of electrical measurements, in-situ thermal imaging and device modelling. This shows that the conduction in lateral metal-oxide-metal device structures is confined to a narrow filamentary path due to self-confinement of the current distribution, and that NDR response is initiated at temperatures well below the IMT temperature where it is dominated by the temperature dependence of the insulating phase; and provides new insights into the NDR mechanism. Finally, we investigate the dynamics of individual and coupled V_3O_5-based relaxation oscillators. These results establish V_3O_5 as an interesting new functional material for the development of solid-state neurons for neuromorphic computing.

2:15 PM EL21.02.03
A 2T Neuromorphic Device based on Metal Oxide Transistor with Self-Assembled Monolayer for High-Precision Artificial Intelligence Seongmin Park, Suwon Seong and Yoonyoung Chung; Pohang University of Science and Technology, Korea (the Republic of)

State-of-the-art artificial intelligence computation consumes tremendous power and requires a long time during training as the separated memory and processor of the current computing architecture hinder data transfer. To deal with this problem, researchers have developed a neuromorphic device that can operate weight storage, update, and matrix-vector multiplication near memory. However, conventional neuromorphic devices based on new non-volatile memories suffer from abrupt conductance shifts and poor uniformity, which degrade the accuracy of the neural network.
This work presents a neuromorphic device with excellent synaptic characteristics by utilizing two InGaZnO (IGZO) transistors. The proposed neuromorphic device consists of a read transistor and a write transistor, where the write transistor's source/drain electrode is connected to the gate electrode of the read transistor so that the write transistor precisely adjusts the gate potential of the read transistor. The ideal synaptic properties were achieved by balancing the gate electrode charging/discharging speed and the transconductance change rate to have an identical programming slope within the operation range. The ultra-low leakage current of IGZO prevents the charge leakage from the read transistor gate through the IGZO channel, preventing the programmed weights change during training. Furthermore, with the large-area uniformity of the IGZO transistor, the programming slopes of the proposed neuromorphic device exhibited a very low standard deviation to the average ratio of less than 3%. For large array compatibility, we regulate the output current of the neuromorphic device by introducing an alkyl-phosphonic acid self-assembled monolayer (SAM) between IGZO and source/drain to form an ultra-thin energy barrier. A phosphonic acid SAM with 12 alkyl chains reduced the current of the IGZO transistor by 30%. In addition, the energy barrier formed by the SAM suppressed leakage current during retention, maintaining the stored weights after 300 seconds from programming. With these strategies, the 2T neuromorphic device exhibited outstanding synaptic characteristics within a low conductance range, which is suitable for a high-precision artificial intelligence system.

2:30 PM EL21.02.04
Dual Synaptic Weights Emulation for Artificial Nociceptors and Energy Efficient Neuromorphic Computing Kuan-Ting Chen, Shi-Cheng Mao, Bo-Ru Lai, Ingann Chen and Jen-Sue Chen; National Cheng Kung University, Taiwan

With the increased diverse sets of information in the era of big data, neuromorphic computation is the crucial technology for advancing the data-processing speed. Electronic devices, which mimic the neural activity with good energy efficiency, will be the key for successful hardware implementation of neuromorphic computing. Inspired by the charge transfer mechanism, the capacitance-based synaptic weight is highly advantageous for the energy efficient neuromorphic computing because the capacitor consumes lower power dissipation and is also free of sneak-path issue due to the voltage-expressed transmitted signal. Furthermore, three-terminal artificial synapse is also realized with the same stacking layer to emulate the synaptic functions and features the concurrent signal transmitting-and-learning.
To be compatible with CMOS process technology, here we fabricated a metal oxide-based synaptic capacitor on p^+-Si substrate. The indium tin oxide (ITO) and tantalum oxide (TaO_x) are stacked as the capacitive device. In parallel, the same stacking layers are employed as the channel layer (ITO) and high-k electrolyte dielectric layer (TaO_x), respectively, to form the synaptic transistor. The relocation of oxygen vacancies in TaO_x under the application and removal of the electric field contributes to the analog transistor conductance and capacitance modulation. Consequently, multiple synaptic functions, including pair-pulse facilitation, high-pass filter, long-term plasticity as well as the transition from short-term memory to long-term memory, can be successfully demonstrated in both transistor and capacitive device. On top of that, it is unparalleled to mimic the nociceptive behavior through capacitance as the response. To confirm the feasibility of both electronics, the dataset classification simulation is carried out by incorporating the results of weight updating process to the CrossSim software. A robust stability of cycle-to-cycle variation is found in capacitive device (0.9%) and transistor (1.8%), causing a high recognition accuracy of 95% and 84%, respectively. It indicates that the ITO/TaO_x-based capacitor shows superior performance and has promising potential in the hardware capacitive neural network.

2:45 PM EL21.02.05
Highly Linear Weight Update of IGZO Photonic-Synaptic Transistors by Controlling Oxygen Vacancy for Neuromorphic Computing Taewon Seo, Juyoung Yun and Yoonyoung Chung; Pohang University of Science and Technology, Korea (the Republic of)

Optoelectronic synaptic devices attract considerable attention for neuromorphic computing due to high bandwidth and ultrafast signal transmission. IGZO-based photonic transistors have been studied for synaptic devices because of their CMOS compatibility, ultralow-off current, and transparency. They exhibit excellent synaptic functions, such as paired-pulse facilitation (PPF), photonic potentiation/electrical depression, and transition from short-term plasticity to long-term plasticity. However, IGZO-based synaptic transistors have a problem with the weight update nonlinearity, the most critical factor for the accuracy of artificial neural network (ANN).
Now, we suggest a method to improve the linearity of potentiation/depression plasticity of IGZO TFTs by controlling oxygen vacancies in IGZO thin film. First, a substrate bias was applied during IGZO deposition to remove unstable oxygen bonds. Second, nitrogen plasma was followed to fill the generated oxygen vacancies. X-ray photoelectron spectroscopy (XPS) data showed oxygen vacancies effectively reduced by 35 % using our approach. As oxygen vacancies in IGZO thin film decreased, the recovery behavior of excitatory post-synaptic current (EPSC) was almost improved by two times. PPF measurement, indicating an increase in the post-synaptic response by the second stimulation compared to the first stimulation, exhibited that oxygen vacancy-controlled IGZO-based synaptic transistors perfectly mimic biological synapses. Especially, the nonlinearity factor of weight update was dramatically improved from 1.55 to 0.41, which is a sufficient level for highly accurate ANN. By solving the problem of the weight update nonlinearity in IGZO-based synaptic transistor, which has a benefit in CMOS compatibility and ultralow off current, our approach enables the implementation of ultra-low-power and high-performance artificial optoelectronic circuits for neuromorphic computing.

3:00 PM BREAK

SESSION EL21.03: Memory Materials
Session Chairs: Isha Datye and Subhash Shinde

Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3011

3:30 PM *EL21.03.01
Phase Change Materials for Energy Efficient Computing Jayakanth Ravichandran; University of Southern California, United States

Neuromorphic computing has gained a lot of interest for the potential to significantly improve the energy efficiency of computing associative tasks. The two key components of this computing methodology focus on mimicking the operation of neurons and synapses. Phase change materials that undergo abrupt volatile and non-volatile changes in conductivity as a function of temperature, and applied electric field are prime candidates to mimic neurons and synapses in an energy and footprint efficient manner. In this talk, I will introduce a novel phase change material, $BaTiS_3$, which belongs to a broader class of phase change materials known as quasi-1D hexagonal chalcogenides. This material demonstrates two properties can be leveraged to mimic simplified forms of neuronal and synaptic processes. At room temperature, the material shows resistive switching behavior, presumably the switching of the ferrielectric dipole moments. Below ~180 K, the material shows voltage tunable and stable changes in conductivity, suggesting the possibility of multistep memory characteristics. The former can be leveraged to mimic low power neurons, and the later as tunable synaptic weights in a neuromorphic computing architecture. This work setups up the potential for novel materials research in creating functionalities necessary to achieve neuromorphic hardware.

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4:00 PM EL21.03.02
Electrochemical Random-Access Memory for Low-Energy Computing Yiyang Li; University of Michigan, United States

Data-intensive processes like artificial intelligence consume substantial amounts of energy. In-memory computing using analog resistive memory can be substantially more efficient that conventional digital approaches. In this work, we discuss our work on developing the electrochemical random-access memory (ECRAM) as the "synapse" for in-memory computing. ECRAM is a type of resistive memory that electrochemically shuttles oxygen vacancy point defects between two transition metal oxides through a solid electrolyte. Its electrochemical process yields ~1V switching and very low currents. Importantly, ECRAM can also attain high-temperature operation and the potential for several years of retention time at 85C.

4:15 PM EL21.03.04
Confined Conducting Filaments in HfO_2-Based Resistive Random Access Memory by Al_2O_3 Nanodome Shaped Arrays (NDSAs) via Glancing Angle Deposition Technology Toward Neuromorphic Computing Ying-Chun Shen and Yu-Lun Chueh; National Tsing Hua University, Taiwan

Resistive random access memory (RRAM) is vital to neuromorphic computing applications. However, filamentary RRAM cells are affected by transitions from abrupt switching to analog switching. In this study, we develop Al_2O_3 nanodome shaped arrays (NDSAs) by glancing angle deposition technology (GLAD) to geometrically confine the conducting filaments (CFs), for which conducting atomic force microscopy (C-AFM) was performed to analyze positions and dimensions of filaments. For the Pt/HfO_2/75 % Al_2O_3 NDSAs/TiN device, the dimension of the CFs can be restricted to 10-12 nm, whereas for the Pt/HfO_2/TiN device, the CFs were formed with the dimension of ~50 nm. Moreover, Pt/HfO_2/75 % Al_2O_3 NDSAs/TiN device exhibited synaptic features with more linear potentiation and depression, demonstrating the analog switching. The controllable coverages of Al_2O_3 NDSAs render the geometric design more promising as a memristor for future applications in neuromorphic computing.

4:30 PM EL21.03.05
Artificial Intelligence Tools and One Dimensional Electronic Materials for Future Computer Chips and Energy Harvesting Shuang Tang, Alexandria Burger and Andrew Lemieszewski; State University of New York Polytechnic Institute, United States

The trend of novel electronic materials development is transitting from thin film based chips into smaller scaled materials systems, such as nanowires, nanotubes and nanoribbons. Among many materials candidates, bismuth antimony nanowires are promising ultra-high mobility, low power consumption, and a great richness of electronic phases and band-edge configurations. When the alloy materials system is made into nanowires, the symmetry between the three L-points and the six H-points in the first Brillouin zone can be either kept or broken, providing much larger flexibility than silicon in chip and circuit designs.

Semi-metals, direct-band-gap semiconductors, and indirect-band-gap semiconductors can coexist in one system. One bottle-neck in materials design is accurately predicting the electronic phase and the band structure. For bulk and pure materials, the band structure can be well described using first principle calculations. However, when the materials are alloyed and made into nanostructures, the calculational time that is needed may not be feasible with the current computer power. In the recent decade, pattern recognition techniques and other artificial intelegence have been widely developed and utilized in research of condensed matter physics and materials science.

In this present work, we will use multiple pattern recognition tools, including the support vectors, the trees, the bagging method, as well as the artificial neural networks, to realize the accurate and convenient describing of electronic phases and band structure of bismuth antimony nanowires. Different values of alloy composition, growth orientation, and wire diameter will be discusses. We will also discuss how the size of training pool will affect the predicting accuracy when different tools are used.

SESSION EL21.04: Energy-Efficient Computing I
Session Chairs: Jayakanth Ravichandran and Heike Riel
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3011

8:00 AM *EL21.04.01

Hybrid 2D/CMOS Microchips for Memristive Technologies Mario Lanza; King Abdullah University of Science and Technology, Saudi Arabia

Two-dimensional layered materials (2D-LMs) materials have outstanding physical, chemical and thermal properties that make them attractive for the fabrication of solid-state micro/nano-electronic devices and circuits. However, synthesizing high-quality 2D-LMs at the wafer scale is difficult, and integrating them in semiconductor production lines brings associated multiple challenges. Nevertheless, in the past few years substantial progress has been achieved and leading companies like TSMC, Samsung and IMEC have started to work more intensively on the fabrication of devices using 2D-LMs. In this talk, I will discuss the state-of-the-art on micro/nano-electronic devices made (entirely or partially) of 2D-LMs, the most sophisticated circuits ever constructed, and the fabrication of CMOS/2D hybrid microchips. I will put special emphasis on devices that employ hexagonal boron nitride, the only 2D-LM with an enough high band gap to be employed as dielectric. I will also discuss the main technological challenges to face in the next years and provide some recommendations on how to solve them.

8:30 AM *EL21.04.02
Two-dimensional Materials for Energy-Efficient Computing Saptarshi Das; The Pennsylvania State University, United States

In this talk, I will focus on describing a new paradigm of devices based on two-dimensional (2D) materials for sensing, computing, storage, and hardware security inspired by various insect, avian, and mammalian brains. We exploit unique electronic and optoelectronic properties of layered 2D materials to design high-performance, ultra-low-power, artificially intelligent, and inherently secure solid-state devices inspired by natural intelligence. For example, we have mimicked auditory information processing in barn owls (*Nature Communications*, *10, 3450, 2019*), collision avoidance by locusts (*Nature Electronics, 3, 646–655, 2020*), and subthreshold signal detection by paddlefish and cricket using stochastic resonance (*Nature Communications, 2020*). We have also mimicked probabilistic computing in animal brains using low-power Gaussian synapses (*Nature Communications*, *10, 4199, 2019*), and memristive graphene synapses (*Nature Communications, 11, 5474, 2020*) and realized biomimetic devices that can emulate neurotransmitter release in chemical synapses (*ACS Nano*, *11, 3, 2017)* and neural encoding in afferent neurons *(Nature Communications, 12, 2143, 2021)*. We have also made thes devices secure through SAT-attack-resistant hardware obfuscation using camouflaged 2D heterostructures (*ACS Nano, 15, 2, 2021*) and by realizing machine learning resilient and reconfigurable physically unclonable functions (*Nature Electronics 4, 364-374, 2021*).

9:00 AM *EL21.04.03
Opportunities and Limitations of Low-Dimensional Channel Materials for Energy Efficient Logic Computing Sheng-Kai Su[1], Edward Chen[1], Gregory Pitner[2], Terry Y.T. Hung[1], Meng-Zhan Li[1], Chao-Ching Cheng[1], H.S. Philip Wong[2,3] and Iuliana P. Radu[1]; [1]Taiwan Semiconductor Manufacturing Company (TSMC), Taiwan; [2]Taiwan Semiconductor Manufacturing Company, United States; [3]Stanford University, United States

Applications of abundant-data computing demand low energy consumption and concomitant high speed of the electronic systems. Increasing transistor density by continuous lateral dimension scaling is still the backbone to meeting such demand [1]. However, short-channel effect increases power consumption. Challenges to scaling Si technology and capabilities of heterogenous integration has stimulated interest in low dimensional materials (LDMs) such as two-dimensional (2D) transition metal dichalcogenides (TMDs) and 1D carbon nanotubes (CNTs) [2].

In this presentation, we explore the potential and challenges of using low dimensional materials as channel for extremely scaled transistors in advanced logic technology nodes. Based on the current hardware data, a multi-physics model to describe the ON current, sources of leakage which limit OFF current of MOSFETs with LDMs is used to project the scaling viability below 45 nm contacted-gate pitch (CGP). The scaling viability are analyzed by separately considering effects from shrinking the gate length, contact length, and extension length for different device architectures.

2D TMDs are high carrier density but low velocity channel materials [3], thus multiple Nanosheets are desired to increase effective device width. CNTs with high mobility and injection velocity in a ~1 nm semiconducting cylinder are especially promising for ON-performance with low power applied voltage V_{DD}. To preserve the advantage of high intrinsic current, low contact resistance and low leakage current are required for energy efficient computing.

Unlike contact to bulk Si, the LDM underneath the contact is atomically thin, therefore maintaining pristine LDM surface during metal deposition becomes even more important than for bulk material. Similarly, doping techniques used in Si technology, which could cause surface damage, might not be suitable for LDM. Uniquely for CNT with long mean free path, the effect of metal coupling could dominate over diffusion limited “current crowding” effect from low mobility materials such as Si or TMDs. The effect of metal coupling to reproduce the experimental observations is important, and we investigate its impact on contact resistance and leakage current [4]. To achieve a good balance between reducing access resistance and leakage, we compare different doping techniques and analyze the challenges of dielectric doping.

It is revealed that contact with strong enough metal coupling and high extension doping generated from dielectrics is desired for short contact length. For CNTs, a trade-off between extension length and contact length reductions to compromise among ON and OFF currents is analyzed from the perspective of CGP scaling. For 2D TMDs with large bandgap, leakage is not a limitation for CGP scaling with a Nanosheet architecture. However, low contact resistance for energy efficient CMOS with large bandgap channel material is challenged. Efforts in advancing contact, doping, and material uniformity (e.g., CNT’s diameter and pitch) for LDMs are necessary before an energy efficient logic technology can be developed.

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9:30 AM *EL21.04.04
Heterogeneous Integration of HfO_2 Resistive Random Access Memories on 2D van der Waals Materials Regina Dittmann[1], Urska Trstenjak[1], Niclas Schmidt[1], Kalle Goss[1], Alexander Gutsche[1], Konstantin Rushchanskii[2] and Silvia Karthäuser[1]; [1]PGI-7, Germany; [2]PGI 1, Germany

In order to make use of the functionality of different material classes for future energy-efficient computing, we investigated to co-integrate HfO_2-based redox-based random access memory (ReRAM) on 2D van-der Waals materials. For that purpose, we investigated the van der Waals epitaxy of HfO_2 thin films and nanoislands on graphene and on highly oriented pyrolytic graphite (HOPG), respectively. We identified a growth window for the pulsed laser deposition of HfO_2 that preserves the graphene transferred to thermally oxidized Si wafers. This enabled us to successfully fabricate HfO_2/Ti ReRAM cells with graphene bottom electrode. Based on the growth process developed for HfO_2 thin films, we deposited HfO_2 nanoislands on HOPG. The electronic and structural properties of these well separated, crystalline HfO_2 nanoislands are investigated by scanning probe methods. The topography reveals homogeneously formed HfO_2 nanoislands with areas down to 7 nm^2 and a thickness of one unit cell. They exhibit several in-gap states in addition to the bulk band gap, implying bulk properties of these ultra-scaled memristive objects. Nanocrystals with a diameter of 2.7−4.5 Å are identified next to carbon vacancies in the topmost HOPG layer, indicating that carbon is incorporated into the islands at early nucleation stages. The comparison of the theoretically determined lowest-energy clusters and electronic states with the experimental results allows us to identify the structure of the most relevant HfO_2 sub-nanometer crystals formed during the first nucleation steps and to assign the in-gap states to the observed carbon incorporation during heterogeneous

integration [1].
[1] N. Schmidt, K. Z. Rushchanskii, U.Trstenjak, R. Dittmann, and S. Karthäuser, ACS Appl. Nano Mater. (2022)

10:00 AM BREAK

SESSION EL21.05: Magnetic and Spintronic Materials I
Session Chairs: Iuliana Radu and Theo Rasing
Wednesday Morning, April 12, 2023
Moscone West, Level 3, Room 3011

10:30 AM *EL21.05.01
Magnetoelectrics at the Nanoscale for Spintronic Computing Applications Florin Ciubotaru[1], Anaïs Guerenneur[1,2], Daniele Narducci[1,2], Moritz Geilen[3], Frederic Vanderveken[1,2], Federica Luciano[1,2], Xiangyu Wu[1], Fanfan Meng[1,2], Sebastien Couet[1], Burkard Hillebrands[3], Inge Asselberghs[1], Sorin Cotofana[4], Iuliana Radu[1], Gouri Sankar Kar[1], Philipp Pirro[3] and Christoph Adelmann[1]; [1]imec, Belgium; [2]KU Leuven, Belgium; [3]TU Kaiserslautern, Germany; [4]TU Delft, Netherlands

Among the technologies that could potentially represent a paradigm shift with respect to CMOS technology, spintronic computation presents several advantages to achieve area and power reduction. The possibility to perform complex logic functions as majority gates, and the non-volatility of the magnetic materials could provide new functionalities to circuit designers for various applications. However, no concept for a complete magnetic/spintronic computing system exists. Therefore, the spintronic devices need to be complemented by CMOS in a hybrid spintronic–CMOS system. A major limitation for the realization of a such hybrid technology is the lack of scalable and energy efficient transducers capable to couple efficiently the electric and magnetic domains.
Current spintronic device concepts are often based on the control of the magnetization by currents, for example via magnetic Oersted fields, or using spin-transfer/spin-orbit torque. However, such approaches are typically not energy-efficient, therefore it would be desirable to control the magnetization by electric fields instead. In the last years, magnetoelectricity has seen a renaissance due to material development, as well as technological and theoretical progress. The promise of magnetoelectricity is a large improvement in energy efficiency compared to electric currents. Furthermore, downscaling the device dimensions would allow for an increase of the magnetoelectric coupling coefficients since they are electric field dependent. Therefore, magnetoelectricity may become an enabling factor for novel low-energy computing devices.
Magnetoelectric composite materials consisting of piezoelectric and magnetostrictive films are one of the most promising approaches for the magnetization control by electric fields. In this case, the magnetoelectric coupling occurs via strain: applying an electric field (voltage) across the structure generates strain in piezoelectric layer, which is then transferred to the adjacent magnetostrictive layer. This leads to an effective magnetic field that can rotate the magnetization of the system, or to generate spin waves if radio-frequency voltages are applied. An analogous inverse effect also exists which links changes in the magnetization direction to strain, and consequently, to electric fields.
For microelectronic applications, magnetoelectric heterostructures must be integrated into devices and miniaturized to the nanoscale. Here we will present an overview of our recent work on magnetoelectric systems and discuss materials, device design and fabrication, as well as the impact of different effects (device geometry, scaling, etc.) on the voltage coupling coefficients. We show that the device downscaling can lead to an enormous increase in the voltage response of magnetoelectric structures. Moreover, many applications require fast responses of the devices with targeted operational frequencies in the GHz range. We will present sub-micron scaled magnetoelectric spin-wave transducers and demonstrate their operation. COMSOL Multiphysics and micromagnetic MuMax software packages were further used to study the mechanical response and the magnetic behaviour, respectively, of different magnetoelectric devices, both in the DC and RF regimes. The magnetoelastic fields were estimated as well. Finally, we discuss the potential of magnetoelectric transducers for spin-wave computing applications.
This work has been funded by the European Union's Horizon 2020 research and innovation program within the FET-OPEN Project CHIRON under Grant Agreement No. 801055, as well as by imec's industrial affiliate program on beyond-CMOS logic. A.G, D.N., F.V., and F.L acknowledge financial support from the Research Foundation – Flanders (FWO) through Grant Nos. 1S97822N, 1SB9121N, 1S05719N, and 1183722N respectively.

11:00 AM EL21.05.02
Galfenol (FeGa) Electrode Material for Magnetic Tunnel Junctions for Low Power Nano-Computing Suyogya Karki[1], Jaesuk Kwon[1], Joe Davies[2], Supriyo Bandyopadhyay[3] and Jean A. Incorvia[1]; [1]The University of Texas at Austin, United States; [2]NVE Corporation, United States; [3]Virginia Commonwealth University, United States

Magnetic materials are an exciting material class for computing due to competitive write speeds, back-end-of-the-line compatibility, radiation hardness, non-volatility, and energy efficiency. Magnetic tunnel junctions (MTJs) are basic building blocks for magnetic devices used in spin transfer torque-magnetic random-access memory (STT-MRAM), magnetic logic-in-memory and neuromorphic computing applications. MTJs are trilayer structures in which a thin insulating layer is sandwiched between two ferromagnetic (FM) layers, where the relative magnetization of the ferromagnetic electrodes (fixed and free layers) can encode either a higher (bit 1) or a lower (bit 0) resistance state. In this work we introduce a 4-layer MTJ where the free layer is a magnetic bilayer comprising exchange-coupled Galfenol (FeGa) and CoFeB layers. The MTJ is fabricated on a PMN-PT piezoelectric substrate that is strained with a voltage to reorient the magnetization of the strongly magnetostrictive FeGa layer, which also rotates the magnetization of the CoFeB layer owing to exchange coupling. This modulates the MTJ resistance. Like highly energy-efficient VCMA switching, straintronic switching is also extremely energy-efficient. Thin films of FeGa are sputter deposited using an AJA sputter system, and X-ray diffraction measurements are used to confirm the preferred (110) crystal orientation of the films. The MTJ stack was grown with layers Si (Substrate)| SiO_2 (100)| Ta (5) | FeGa (5) |CoFeB (4) | MgO (2) | CoFeB (6) |Ta (5) | Ru (5); numbers are in nm and the stack was post annealed at 270 °C for 1 hr. The in-plane hysteresis loop of the stack shows two distinct switches of the top CoFeB and the bottom CoFeB|FeGa layers. In collaboration with NVE corporation, CIPT measurements show promising on/off ratio of the stack. The successful demonstration of piezoelectric/FeGa MTJs is a promising result for high-efficiency magnetic write performance in nanomagnetic computing.

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11:15 AM EL21.05.03
Chiral Non-Collinear Spin Textures in Nominally Centrosymmetric Magnets Rana Saha, Holger L. Meyerheim and Stuart S. Parkin; Max Planck Institute of Microstructure Physics, Germany

One of the major topics in spintronics today is to study magnetic materials in which neighboring magnetic moments are neither parallel nor anti-parallel but are rather non-collinear and can thereby form complex, topological, spin textures. Perhaps the most extensively studied of these is the skyrmion; this is a tiny magnetic nano-object with a chiral magnetic boundary and which is typically circular in shape. A prerequisite for the formation of such chiral nano-objects is that the parent material has a structure that is non-centrosymmetric. What has surprised the spintronics community recently is the observation of skyrmions in several materials that are centrosymmetric. Here we show evidence for skyrmions in a member of the family of van der Waals materials, $CrTe_2$, that is nominally centrosymmetric. The symmetry of the structure of this 2D compound is lowered in a very special manner by self-intercalation of Cr atoms within the so-called van der Waals gaps between tri-layers of Te-Cr-Te from which the structure is formed. Furthermore, we show from detailed, high-resolution, x-ray structure analysis that the self-intercalated Cr atoms form an ordered 3D superstructure that hasn't previously been observed in any known van der Waals compound. The superstructure gives rise to two inequivalent van der Waals gaps, both partially filled by Cr atoms but in different ways. As a consequence, neighboring Te-Cr-Te tri-layers experience an asymmetric environment involving relaxations of the atomic positions along the vertical *c*-axis, thereby reducing the crystal symmetry from Pm to P3m1, the latter being non-centrosymmetric. The latter has a C_{3v} point group that is compatible with the appearance of Néel-type skyrmions, which were directly imaged using state-of-the-art Lorentz transmission electron microscopy over a wide temperature range.

11:30 AM *EL21.05.04
Spintronics-Enabled Low Power Computing Louis Hutin[1], Kevin Garello[2], Laurent Vila[2], Philippe Talatchian[2], Ursula Ebels[2], Kamal Danouchi[2], Guillaume Prenat[2], Denys R. B. Ly[1], Olivier Billoint[1], Gregory Di Pendina[2], Franck Badets[1], Corentin Bouchard[1], Bernard Viala[1], Bertrand Delaet[1], Catherine Carabasse[1], Florian Disdier[2], Jérôme Faure-Vincent[2], Ricardo Sousa[2], Aymen Fassatoui[2], Pierre Noé[1], Jean-Philippe Attané[2], Lorena Anghel[2], Elisa Vianello[1], François Andrieu[1] and Ioan Lucian Prejbeanu[2]; [1]CEA-Leti, France; [2]Spintec, Université Grenoble Alpes / CEA / CNRS, France

In the context of a growing demand for data-intensive applications, the ubiquitous von Neumann computer architecture suffers from throughput limitations due to the memory transfer rates lagging behind CPU speed, as well as from the energy cost of information shuttling. This can be mitigated by innovative architectures and nanodevices enabling a higher degree of locality in information processing, blurring the lines between memory and compute functions, extending beyond the boundaries of purely charge-based and/or conventional Boolean logic paradigms. We hereby review some recent advances in the field of spintronics-based component research and illustrate how they may, at different levels, contribute to the advent of more energy-efficient computing systems.
Trade-offs between programming energy, speed and endurance prevent most emerging NVM technologies from moving up the memory hierarchy. Among the more promising candidates, Spin Transfer Torque (STT) MRAM is considered as a denser and low power alternative to SRAM for last-level cache. Yet, sub-10ns programming conditions would be hardly compatible with standard lifetime requirements, due to the need for large currents across the MgO-based magnetic tunnel junction (MTJ). Leveraging the strong spin-orbit coupling in some heavy metals or topological insulators, Spin Orbit Torque (SOT) MRAM enables switching the state stored in the MTJ by flowing a charge current near it rather than through it, effectively decoupling the read and write paths. While nanosecond switching and high (>1^{e}12 cycles) endurance are reachable, future work on material and interface engineering directed at charge-spin conversion efficiency and selective addressing should help further density improvements.
From the standpoint of digital logic, a number of spin-based components using spin-polarized transport have emerged over the years as possible beyond CMOS substitutes combining low switching energy, built-in non-volatility and possibly higher logic density. In many cases however, these benefits could be overshadowed by circuit overhead for either signal amplification (maintaining logic levels for long range transfer, cascading, fanout) or error correction. In an effort to alleviate this issue, some recent proposals combine transduction mechanisms to couple hybrid spintronic devices through charge-driven interconnects. Two such examples are the MESO (MagnetoElectric Spin Orbit) and FESO (FerroElectric Spin Orbit) devices. The latter relies on the property that the direction of a charge current generated by spin-orbit coupling may be controlled by the polarization of a ferroelectric. This effect was demonstrated in two classes of materials: two-Dimensional Electron Gases (2DEG) appearing at oxides surfaces or interfaces, and ferroelectric Rashba semiconductors, opening intriguing perspectives towards the integration of non-volatile logic with aJ switching energy and manageable error rates.
Finally, other more disruptive computational paradigms can not only cope with, but benefit from noise or stochasticity. Some learning or inference algorithms were initially inspired by the physics of interconnected non-linear elements probabilistically evolving towards collective states minimizing their energy. Conversely, hardware networks of directly interacting components could be designed to naturally execute those energy-based computing algorithms with a much reduced need for data movement or auxiliary functions. For instance the so-called Ising machines, particularly suitable as combinatorial optimization solvers, can take many shapes and forms such as dynamical systems of coupled oscillators or networks of binary stochastic neurons. The latter are functionally equivalent to random telegraph signal generators with tunable dwell times, thus distinguishing superparamagnetic MTJs and their unique property of thermally-induced switching as elegantly simple and efficient building blocks.

SESSION EL21.06: Ferroelectric Materials I
Session Chairs: Stefano Brivio and Subhash Shinde
Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3011

1:30 PM *EL21.06.01
Ultrathin Ferroelectric Films for Next Generation Logic and Memory Applications Sayeef Salahuddin; University of California, Berkeley, United States

Compared to archetypical perovskites, fluorite HfO_2 based ferroelectric materials are process-compatible with advanced CMOS transistors. As a result, they promise to bring ferroelectric technologies into wide-spread applications. At the same time, ferroelectricity in these materials is also different. In conventional perovskites, the polarization becomes weaker as the thickness is decreased due to 'size effects'. Balking this conventional trend, our recent work has shown that ferroelectricity in HfO_2-like fluorite films in fact enhances as the thickness goes down. The ferroelectricity can be demonstrated even in a 0.5 nm thick film, which is just one cell! In this presentation I shall discuss these results. In addition, I shall also discuss Negative Capacitance transistors with just 18A thick ferroelectric material- the same thickness of high- dielectric used in today's advanced transistors. I shall further present ferroelectric field effect transistors with thin ferroelectric gate oxide. These results demonstrate substantial potentia for ultrathin, integrated ferroelectric materials for next generation logic and memory devices.

2:00 PM EL21.06.02
Manipulation of Antiferromagnetism in Freestanding BiFeO$_3$ Membranes Siang Hong Tan[1], Xuheng Diao[1], Chang-Yang Kuo[1], Qi-Wu Shi[2], Shang-Jui Chiu[3] and Yen-Lin Huang[1]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]Sichuan University, China; [3]National Synchrotron Radiation Research Center, Taiwan

BiFeO$_3$ (BFO) is arguably the only material that exhibits two order of parameters above room temperature with a Curie temperature of 1100 K and Nèel temperature of 653 K. Moreover, these two order parameters, ferroelectricity, and antiferromagnetism, are strongly coupled, known as magnetoelectric coupling. Owing to this magnetoelectric coupling, extremely low switching energy to alter the states of orderings can be realized by reducing the ferroelectric switching voltage as well as the ferroelectric polarization of BFO. Recent studies show that by optimizing the chemical composition of BFO, size scaling, and the removal of substrate clamping effect, the BFO ferroelectric switching voltage can be well improved[1]. Freestanding BFO membranes exhibit ~30% coercive voltage reduction and ~50% switching speed enhancement[2]. However, the methods to obtain large area of freestanding BFO films are still challenging as well as the understanding of its antiferromagnetic ordering. Here, we synthesized high-quality BFO epitaxial thin films on SrTiO$_3$ single crystal substrates by pulsed laser deposition, and optimized the freestanding process of BFO membranes by introducing various oxide buffer layers, such as SrRuO$_3$, and SrTiO$_3$, in between the sacrificing layer, La$_{0.7}$Sr$_{0.3}$MnO$_3$, and the BFO layer. Moreover, we used XMLD (X-ray Magnetic Linear Dichroism) to characterize the antiferromagnetic orientations of BFO membranes, we found that the antiferromagnetic axis of BFO is lifted from in-plane toward out-of-plane direction ~<112>$_C$, where C is noted as a cubic system, after the substrate was removed. We also notice that the tilting angle of the antiferromagnetic axis of BFO is strongly influenced by the thickness of the BFO layer and the buffer layer and that implies the antiferromagnetic axis degree of freedom is tunable by altering the elastic boundary conditions. Finally, we further conduct magnetotransport measurements to confirm whether the efficiency of magnetoelectric coupling can be improved after the freestanding process.

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2:15 PM EL21.06.03
The Polar Phase and Ferroelectricity Properties of Hf0.5Zr0.5O2 Freestanding Thin Films Xuheng Diao and Yen-Lin Huang; National Yang Ming Chiao Tung University, Taiwan

The polar phase and ferroelectricity properties of Hf0.5Zr0.5O2 freestanding thin films
Xu-Heng Diao1, Siang-Hong Tan1, Shang-Jui Chiu2, Yen-Lin Huang1
Department of Materials Science and Engineering, National Yang Ming Chiao Tung University Hsinchu, Taiwan.
National Synchrotron Radiation Research Center, Hsinchu, Taiwan.

Hafnium-based oxide thin films, such as Hf0.5Zr0.5O2 (HZO) have great potential for nanoscale device applications with their low power, high-speed, non-volatility, and compatibility with modern CMOS technology. However, fabricating a stable phase of HZO thin films exhibiting robust ferroelectricity is not an easy task. The major mechanism to stabilize the ferroelectric phase of HZO is to utilize an epitaxial strain imposed from a lattice-mismatched substrate. This limits the process window for ferroelectric HZO thin films. In addition to strain effect, the chemical composition of the bottom electrodes and the oxygen vacancies level will also affect the polar stability of the HZO thin-film. How to stabilize the polar phase of HZO and explore the boundary of ferroelectricity of HZO thin films are the central challenges for HZO-related devices and applications.
In this study, we demonstrate the robust ferroelectricity of HZO epitaxial thin films in three different types of phases, which are pure polar-O-phase(orthorhombic), pure nonpolar-M-phase (monoclinic) and mixed O and M-phases. We then obtain HZO films without substrates (freestanding) at a millimeter scale. Through XRR (X-ray Reflectivity) and XRD fringes, we found that the nonpolar-M-phase started to appear from the polar-O-phase after the thickness is thicker than 7 nm resulting in the suppression of ferroelectric polarization. Finally, we discuss the phase competition between the polar O-phase and non-polar M-phase with and without the substrate clamping effect. Our approach can provide fundamental insights into the limit of ferroelectric switching of HZO-based films and the role substrate plays in polar phase stabilization.

2:30 PM *EL21.06.04
Ferroelectric Field-Effect Transistors—Logic Compatibility and Microstructure Asif I. Khan; Georgia Institute of Technology, United States

Over the last decade, the discovery of ferroelectricity in fluorite-structured binary oxides, namely HfO$_2$ and its alloyed variant, led to resurgent interests into ferroelectric devices for embedded memory applications [1,2]. In this talk, we will highlight recent advancements in ferroelectric field-effect transistors (FEFETs). First, we will present our work on reducing write voltage in FEFETs down to logic compatible levels for embedded memory applications by engineering the interfacial oxide layer and gate metal electrodes. Next, we will highlight our efforts on understanding and controlling the microstructure of ferroelectric layer in FEFET gate stacks to address the variability challenge, using multi-scale transmission electron microscopy including in-situ, electrical biasing approaches [3]. The talk will end with an outlook for FEFETs for different domains, such as embedded, storage class and storage applications.

The research is supported by the National Science Foundation, the Defense Advanced Research Program Agency (DARPA), the Applications and Systems-Driven Center for Energy-Efficient Integrated Nano Technologies (ASCENT), one of six centers in the Joint University Microelectronics Program (JUMP), a SRC program sponsored by the DARPA, and an Intel Rising Star award.

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3:00 PM BREAK

SESSION EL21.07: Panel Discussion: Exploratory Materials
Session Chairs: Heike Riel and Hui Jae Yoo

Wednesday Afternoon, April 12, 2023
Moscone West, Level 3, Room 3011

3:15 PM *EL21.07.01
BEOL-Compatible Diamond Growth for Thermal Management for Efficient Computing Srabanti Chowdhury; Stanford University, United States

Efficient computation demands of 21st -century applications far exceed the capabilities of today's systems. Traditional approaches are stalling to serve the roadmap for next generation computation where large efficiency and speed improvements are needed. These challenges get worse as 2D scaling of transistors hits fundamental limits: the 'miniaturization wall'. The next leap in performance and energy efficiency requires the next surge in integration. Ultra-dense on-chip 3D integration with inter-layer via pitch of 100 nm are the chips especially for abundant-data applications (e.g., AI, analytics, graphs) [1]. 3D chip integration can be realized in more than one way: monolithically, or heterogeneously. Regardless of the device technology proposed, fast compute units must operate in 3D layers to overcome the memory wall and the miniaturization wall. This criterion, alone, imposes an enormous thermal challenge and demands solutions beyond the traditional ones such as improved heat sinks outside the chip or thermal vias within the chip. It should be noted that thermal vias including dummy thermal vias are not enough and comes with significant electrical performance penalty. Novel approaches like spreading the heat inside chips using thermally conductive material are necessary. Our current demonstration of thin-film diamond grown at BEOL compatible temperatures (400oC) positions itself as a potential solution for heat spreading [2]. Diamond is perhaps the most attractive candidate for high thermal conductivity (>2000W/m/K in its single crystalline form). Due to its large bandgap (5.47 eV) and highly insulating nature, diamond is excellent for integration with device where electrical behavior should be preserved, and phonon bottleneck is removed. At the device level, Joule heating and resulting high temperature in the channel due to the increased power density results in performance degradation and premature failure. Diamond integration near the hot spot can spread the heat by increasing the heat transfer coefficient. Diamond is mostly grown at high temperatures (700-1000°C), which limits its integration with many semiconductor technologies. We have recently demonstrated a high-quality 400°C-diamond by modifying the gas chemistry at different nucleation stages, with a sharp sp3 Raman peak (FWHM≈6.5 cm-1) and high phase purity (97.1%), like 700°C-diamond (>98%) is demonstrated. An average grain size of 650 nm with a thickness of 790 nm corresponding to an anisotropy ratio of 1.21 at 400°C close to the best-reported of 1.12 at 700°C is achieved. This near-isotropic diamond exhibits a relatively high thermal conductivity of ~300 W/m/K and a thermal boundary resistance as small as only 5 m2K/GW on BEOL compatible dielectric layers.
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3:45 PM *EL21.07.02
Ferroelectric Tunnel Junctions for Compute-in-Memory Saima Siddiqui, Chia-Ching Lin, Sou-Chi Chang, Nazila Haratipour, Bernal G. Alpizar, Sarah Atanasov, Jason Peck, Tristan Tronic, Anandi Roy, Dominique Adams, I-Cheng Tung, Adedapo Oni, John Richards, Matthew Metz and Uygar Avci; Intel Corporation, United States

Energy efficient computing is one of the major challenges of today's semiconductor industries. To support the artificial intelligence (AI), the computation is more memory centric and requires frequent access beyond the cache. Data shuttling (known as "memory wall") is identified as the main bottleneck for such implementation of AI with the current von Neumann architecture. Modifying the computing system is a potential option for circumventing this bottleneck, and among different computing architectures, computing inside memory (CIM) is the most energy-efficient for eliminating the memory wall of state-of-the-art processors. It has been shown that the non-volatile memories in the cross-point architecture can potentially improve the system efficiency significantly from below one to a few hundred TOPS/W. Different non-volatile memories including resistive random-access memory (RRAM), phase change memory (PCM), magnetic RAM and ferroelectric (FE) based devices i.e., FeRAM, FeFET and tunnel junctions (FTJs) are actively studied for efficient non-volatile memory and CIM applications. Recently, HfxZr1-xO2 (HZO) FE materials have attracted significant attention as embedded non-volatile memory (eNVM) due to thickness scalability and CMOS back-end-of-line (BEOL) compatibility [1]. In particular, it has been shown experimentally that cache-level memory with much lower refresh power can be enabled by HZO-based low-voltage FeRAM with endurance of >1012 cycles for high-speed read/write operations at elevated temperatures [2-4]. These devices are designed based on the fundamental understanding from multi-domain phase-field device-level framework for polycrystalline HZO FE and anti-ferroelectric (AFE) thin films [5]. However, compared to memory options in conventional memory hierarchy, the performance requirements such as write and read energies, endurance as well as retention are different in CIM applications, and thus device technology co-optimization is critical. Among different resistive memory devices, FTJs are of particular interest as they offer the lowest switching energy, high endurance and retention.
FTJ is a two-terminal device with a ferroelectric layer sandwiched between two electrodes. The resistance of this device changes based on the polarization of the FE layer. Depending on either complete or partial switching of the FE layer, FTJ can be used for digital or analog CIM. In this work, we will demonstrate HZO- based planar FTJs with very low write current (3.8×101 A/cm2) and voltage (1 V) by material and structural engineering. Here, we optimize FTJs' performance for read ON current (10-3 A/cm2 at 0.3V), ON/OFF ratio (7), endurance (>1010), retention (100 s), and nonlinearity (0.01/-2.4) with 16 individual states for analog CIM. The write pulse of our planar FTJs can be scaled down to 250 ns without degradation in performance, and it is expected that polarization switching can be as fast as 2 ns in scaled dimensions [2]. There are still challenges (i.e., low read current, ON/OFF ratio, retention etc.), which need to be solved for the technological implementations of FTJs for CIM. However, we show that a high accuracy of ~90% is achieved in recognizing digits from Modified National Institute of Standards and Technology (MNIST) dataset by our FTJs with both binary and multiple states [6]. These results highlight that HZO-based FTJs are promising for high performance non-volatile memories and electrical synapses. [1] T. Mikolajick et al., "Next generation ferroelectric materials for semiconductor process integration and their applications," J. of Appl. Phys. 129, 100901 (2021). [2] S. -C. Chang et al., " Anti-ferroelectric HfxZr1-xO2 Capacitors for High-density 3-D Embedded-DRAM," 2020 IEEE International Electron Devices Meeting (IEDM), 2020, pp. 28.1.1-28.1.4.

4:15 PM EL21.07.04
Room Temperature Low-Energy Resistive Switching in Flux-Grown Quasi-1D Chalcogenide $BaTiS_3$ Huandong Chen and Jayakanth Ravichandran; University of Southern California, United States

Low energy switching in the form of either volatile or non-volatile is critical in achieving energy efficient computing. Asymmetric resistive switching between two different phases or states are typically achieved by phase transitions such as metal-to-insulator transitions, but the energy consumption to overcome the barrier is usually substantial. On the other hand, resistive switching between bistable states such as ferroelectric switching is much more energy efficient. $BaTiS_3$ is a 'ferroelectric-like' semiconductor that features large Ti out-of-plane displacements at room temperature like $BaTiO_3$ and is promising in demonstrating such bistable switching. Here, we show the non-volatile resistive switching over one order of magnitude achieved below 0.5 V from a bulk $BaTiS_3$ device with the channel size ~ 100 µm in plane, and the status can be reset via a reverse scan. The scaling of the switching voltage with respect to channel sizes is also discussed. Our study identifies $BaTiS_3$ as a unique ferroelectric semiconducting system that achieves low energy resistive switching at room temperature.

4:30 PM PANEL DISCUSSION

SESSION EL21.08: Poster Session
Session Chairs: Subhash Shinde and Hui Jae Yoo
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EL21.08.01
Low-Voltage Control of Synaptic Behavior in WO_3 based Two Terminal Protonic Devices Satya Prakash Pati, Satoshi Hamasuna and Takeaki Yajima; Kyushu University, Japan

Artificial neuromorphic devices are capable of processing information by consuming much lower power in comparison with traditional computing technology [1]. Among diverse synaptic structure, conductance switching in metal/insulator/metal type memristive devices are promising candidate owing to their analogous working mode. Most of the conventional memristive devices are filamentary type, where electrical control of migration of ions (Li^+, Na^+, K^+, Ca^{2+} etc.) or oxygen defects result in the change of conductance state. Due to the formation of random filament and relatively low diffusion capability of such ions, these devices suffer from poor reproducibility and relatively high voltage. To circumvent the issue, proton (H^+) could be a promising candidate owing to its lowest ionic size and high diffusability [2]. Moreover, most of the conventional protonic devices reported are 3-terminal type having an insulating barrier layer, and therefore, their operating voltage is still over 1-Volt range [3-6]. To avoid the issues of power consumption, further reduction of operating voltage should be verified. In this concern, we propose a 2-terminal protonic device in the stacked geometry without any barrier layer. Herein, we have demonstrated the ultra-low voltage switching of conductance state in a 2-terminal protonic device comprising an amorphous WO_3 layer as proton conductor.
Heterostructure of Si (Sub.)/SiO_2 (500nm)/Ti (3nm)/Pt (30nm)/WO_3 (120nm)/Pd (30nm) was fabricated by using e-beam evaporation and pulsed laser deposition. Microstructural measurements confirm the fabricated WO_3 layer is amorphous and atomically flat having roughness ≈1.5nm. Additionally, WO_3 film is highly porous having density 5.76 gm/cm^3 which is less than its bulk value 7.16 gm/cm^3. In order to define the chemical potential of hydrogen, proton transport measurements were performed under Ar+H_2(5%) mixture gas with a fixed pressure 6.86 kPa. To understand the hydrogen incorporation process in WO_3, conductance was measured as a function of H_2 exposer time with different applied voltages. The result exhibits a gradual increase in conductance up to 3-order of magnitude over time, and the increasing rate is dramatically changed as a function of the applied voltage. At negative voltages, WO_3 still maintains its semiconducting properties while application of positive voltages induces a large change from semiconducting to conducting state. The results clearly indicate the hydrogen incorporation is strongly affected by the applied voltage, where the H-ions from Pd reservoir progressively drifts into WO_3 channel through the electrochemical reactions in the two-terminal device. We also investigated the conductance change from the viewpoint of hydrogen chemical potential rather than the applied voltage, where H_2 pressure was varied while the applied voltage was kept constant at 0.5 volt. The result shows that the device response time is largely delayed by decreasing the H_2 pressure, corroborating the underlying electrochemical reaction. Based on these thorough understandings, the reversible conductance change as like potentiation and depression in biological synapses was achieved by switching the polarity of input voltage from -0.2V to +0.2V. Despite this low operation voltage, we have obtained the conductance modulation of 22% at room temperature. These findings will pave a way to the design of low power consumption protonic neuromorphic devices.
This work was supported in part by JST CREST Grant Number JPMJCR19K2.
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5:00 PM EL21.08.02
Low-Operation Voltage Non-Volatile Memory Characteristics with Oxide-Semiconductor Thin-Film Transistors Through Interaction Between Oxide Semiconductor Channel and Gate Oxide Jimin Han, Boyoung Jeong and Tae-Sik Yoon; Ulsan National Institute of Science and Technology, Korea (the Republic of)

The demand on high-density and high-performance non-volatile memories is increasing for emerging data-centric applications. Among various non-volatile memories, a memory adopting a single metal-oxide-semiconductor field-effect transistor (1-MOSFET) operates with the modulation of the channel conductance to store the information. Mechanism of the channel conductance modulation is largely dependent on the properties of gate stack composed of semiconductor channel and gate oxide layers. One of the most representative 1-MOSFET memory to modulate the channel conductance is a floating-gate (charge-storage node or charge-trap layer) memory cell comprising a flash memory. This cell performs memory functions in the charge-storage-based way that the threshold voltage is shifted as a result of electrical charging of the floating gate (or charge-storage node) by tunneling of electrons through tunneling oxide upon voltage application to the control gate. Alternative way includes the use of a non-charge-storage-based (or ion-based) memory operation by tuning gate stack properties such as the changes in carrier mobility and dopant concentration in the channel layer, and gate oxide capacitance. There have been extensive efforts to make advance in 1-MOSFET memory to fully exploit its high density integration capability with a low cost per bit. Nevertheless, it is still challenging to achieve low operation voltage as well as high operation speed, which are particularly crucial for the application to energy-efficient computing systems that perform data-processing cooperated with memory units. In this study, charge-storage-based and non-charge-storage-based 1-MOSFET non-volatile memory were investigated to achieve low voltage operation in oxide-semiconductor thin-film transistor (TFT) with various gate stacks. For example, the memory with an indium-zinc oxide (IZO) channel layer and an oxygen-deficient HfO_{2-x} gate oxide deposited by sputtering exhibited non-charge-storage-based non-volatile memory characteristics, where the channel conductance was modulated as driven by oxygen ion exchange between gate oxide and channel layers. The device with an indium-gallium-zinc oxide (IGZO) channel layer and HfO_{2-x} gate oxide deposited by atomic layer deposition showed the charge-trap memory properties with threshold voltage shift by electrical charging in the oxygen-deficient low-temperature ALD HfO_{2-x} charge-trap layer. In particular, the UV/ozone treatment of interface between gate oxide and oxide semiconductor channel layer adjusted the electrical charging and oxygen ion exchange behaviors. The memory with ZnO channel layer and NbO_x gate oxide showed also the charge-trap memory characteristics thanks to the high trap density in NbO_x as a charge-trap layer. These presented devices exhibited various non-volatile memory characteristics such as gate voltage polarity-dependent programming and erasing operations, the good retention of memory states and endurance properties upon repeated operations. In addition, since these devices did not adopt the tunneling oxide, thus enabled lower voltage operation compared to conventional floating-gate memory cell. These results demonstrated that the properties of gate stack layers including oxide semiconductor, ion-exchange layer, charge-trap layer, and interfacial tunneling oxide formation by post-deposition treatments could be adjusted, and consequently determine charge-storage-based or non-charge-storage-based non-volatile memory functions with the low voltage operation for energy-efficient computing systems.

5:00 PM EL21.08.03

Non-Charge Storage Based Nonvolatile Memory with IGZO Oxide Semiconductor and $LiCoO_x$ Charge Trap & Ion Supplying Layer with Large Memory Window Boyoung Jeong, Jimin Han, Taeyun Noh and Tae-Sik Yoon; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Demand for developing advanced nonvolatile memories significantly increases as emerging data centric applications such as artificial intelligence, the Internet of Things, and automated systems have evolved [1]. Among various nonvolatile memories, charge storage-based flash-type memory has been the most representative. However, adopting charge storage-based nonvolatile memory has some reliability issues such as unintended shift of threshold voltage (V_T) or electrostatic coupling effects [2]. In this study, we investigated non-charge storage-based nonvolatile memory with IGZO channel layer and $LiCoO_x$ as ion supplying layer and charge-trap layer. To demonstrate non-charge storage-based memory behavior, two thin-film transistors (TFTs) having different HfO_2 tunneling oxide thickness, i.e., IGZO/HfO_2(5 nm)/$LiCoO_x$ and IGZO/HfO_2(2 nm)/$LiCoO_x$ stacks, were prepared, and their memory performances were examined. The IGZO/HfO_2(5 nm)/$LiCoO_x$ device showed the clockwise hysteresis in transfer curves with $\Delta V_T \sim 5$ V due to electrical charging in the $LiCoO_x$ layer upon applying the gate voltage sweep of -5 ~ +25 V in forward and backward direction. On the other hand, IGZO/HfO_2(2 nm)/$LiCoO_x$ device with a thinner HfO_2 layer showed much enhanced memory window with ΔV_T up to approximately 20 V in clockwise hysteresis in the same measuring condition. The V_T shift could be induced by the electron charging in the $LiCoO_x$ layer as well as the Li ion migration between IGZO and $LiCoO_x$ layer that depends on the thickness of HfO_2 tunneling oxide. In particular, Li ions could pass through the 2 nm-thick HfO_2 tunneling oxide and modulate the channel conductance as dopants in the case of 2 nm-thick HfO_2 device, while only electron charging would induce the V_T shift in the case of 5 nm-thick HfO_2 device because Li ion cannot penetrate through 5 nm-thick HfO_2. Since Li ions act as p-type dopants in IGZO channel layer, the IGZO channel conductance decreases and V_T shifts positively during application of positive gate voltage as a result of Li ion migration from $LiCoO_x$ layer to IGZO channel layer, in addition to the electrical charging of $LiCoO_x$ layer. Thanks to the use of thinner HfO_2 tunneling oxide, both electron charging and Li ion migration in response to the applied gate voltage lead to the wide memory window more efficiently. This study demonstrates non-charge storage based nonvolatile memory characteristics through viable approach of introducing Li ion as dopants in order to improve the nonvolatile memory performance for advanced nonvolatile memory application.

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5:00 PM EL21.08.04

Analog Synaptic Characteristic in Bilayered Gd-Doped Ceria and CeO_2 Memristors for Neuromorphic Computing Sola Moon, Kitae Park, Peter H. Chung, Dwipak P. Sahu and Tae-Sik Yoon; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Neuromorphic computing, inspired by the human brain that consumes less than 20 W of power, is emerging as an alternative to the existing von Neumann computing system suffering from its limits in device scalability and delayed data transfer between memory and processing unit [1]. In order to develop neuromorphic computing systems, significant efforts have been made to develop artificial electronic synaptic devices that mimic biological synaptic functions. Among various synaptic devices, analog resistance switching-based oxide memristive devices have promising opportunities due to their unique properties such as high density, good scalability, and high energy efficiency. In this study, we have demonstrated linear, symmetric, and analog synaptic characteristics in the bilayer structures of Pt/Gd-doped ceria (GDC)/CeO_2/Pt and Pt/CeO_2/Gd-doped ceria (GDC)/Pt memristors with different oxide stacking order. In particular, Gd-doped ceria, being one of the oxides having high ionic conductivity among mixed oxygen ionic-electronic conductors. Also, Gd-doped ceria has been reported to form a high concentration of oxygen vacancies [2]. As the concentration and mobility of oxygen-based defects play a significant role in oxide-based memristors, the bilayered CeO_2 and GDC memristors were fabricated and their synaptic properties were investigated. The use of bilayer memristors by stacking CeO_2 with more oxygen-deficient GDC turned out to have improved linearity and symmetry in potentiation and depression behaviors thanks to redistribution of oxygen vacancies between CeO_2 and GDC. The Pt/GDC/CeO_2/Pt memristors showed the potentiation behavior with decreasing resistance upon applying positive voltage at top Pt electrode while the application of negative voltage caused the depression with increasing resistance. The Pt/CeO_2/GDC/Pt memristors with reverse stacking order of GDC and CeO_2 exhibited opposite dependence of resistance change on the applied voltage polarity, which is associated with the resistance switching mechanism of energy barrier modulation at GDC/CeO_2 interface and Schottky barrier modulation at the interface with electrodes. Pattern recognition simulations using the modified MNIST dataset showed accuracy levels of up to 88% in bilayer memristors, confirming the potential of these bilayer memristors as artificial synapses for neuromorphic computing.

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5:00 PM EL21.08.05

Effects of *In Situ* SiN Layer on the Leakage Current of AlGaN/GaN HEMTs Juyeong Park[1], Jong Bae Kang[2] and Jaehyung Jang[2,3]; [1]Gwangju Institute of Science and Technology, Korea (the Republic of); [2]KENTECH Institute of Energy Materials and Devices, Korea Institute of Energy Technology, Korea (the Republic of); [3]Korea Institute of Energy Technology, Korea (the Republic of)

For conventional GaN based high electron mobility transistors (HEMTs) fabrication process, Au based ohmic contacts are usually adopted to form low resistance ohmic contact. However, Au based ohmic contact usually needs high temperature annealing process and it induces high density of surface states which causes high leakage current of devices [1]. In this work, in-situ SiN layer is employed to prevent degradation of the GaN surface from high temperature annealing during fabrication of GaN HEMT. Since in-situ SiN was grown at high temperature environment, it is heat resistant enough to protect GaN surface from high temperature stress. Three samples were fabricated and compared to analyze the effect of in-situ SiN layer.

The heterostructures was grown on a Si substrate consisting of 50-nm-thick SiN cap layer, 20-nm-thick $Al_{0.25}Ga_{0.75}N$ barrier, GaN channel and buffer layer. The fabrication process starts with mesa-isolation with inductively-coupled-plasma reactive-ion-etching (ICP-RIE) using BCl_3/Cl_2 gas. The in-situ grown SiN on the region of ohmic contact was etched with ICP-RIE using SF_6 gas. The multilayer Ti/Al/Ni/Au (30/180/40/150 nm) metallization was deposited using e-beam evaporator. Rapid thermal annealing (RTA) process was followed to form the ohmic contacts. The samples were annealed at the temperatures of 900°C for 70s in nitrogen ambient. For a sample A, any surface treatments or etching processes were not applied. For the sample B, TMAH treatment was applied on the surface of sample for 1min at the temperature of 100°C to remove high temperature stress related surface states [2]. For the sample C, the in-Situ SiN layer was etched with low power ICP-RIE using SF_6 gas. The Ti/Au (20/300 nm) pad metallization was deposited using e-beam evaporator. Finally, Ni/Au (20/300 nm) was deposited to form the gate electrodes using e-beam evaporator. The fabricated GaN HEMTs have an 8.5-µm source-drain spacing, 3-µm gate length and 2×50µm gate width. The electrical characteristics of the GaN HEMTs were measured using HP4155A semiconductor parameter analyzer.

The leakage currents of fabricated samples were compared to analyze the effects of in-situ SiN. The gate leakage current densities of sample A, B and C were 73 µA/mm, 142 nA/mm, 5 nA/mm respectively at the gate bias of -10 V. The sample C exhibited the lowest gate leakage current, followed by the sample B and sample A. It was found that the TMAH treatment reduces the leakage current by removing surface states on SiN. The removal of SiN damaged due to the thermal stress further reduced the leakage current. The low leakage current of sample C implies that the in-situ SiN successfully protected the GaN surface from high temperature stress suppressing the formation of surface states on the GaN surface.

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5:00 PM EL21.08.06

Analog Synaptic Characteristics of CeO$_2$-based Memristor Crossbar Array for Neuromorphic Computing Kitae Park, Jiyeon Ryu, Dwipak P. Sahu and Tae-Sik Yoon; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Artificial synapses with analog resistive switching devices have been actively researched since they are essential elements for brain-inspired neuromorphic systems as promising computing systems particularly for data-centric applications such as artificial intelligence.[1] In this study, the CeO$_2$-based memristor was fabricated as 32x32 crossbar array structure. Two-terminal of access lines with Pt electrodes were deposited by e-beam evaporation and patterned with 10 µm width by photolithography and lift-off process and the switching layer (CeO$_2$) was deposited by RF magnetron sputtering. The synapse array exhibited analog, gradual, and voltage-polarity dependent resistive switching, which emulates biological synaptic behaviors of synaptic weight updates. The conductance of the device in array, corresponding to synaptic weight, increased upon consecutive positive voltage pulses and reversibly decreased upon negative pulses. In addition, its non-linear current-voltage characteristics matched well with Schottky conduction, which efficiently reduced sneak current in array architecture working as Schottky diode selector at the same time. Moreover, several electrical properties analogous to those of biological synapse were observed such as paired-pulse facilitation, spike rate-dependent plasticity. Time-dependent conductance decay could also be fitted well with multiple exponential decay functions that could separately assess short-term memory and long-term memory, and the retention at long-term memory turned out to be ~55 % after 1 hour. The resistive changing is thought to be induced by redistribution of oxygen vacancies in CeO$_2$ switching layer, particularly at the interface with electrodes. X-ray photoelectron spectroscopy analysis unveiled that CeO$_2$ layer has considerable amounts of oxygen vacancies to induce resistive switching. Furthermore, memristor with NbO$_x$/CeO$_2$ bilayer exhibited enhanced resistive switching dynamic range and non-linearity. This is because NbO$_x$ layer worked as not only an oxygen vacancies reservoir, but also threshold switching selector.[2] This study demonstrated that analog synaptic CeO$_2$-based memristor crossbar array could be promising synaptic elements for neuromorphic computing.

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5:00 PM EL21.08.07

Sub-1.0 V Low Voltage Resistive Random Access Memory Operations with Ag/VO$_x$/Pt Structure Jiyeon Ryu, Kitae Park and Tae-Sik Yoon; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Recently, as the importance of date-centric applications increases such as artificial intelligence which requires huge amount of real-time data processing, high performance non-volatile memories are highly required, particularly enabling high density integration and low voltage operations for stand-alone memory and computing elements in processing-in memory applications. Among various non-volatile memories, resistive random access memory (RRAM), which has a simple metal-insulator-metal (MIM) structure, has excellent scalability, easy fabrication also for 3D architecture, and has been reported to have potential for low voltage and high speed operations. In this study, the Ag/VO$_x$/Pt RRAM devices were demonstrated to show sub-1.0 V low voltage and high speed operation with low switching current, high endurance, and high memory window. Resistive switching was induced by the formation and rupture of silver filament through VO$_2$ layer by applied bias. The DC current-voltage curves showed average value of V_{SET} of +0.23 V, V_{RESET} of -0.07 V without electroforming step. In addition, highly stable cycle-to-cycle endurances up to 3000 cycles with on/off resistance ratio > 10^2 without any degradation. Voltage pulse measurements also revealed the low voltage and fast switching with V_{SET} < 1.0 V with the switching time < 1 µs in our measurement setup. Auger electron spectroscopy, Rutherford backscattering spectroscopy, and X-ray photoelectron spectroscopy analysis confirmed that the VO$_x$ layer is composed of mixture of VO$_2$ and V$_2$O$_5$ phases. Transmission electron microscopy analysis revealed that VO$_x$ layer is mostly in amorphous state with small fraction of crystallites. This amorphous structure of VO$_x$ layer in addition to its inherent structural nature enabling to hold metallic elements within the lattice was advantageous in conductive-bridge random access memory of RRAM to achieve facilitated filament formation at low voltage thanks to the abundant oxygen vacancies in the amorphous phase. In addition, the homogeneous amorphous structure is desirable to achieve uniform device-to-device distribution. The presented results of highly stable, forming-free, low voltage and high speed switching operation of Ag/VO$_x$/Pt RRAM devices demonstrated their potential for stand-alone non-volatile memory and computing elements in the processing-in-memory applications.

5:00 PM EL21.08.08

Synaptic Characteristic of Li Doped HfO$_2$ with TiN Electrode Gyumin Park and Byung Joon Choi; Seoultech, Korea (the Republic of)

The human brain is capable of simultaneously processing and memory with low power consumption. A computing method that imitates these characteristics is called neuromorphic computing. Neuromorphic computing has high energy efficiency by mimicking brain works in hardware. To mimic the brain, we need to imitate synaptic behavior: electrical stimulus causes a continuous resistance change in the synaptic device. Resistive random access memory(RRAM) is one of the strong candidates attended for the synaptic device. The two-terminal structure of RRAM enables high-density integration. The simple structure makes crossbar array: Structure used in neuromorphic semiconductors. But RRAM needs the forming process, higher than the operating voltage. The forming process degrades the endurance of RRAM.

In this study, we confirmed the synaptic behavior, forming voltage controllability of lithium-doped hafnium oxide with a titanium nitride electrode. The structure is Pt/Li: HfO$_2$/TiN. The bottom electrode, 85nm-thick TiN as Li reservoir was deposited by magnetron sputter. The switching layer, Li:HfO$_2$ was co-sputtered in a lithium-rich to have a forming-free characteristic by Magnetron sputter. The top electrode, 200nm-thick Pt was deposited by Magnetron sputter. The richer lithium concentration (Li:Hf = 1:1) modulates the forming voltage from 2.5V to 2V. The device shows synaptic characteristics. The synaptic characteristics are Habituation, Sensitization, and Paired Pulse Facilitation (PPF). Habituation is that the conductivity increases as the pulses are applied, and the element becomes insensitive to the electrical pulse. Sensitization is when the conductivity decreases as the pulse is applied, making the device sensitive to the electrical pulse. PPF is a phenomenon in which short intervals of electrical pulses are input like a signal with strong conductivity, and wide intervals are input as a weak signal. We also checked the 8x8 crossbar array learning speed simulation of the learning speed based on the nonlinearity : (G : synaptic weight, G_0 : initial weight A : Constant to fit the graph, B : nonlinearity, P : number of pulses, P_0 : initial number of pulses) Our device’s nonlinearity was 0.1/3.6 (Potentiation/Depression). When simulated with this nonlinearity, the accuracy was confirmed to be 96.3% at 500epoch. —through simulation, the accuracy increased to 97.9% at 500epoch when the nonlinearity of depression was only 1— our research showed the possibility of a forming-free device with modulation of lithium concentration. We confirmed even if the synaptic device has insufficient linearity and symmetry, it can be used as a neuromorphic device.

5:00 PM EL21.08.09

Modulation of Ion Dynamics by Interfacial Ferroelectricity for Electrolyte-Gated Synaptic Transistors Minho Jin, Jae Hak Lee, Haeyeon Lee, Jiyeon Kim and Youn Sang Kim; Seoul National Univeristy, Korea (the Republic of)

With becoming the era of artificial intelligence (AI) and processing of big data, conventional von-Neumann architecture in computing technology has reached its limits in processing large amounts of data, such as low processing speed referred to as von-Neumann bottleneck, high energy consumption, and low integration density. To overcome these limits, neuromorphic computing architecture that mimics the relationships between neurons and synapses in the human brain has been newly proposed for energy-efficient analog computing.

As resistors constituting a neuromorphic architecture, Li^+ electrolyte-gated transistors (EGTs) with the channel of oxide semiconductors have attracted significant attention as a promising candidate for artificial synapses because of mitigating the limitations of 2-terminal devices, the fast response of Li^+ ions, low energy consumption with low operating voltage, and high applicability to flexible electronics. Due to the inherent nature of Li^+ EGTs show, however, limitations such as poor long-term synaptic plasticity and nonlinear/nonsymmetric conductance update for analogy computing. Because Li^+ ions under the external electric field are abruptly transported at the channel/electrolyte interface, electrical conductance modulated by an electrochemical reaction between Li^+ ions and the channel also changes abruptly, hindering the practical applications of artificial synapses. Considering the ion dynamics at the interface, therefore, is necessary to develop Li^+ EGTs.

One of the solutions for the preventing abrupt transport of Li+ ions is the introduction of the ion dynamics-modulating interlayer. Herein, we present Li^+ EGTs integrated with ferroelectric poly(vinylidene fluoride-*co*-trifluoroethylene) (PVDF-TrFE) polymer as a channel/electrolyte interlayer. Due to the polarized domains of PVDF-TrFE, the transport of Li^+ ions at the channel-electrolyte interface is accelerated and Li^+ ions effectively penetrate the channel along the fluorine sites in PVDF-TrFE. Partial polarization switching in ferroelectric domains also enables the sequential transport of Li^+ ions at the interface. Moreover, the self-diffusion of Li^+ ions from the channel to the electrolyte is suppressed by the downward polarized domains. We verify the changes in ion dynamics by electrochemical impedance spectroscopy (EIS) measurement, where the data shows that PVDF-TrFE reduces the charge transfer resistance at the interface. Also, the electrochemical reaction by Li^+ ions majorly occurs in the oxide channel, rather than the PVDF-TrFE interlayer. This indicates that the changes in electrical conductance of Li+ EGT is due to the electrochemical doping of Li^+ ions into the oxide channel. We confirm, therefore, that Li^+ EGTs successfully demonstrate various synaptic characteristics, such as excitatory postsynaptic current, long-term synaptic plasticity over 500 s, and paired-pulse facilitation. Also, confirming availability as an artificial synapse, conductance modulation in Li^+ EGTs shows a high dynamic range (G_{max}/G_{min}) of 92.42, high linearity, and superior stability over 100 cycles. Based on their synaptic characteristics, simulations of image classification and recognition using a convolution neural network for the CIFAR-10 dataset indicates that Li^+ EGTs are suitable as artificial synapses with high inference accuracy of 89.13%. We present materials discovery and novel methodological approaches for the modulation of ion dynamics at the interface to develop practical artificial synapse.

5:00 PM EL21.08.10

Facile Solvent-Dipping Method to Control Sulfur Vacancy for MoS_2 Synaptic Memristor Jiyeon Kim[1], Jae Hak Lee[1], Minho Jin[1], Haeyeon Lee[1], Ji Soo Kim[1], Eunho Lee[2] and Youn Sang Kim[1]; [1]Seoul National University, Korea (the Republic of); [2]Kumoh National Institute of Technology, Korea (the Republic of)

Neuromorphic computing is emerging compared to conventional computing systems based on Von Neumann structure which have limitation of processing delay when massive data is delivered between CPU and memory. To overcome this Von Neumann bottleneck, human-brain imitating synaptic devices have been attracted in neuromorphic system. Especially, memristors have attracted great attention due to the low switching voltage, enabling low-power consuming devices. Also, non-volatile memory characteristics of memristor can emulate potentiation process in synapse. In order to determine whether the memristor exhibits neuromorphic properties, synaptic behaviors such as synaptic plasticity and linearity need to be accompanied. To implement synaptic memristor, molybdenum disulfide (MoS_2), which is a representative example of transition-metal dichalcogenides (TMDs), has been used for channel layer of synaptic memristor because its eletrical properties such as high mobility and large bandgap can be easily controlled by number of layers, which is available due to its two-dimensional structure. Among its distinctive characteristics, many researchers are focusing on precisely controlling sulfur vacancies of MoS_2, which is directly related to synaptic memristor operation according to conductance change. However, traditional fabrication methods to make sulfur vacancies showed some limitations such as plasma damage, complicated process by chemical vapor deposition (CVD) and contamination of CVD reactor, suggesting necessity of concise and non-destructive method. Herein, we introduced facile solvent-dipping method immersing the samples in the solvent to control sulfur vacancies, considering polarity index and Hansen solubility parameter (HSP). We selected three solvents with similar HSP but different polarity: tetrahydrofuran, chlorobenzene, and toluene. Toluene has been reported as a common solvent to make sulfur vacancies in MoS_2. Moreover, in this study, polarity index was newly proposed to confirm if the polarity of solvent affects sulfur vacancy generation in MoS_2 when selected solvents have similar HSP values. We confirmed tetrahydrofuran-treated synaptic memristor generated the highest sulfur vacancies because bipolar solvent can remove both polar and nonpolar sulfur. This unique solvent-dipping process resulted in great performance of tetrahydrofuran-treated synaptic memristor; non-volatile memory characteristics such as high programming/erasing current ratio ($>10^3$) and long retention ($>10^4$ s) and synaptic behaviors of paired-pulse facilitation (PPF) about 170% and 8-times increased linearity. Neuromorphic computing was conducted by Modified National Institute of Standards and Technology (MNIST) to show synaptic behavior clearly, demonstrating increased recognition accuracy after solvent treatment. Visual simulation was illustrated to verify long term potentiation/depression (LTP/LTD) of synaptic devices. Flexible synaptic memristor was also fabricated and maintained its performance without noticeable degradation while bending test was operated, suggesting possible application in next-generation flexible devices. We suggested concise, non-destructive, and reliable solvent-dipping method to control sulfur vacancies in TMDs, and this is a novel study to our knowledge. Our research provides the framework for TMD-based neuromorphic devices, requiring further research for real application in brain-imitating neuromorphic system.

5:00 PM EL21.08.11

Enhancement of Long-Term Memory Characteristics of Ion-Gated IGZO Synaptic Transistors Using UVO Interface Treatment Haeyeon Lee, Jae Hak Lee, Minho Jin, Jiyeon Kim and Youn Sang Kim; Seoul National University, Korea (the Republic of)

Neuromorphic architecture mimicking the signal transmission method of biological neurons has attracted much attention for next-generation computing with the advantages of fast response speed and high energy efficiency by parallel weight update processing. Especially, synaptic transistors have been extensively studied since they perform both calculation and memory functions and easily control channel conductance without channel damage by electrical pulses from a separated gate terminal. Among various types of transistors, electrolyte-gated transistors (EGTs) using electrolytes (e.g., solid polymers, gels, ionic liquids) as gate-insulator are a promising candidate for synaptic transistors due to the low operation voltage by electrical double layer (EDL) and high applicability to flexible electronic devices. However, conventional EGTs show volatile and irregular memory characteristics because of the rapid self-dissipation of ions in the electrolyte. Here, we have demonstrated the WiBS/polymer electrolyte-gated synaptic transistor (WEST) with ultra-violet ozone (UVO) surface treatment which highly improves the long-term memory characteristics and other synaptic functions as well. Super-concentrated WiBS electrolyte composed of excess lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium trifluoromethanesulfonate (LiOTf) in water enables the WEST to conduct synaptic functions in a voltage range of 1.23 V or higher, which is the electrochemical stability window of water. Also, the WiBS electrolyte can take advantage of the characteristics of pure water: high dielectric constant and biocompatibility. UVO treatment is one of the effective post-treatment that has been widely used to surface modification by controlling the oxygen vacancy concentration on the surface in various fields. Ultra-violet (UV) in the two different wavelengths of 185 and 254 nm decomposes metal-oxide bonds of InGaZnO (IGZO) thin film and the bonds are broken more intensively by the supplied ozone, which generates reactive oxygen radicals and they trigger the excessive ion bombardment process. We performed XPS analysis and measured hysteresis characteristics to calculate the memory window to verify the cause of the improvement in long-term memory performance of the WEST. As a result, the oxygen vacancy ratios of the UV-only and UVO-treated WEST calculated by XPS data are 0.35 and 0.44, respectively, 1.5 times and 2 times higher than the non-treated WEST, respectively. These increased oxygen vacancies act as trap sites at the interface, trapping lithium (Li) ions in the electrolyte and suppressing the self-diffusion of the Li ions. Also, the UVO-treated WEST performs long-lasting nonvolatile memory characteristics longer than 10,000 s, which is 1186 times higher than the non-treated WEST. Residual Li ions are detected only in the UVO-treated WEST and appeared as interstitial defects and Li-O bond peaks at 54.9 and 55.7 eV, respectively. After the UVO treatment, both the nonlinearity and asymmetricity of synaptic weight update characteristics are greatly improved from 5.91 to 0.32 for potentiation and from -6.11 to -0.55 for depression. By using the surface post-treatment, the WEST has shown great suitability as a neuromorphic device capable of long-lasting memory functions and elaborate weight controllability comparable to real human brains.

SESSION EL21.09: Magnetic and Spintronic Materials II
Session Chairs: Florin Ciubotaru and Louis Hutin
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3011

9:15 AM EL21.09.01
Engineering Large Spin-Orbit Torque in Silicides for Low-Power Spintronics Applications Cheng-Hsiang Hsu[1,2], Julie Karel[3], Hannah Kleidermacher[1], Niklas Roschewsky[1], Emma Blenkinsop[1], Jonathon Webster[1], Shang-Lin Hsu[1], Shehrin Sayed[1], Alpha T. N'Diaye[2], Frances Hellman[1,2] and Sayeef Salahuddin[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Monash University, Australia

Magnetic memory has been a strong candidate for next-generation low power memory solution. In fact, magnetic memory has been commercialized in both standalone and embedded memory markets for the past few years. However, there are still several challenges in the current spin-transfer torque technology in magnetic memory applications. As a result, spin-orbit torque emerges as a candidate to replace spin-transfer torque due to advantages such as separate read-write current path, faster switching speed and larger material design space. To this regard, efforts in studying spin-orbit torque has been geared toward addressing several issues including material compatibility with silicon platform, trade-off between conductivity and spin-torque efficiency, and engineering field-free switching designs. Here, we propose to use silicides, a decades-old CMOS technology, for efficient spin current generation to manipulate magnetizations. In both amorphous iron silicide and cobalt silicide, we discovered a strong spin current generation efficiency that rivals the largest efficiency values discovered in topological insulators. Moreover, we discovered clear Fe (Co) concentration dependence of spin current generation efficiency in both systems that can potentially be signatures of Fermi level tuning in amorphous materials for manipulating spin current generation. At last, we show that the scaling trend between conductivity and spin current generation efficiency in both silicides are opposite to the conventional scaling trend. In the conventional scaling trend, the efficiency increases as the conductivity decreases. This is a fundamental bottleneck to adopt spin-orbit torque technology for magnetic memory applications. In silicides, the trend is opposite with an increasing efficiency as the conductivity decreases. This novel trend can lift the conventional trade-off and further enable the adoption of spin-orbit torque in magnetic memory applications. This work presents an efficient way of generating spin current in a silicon platform compatible material system – silicides – for energy efficient computing.

9:30 AM *EL21.09.02
All-Optical Control of Magnetism—Towards Energy-Efficient (Brain-Inspired) Computing Theo Rasing; Radboud Universteit. Nijmegen, Netherlands

The ability to switch magnets between two stable bit states is the main principle of digital data storage technologies since the early days of the computer. However, the explosive growth of digital data and its related energy consumption is pushing the need to develop fundamentally new physical principles and materials for faster and more energy-efficient processing and storage of data.
Since our demonstration of magnetization reversal by a single 40 femtosecond laser pulse, the manipulation of spins by ultra-short laser pulses has developed into an alternative and energy efficient approach to magnetic recording[1]. Plasmonic antennas have allowed to push this even down to nanometer length scales[2], while photonic networks allow the development of an optically switchable MRAM[3].
However, new ICT technologies, such as Artificial Intelligence push the exponentially increasing energy requirement of data manipulation even more. Therefore, the development of radically new physical principles that combine energy-efficiency with high speeds and high densities is crucial for a sustainable future. One of those is neuromorphic computing, that is inspired by the notion that our brain uses a million times less energy than a supercomputer while, at least for some tasks, it even outperforms the latter. Ultimately, future brain-inspired technology should provide room temperature operation down to picosecond timescales, nanoscale dimensions and at an energy dissipation as low as the Landauer limit (~zJ). In this talk, I will discuss the state of the art in ultrafast manipulation of magnetic bits and present some first results[4] to implement brain-inspired computing concepts in magnetic materials that operate close to these ultimate limits.
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10:00 AM BREAK

SESSION EL21.10: Energy-Efficient Computing II
Session Chairs: Mario Lanza and Heike Riel
Thursday Morning, April 13, 2023
Moscone West, Level 3, Room 3011

10:30 AM EL21.10.02
Graphene-based Artificial Dendrites for Spatio-Temporal Processing in Spiking Neural Networks Samuel Liu[1], Dmitry Kireev[1], Maya Borowitz[1], Tianyao P. Xiao[2], Christopher Bennett[2], Deji Akinwande[1] and Jean A. Incorvia[1]; [1]The University of Texas at Austin, United States; [2]Sandia National Laboratories, United States

Neuromorphic computing has emerged as an important field to reduce the energy impact of artificial neural networks (ANNs). Among the types of neural networks, spiking neural networks (SNNs) rely on spatio-temporal spikes to transmit information, allowing even greater energy efficiency than the constant signals in ANNs. Due to increased complexity in the time domain, nonlinear dynamics in artificial neurons can significantly impact the performance of an SNN. These nonlinear dynamics can be mediated by dendrites, an SNN component that is relatively unexplored in neuromorphic computing, with few device candidates.

In this work, we propose a biocompatible graphene-based artificial dendrite that can implement tunable dendritic kernels at variable timescales, presenting a platform that can bridge between artificial and biological neural systems. We fabricated mesoscale (few mm2) and microscale (few µm2) synaptic transistor devices by interfacing graphene with a Nafion membrane. We used the dual-gate operation of the device in current mode to model alpha and Gaussian dendritic kernels, showing a transformation of input spikes to a non-spiking spatio-temporal output signal. The timing can be adjusted several orders of magnitude between microsecond to second, allowing a wide range of tunability. Device characteristics of conductance range, energy dissipation, and temperature dependence are also evaluated. A SNN constructed using the Linear Solutions of Higher Dimensional Interlayers (LSHDI) methodology is used to evaluate the performance of the artificial dendrites. We train the network offline on spoken digits from the Texas Instruments 46-word corpus using the modeled dendrites, then translate the software inputs to the dendrites into electrical signals to demonstrate functionality on a collection of hardware artificial dendrites. The results propose an artificial dendrite that is biocompatible, energy efficient, and highly tunable.

10:45 AM *EL21.10.03
Photonic Computing with Reconfigurable Integrated Circuits Wolfram Pernice; Heidelberg University, Germany

Conventional computers are organized around a centralized processing architecture, which is well suited to running sequential, procedure-based programs. Such an architecture is inefficient for computational models that are distributed, massively parallel and adaptive, most notably those used for neural networks in artificial intelligence. In these application domains demand for high throughput, low latency and low energy consumption is driving the development of not only new architectures, but also new platforms for information processing.
Photonic circuits are emerging as one promising candidate platform and allow for realizing the underlying computing architectures, which process optical signals in analogy to electronic integrated circuits. Therein electrical connections are replaced with photonic waveguides which guide light to desired locations on chip. Through heterogeneous integration, photonic circuits, which are normally passive in their response, are able to display active functionality and thus provide the means to build neuromorphic systems capable of learning and adaptation. In reconfigurable photonic architectures in-memory computing allows for overcoming separation between memory and central processing unit as a route for designing artificial neural networks, which operate entirely in the optical domain.

SESSION EL21.11: Oxide Based RERAM and Synapses I
Session Chairs: Heike Riel and Ahmad Zubair
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3011

1:45 PM *EL21.11.01
Resistive Memory Technologies as Dynamic Elements for Neuromorphic Computing Sabina Spiga, Mrinmoy Dutta, Manuel Escudero, Emanuele Gemo and Stefano Brivio; CNR-IMM, Italy

Hardware spiking neural networks (SNNs) and emerging unconventional computing concepts hold the great promise to build future low-power computing systems. The co-development of novel efficient neuromorphic hardware and brain-inspired learning protocols aims to deliver on this promise: it will bring a paradigm shift towards edge computing, where information processing is performed close to the data generated by portable and IoT devices, and will enable applications relying on smart analysis of sensory signals in real time.

Recently, the research in the field of neuromorphic computing has been receiving a significant boost by exploiting the physics of the broad class of memristive devices as new hardware building blocks enabling neural behavior, and then substituting or complementing CMOS circuits. These devices can support '*in memory computing*' in neural networks, thus avoiding the energy cost associated with data transfer between the memory and the processor, and then surpassing the limit of the von-Neumann computing architecture. Furthermore, as our brain uses neuronal and synaptic dynamics as working memory, it is desired that also neuromorphic chips compute with dynamics, encompassing devices and circuits with useful transients or evolution in time.

Our work focuses on resistive switching memory (RRAM), i.e. metal/insulator/metal devices that undergo reversible resistance change upon voltage application. RRAM devices, also depending on the used material stacks and programming strategies, allow the engineering of many functionalities for neuromorphic computing, such as analog dynamics response to input stimuli, and controllable stability of the device resistance states over various time scales. Therefore, RRAMs can act as volatile or non-volatile dynamic memory elements mimicking the short/long term plasticity of synapses in nervous system, or even as stochastic and non-linear elements in neuronal units. In our work, we engineered both analogue non-volatile HfO_x-RRAM as synaptic nodes in SNNs and Ag/SiO_x devices with tunable retention properties (from µs to seconds range), and exhibiting a conductance modulation as a function of input stimuli.

In an alternative approach, we developed analogue nonlinear dynamical circuits, exploiting the programmable nonlinearity of non-volatile HfO_2 RRAM devices. In particular, HfO_2-RRAMs can be programmed in different resistance states exhibiting a different nonlinearity of the current-voltage characteristic, which is used to generate complex circuit oscillations. Moreover, we have demonstrated that the circuit can be tuned from periodic (ordered) and chaotic behavior through the modulation of an input signal. In this manner, it can be used as a processing machine expanding the dimensionality of the input and enabling subsequent linear classification, in a reservoir computing scheme.
To summarize, in this talk we will show how various types of RRAMs, relying on different material stacks and mechanisms, can be used for computing by exploiting their intrinsic dynamics.
[*This work is partially supported by the Horizon 2020 EU MeM-Scales project, under the grant n. 871371].*

2:15 PM EL21.11.02
Conductive-TaOx/HfOx Based RRAM Devices with Enhanced Properties for Training Deep Neural Networks Tommaso Stecconi[1], Donato F. Falcone[1], Youri Popoff[1,2], Folkert Horst[1], Bert Offrein[1] and Valeria Bragaglia[1]; [1]IBM, Switzerland; [2]ETH Zürich, Switzerland

With the end of Moore's law approaching and the surge in compute effort required by Artificial Intelligence (AI), the quest for alternative computing schemes to the Von-Neumann architecture has intensified. In this context, in-memory computing is emerging as a promising hardware solution to improve both speed and energy efficiency [1].

By using analogue memory elements arranged in a crossbar array, we enable a fast and massively parallel computation of Vector-Matrix-Multiplications (VMM), the most called on algebraic operation in AI. Executing VMMs directly in analogue hardware enables enhanced power-efficiency compared to today's conventional computing approach based on highly advanced, digital Complementary Metal-Oxide-Semiconductor (CMOS) technologies. For the analogue alternative to be successful, it must embed memory elements with low programming and reading energy, which translates into requirements such as low-conductance, fast resistive-switching dynamics, and low operating voltages.
At the same time, many other fundamental properties such as unit cell area scalability, programming endurance and multi-state retention must be evaluated.

In this work we present RRAM devices based on an oxide bilayer structure of TaOx/HfOx, sandwiched between TiN electrodes. The bilayer structure improves the resistive switching symmetry, stochasticity and graduality. At the same time, with the TaOx resistivity being orders of magnitude lower compared to the HfOx, the forming voltage does not increase excessively compared to the baseline case of an oxide monolayer only.

By developing an ultrathin 4nm defective-rich HfOx material by ALD, we achieve forming voltages of ~4 V for $(200\ nm)^2$ devices, improving by more than 20% this specific compared to the previous generation of bilayer RRAMs (Gen_1) [2].
The reduction of the forming voltages enables a better control of the filament, leading to a ~10x lower conductance of the devices compared to Gen_1.

Our colleagues working on deep learning solutions for networks of memristors have recently developed the "Tiki-Taka" algorithm, relaxing the requirements on the conductance updates symmetry and linearity [3]. For the algorithm to accurately train a network of memristors, we update their conductive states by a train of either positive or negative voltage pulses, with fixed amplitude and duration.
We successfully demonstrate the Tiki-Taka's "symmetrization procedure" on our devices, which is an essential step for the correct execution of the algorithm. This procedure requires analogue and non-volatile bidirectional tunability of the device conductance. Both properties are excellently met by our new generation of TaOx/HfOx devices.

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2:30 PM BREAK

SESSION EL21.12: Oxide Based RERAM and Synapses II
Session Chairs: Hui Jae Yoo and Ahmad Zubair
Thursday Afternoon, April 13, 2023
Moscone West, Level 3, Room 3011

3:30 PM EL21.12.01
Origin of Discontinuous Negative Differential Resistance in Metal-Oxide-Metal Devices Robert G. Elliman[1], Sanjoy Nandi[1], Shimul K. Nath[1], Shuai Li[1], Thomas Ratcliff[1], Xinjun Liu[2], Peter Raad[3] and Assaad El Helou[3]; [1]Australian National University, Australia; [2]Tianjin University, China; [3]Southern Methodist University, United States

Metal-oxide-metal cross-bar devices that exhibit current-controlled negative differential resistance (CC-NDR) can be used to fabricate nanoscale oscillators, and are of interest as a fundamental building block for brain-inspired neuromorphic computing. For devices based on binary metal-oxides the CC-NDR response is typically manifest as S-type current-voltage characteristic that can be attributed to an increase in the oxide conductivity due to local Joule heating. However, recent studies have shown that such devices also exhibit a range of more complex behaviour that may provide additional functionality. These include an abrupt 'snap-back' response, as well as compound characteristics comprising various combinations of S-type and snap-back characteristics. Understanding such behaviour is complicated by the fact that conductivity changes can involve a combination of electronic and thermal processes, material-specific phase transitions (e.g. crystallization or metal-insulator transitions), non-linear current redistribution and measurement artifacts.

This presentation summarizes our current understanding of the mechanisms underpinning the snap-back and compound CC-NDR modes and shows how this understanding can be used to develop devices with new functionality [1, 2]. Specifically, we combine electrical, physical and thermal characterisation of NbOx-based devices, including in-situ thermoreflectance imaging of device temperature distributions, to understand the origin of the CC-NDR modes and their dependence on material and device parameters (e.g. oxide stoichiometry, electrode metal, film thickness, device area). These results are then compared with the predictions of an electro-thermal model of filamentary conduction that employs a core-shell structure to represent conduction in the filamentary path (core) and the surrounding oxide film (shell). These results show that both the snap-back and compound CC-NDR characteristics can be explained by current redistribution between the core and shell regions, with the snap-back response resulting from an abrupt current bifurcation process in which the current distribution separates into regions of low and high current density. Further analysis shows that the criterion for bifurcation is determined by the relative magnitudes of the shell-resistance and the NDR of the core region. Based on this understanding, we demonstrate how the asymmetric contact resistance of a Schottky-barrier contact can be used to construct devices with a bias-polarity dependent CC-NDR response [3].

Significantly, the results of this study demonstrate that a diverse range of CC-NDR responses can be explained by a relatively simple model that accounts for current redistribution within metal/oxide/metal device structure. Within this framework, the continuous S-type and abrupt snap-back CC-NDR responses have the same physical origin, precluding the need to invoke additional mechanisms such as an insulator-metal transition.

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3:45 PM EL21.12.02
Assessing the Impact of Ti Doping and MAX-Phase Ti_2AlN Electrode in HfO_x Neuromorphic Devices Fabia Farlin Athena[1], Moses Nnaji[1], Matthew P. West[1], Samuel Graham[2] and Eric M. Vogel[1]; [1]Georgia Institute of Technology, United States; [2]University of Maryland, United States

Oxide-based non-volatile memories have great potential for neuromorphic computing applications.[1] In HfO_xfilamentary memory, when bias is applied, a conductive filament (CF) is formed, within which O ion motion in and out causes rupture and reformation of the CF, and this process primarily governs the switching. However, challenges such as high forming voltage (V_F), abrupt resistance change, and high off-state current prohibit its widespread adoption.[2]

In this study, we independently assess the impact of Ti doping and electrode material optimization on HfO_x devices with the goal of overcoming the problems in HfO_x filamentary memory. The Ti-doped HfO_x devices were fabricated, where the ~5 nm oxide was deposited via atomic layer deposition. Electrical characterization shows that the **V_F decreases** (~2.1 V) with the increase of Ti doping.[3] In addition, analog pulse measurements show that a 25% Ti doping **improves the linearity in resistance change** during the reset. However, the switching is not substantially impacted, and the **off-current is high**.[4] A few O ion motion at the CF break region governs the switching. We determined the location of the break via a direct tunneling electron transport model and a finite element analysis. Both analyses show that the break is close to the reset anode electrode; thus, the electrode has a significant impact on the switching. We hypothesize that a reduction in thermal conductivity (K) of the electrode will lower the off-current. A low electrode will cause less heat removal and more oxygen ion motion, thus will result in a thicker break in CF and less off-current. However, the challenge is that most of the electrodes have high K (e.g., K_{Au} = 310 W/m.K., K_{TiN} = 29 W/m.K). Ti_2AlN, like many other MAX phase materials, has unique metallic (high electrical conductivity) and ceramic properties (low thermal conductivity, $K_{MAX\ phase}$ ~4.63 W/m.K) as it contains alternating layers of metallic and covalent bonds.[5] Thus, HfO_x devices with Ti_2AlN MAX phase as the bottom electrode were fabricated. Alternating layers of Ti and AlN were first deposited at room temperature via magnetron sputtering and then thermally annealed to obtain Ti_2AlN. Raman spectroscopy of the electrode showed the characteristic spectra of Ti_2AlN. The HfO_x devices with MAX phase BE show a **one-order-of-magnitude improvement in the off-current** (HRS ~ 450 kΩ), a large switching window (~200), good endurance (>100) and retention (~10^4 s) of states. Furthermore, analog pulsing measurements are conducted to analyze the synaptic behavior of the devices. A COMSOL Multiphysics® model is used to develop a fundamental understanding of the observed results.
Overall, this study demonstrates that through optimization of the materials in HfO_x memory, the electrical responses can be tailored for neuromorphic application.

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4:00 PM EL21.12.03
Electroforming-Free Low Switching Operation in CeO_2-based 1S1R Memristor Device for Neuromorphic Computing Applications Dwipak P. Sahu, Kitae Park, Peter H. Chung, Sola Moon and Tae-Sik Yoon; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Resistive random-access memory (RRAM) devices with crossbar array (CBA) configuration have been considered as promising next-generation non-volatile memory as well as future computing paradigms, such as in-memory computing and neuromorphic computing [1]. However, the generation of sneak path currents through unselected cells in a CBA architecture affects the efficiency and power consumption of the cells. Therefore, the sneak current issues can be resolved by vertical integration of a memristor (R) with a selector (S) in a 1S1R crossbar array [2]. However, it is also essential that the material composition and electrical properties of both the memristor and selector should be compatible for the proper functioning of 1S1R integrated device. Among various oxide switching layers, here, we have considered CeO_2-based rare-earth oxide as a dielectric switching layer for memory and selector devices due to its large bandgap, high oxygen ionic conductivity, and strong oxygen-getting ability of Ce [3]. For this, we have fabricated a memristor with $TiN/CeO_2/TiN$ structure and vertically stacked it with a selector device made of $Ag/CeO_2/SiO_2/TiN$ through a shadow mask in a capacitor structure. The selector (S) device with Ag as the top electrode (TE) acts as a volatile memory under a low current operation of 1 µA and could help in reducing the leakage current on integration with the memory (R) device. The memory device shows analog switching characteristics under a bias voltage of ±4 V with a leakage current of 430 nA at a read voltage of 1V. In memory devices with TiN electrodes, the possibility of the formation of a TiO_xN_y interface layer during the fabrication process can serve as a reservoir of oxygen vacancies which may act as a leaky dielectric layer. Upon repeating +V sweep from 0 to +4 V, the current increased by more than 10 times indicating a potential application of the memory device for synaptic weight update. However, the continuous negative voltage sweep does not return the device current to its initial stage which could be due to the formation of different interface barriers between top TiN/CeO_2 interface and bottom CeO_2/TiN interface although the device is structurally symmetric. In comparison, the 1S1R device also shows an analog switching with ±4 V and requires no electroforming process prior to the switching operation. Due to the addition of a selector device, the leakage current was suppressed by nearly four orders to 28 pA at a read voltage of 1V. Initially, both memory and selector devices are at HRS and most of the voltage drop is on the selector due to its large off-state resistance. The device shows memory switching after the selector turns on which reduces the leakage current. The present 1S1R device shows reliable data retention of 68.7% after 30 min which has the potential for studying its long-term plasticity behavior. A detailed analysis will be carried out by fabricating 1S1R in crossbar array architecture to study the synaptic behavior for the implementation of a hardware neural network.

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4:15 PM EL21.12.04
Novel and Tunable Wavelength-Selective Artificial Synapses Based on Inorganic Thin Film Photovoltaic Devices Kunal Tiwari, Axel Gon Medaille, Alex Jimenez, Eloi R. Costals, Sergio Giraldo, Marcel Placidi, Edgardo Saucedo and Zacharie Jehl Li-Kao; Polytechnic University of Catalonia, Spain

Artificial synapses are an important building block for neuromorphic computing, holding the promise to reproduce fundamental brain functions and markedly improve the energy efficiency of future computers beyond the Von Neumann architecture while offering new possibilities in terms of unsupervised learning and parallel computing with a high resilience to faults. As the human brain receives nearly 80% of its inputs from visual perception, the development of efficient and tunable optoelectronic artificial synapses appears as the next frontier going forward, and several proof-of-concept devices have been reported using both organic and inorganic materials, albeit with a comparatively low degree of tunability. While carrier trapping from native and extrinsic defects is often seen as a drawback in inorganic thin film photovoltaic devices, it holds a remarkable yet currently untapped potential to simulate synaptic plasticity.
In this work, we demonstrate for the first time the properties of **long term potentiation, short term potentiation, and synaptic depression using light as a stimulus** and persistent photoconductivity as a figure of merit to characterize the plasticity in a $Cu_2ZnSnSe_4$/CdS/ZnO-based photovoltaic device artificial synapse. The dark persistent photoconductivity was found to last for **several days after a stimulation** with white light ranging from durations of a few minutes to several hours and at a power of 1000 $W.m^{-2}$. Furthermore, illumination in short bursts (few seconds and less) reveals a typical **short term plasticity behavior with a memory effect akin to that of an RC integrator**, a key element for digital computing. It is to our knowledge the first time that such behaviors are deliberately achieved and characterized for this class of materials and devices.
Even more remarkably, the fabricated devices are found to operate with some level of **wavelength selectivity**. By maintaining the incident illumination power constant and varying the illumination wavelength with 28 different LEDs over a range from 350 nm up to 1500 nm, significant changes in the synaptic response are observed which widens the number of possible programming states of the system, and relates to the different transition energies of the trapping states involved in the plasticity of the device. The response to **ultraviolet and blue illuminations below 500 nm is particularly efficient at producing both a long term and short term potentiation of the synapse**, hinting at the charging of trap states located at the vicinity of the front p-n interface. In contrast, most of the wavelengths from the visible spectrum do not lead to a measurable short term plasticity response, which could be interpreted as either the absence of transition corresponding to those wavelengths or to a screening of the photoconductivity by the photocurrent. The case of infrared illumination beyond 1200 nm is particularly peculiar as it **simultaneously can lead to a short term synaptic potentiation following illuminations of a few seconds or less, and a long term synaptic depression following an illumination of fifteen minutes** of an already potentiated synapse. Such reaction to a single stimulus has to our knowledge never be observed in either electronic or optoelectronic synapses.
Finally, it is found that the synaptic behavior of the devices can be tuned through the variation of the oxygen content in the ZnO window layer, offering further insights on the defect trapping mechanics involved in the plasticity of those artificial synapses. The complete set of results will be presented, including the current limitations of this work, and a model involving two trap levels located at the vicinity of the p-n interface will be proposed and discussed in the context of the electrical characterizations of the artificial synapses and previous knowledge acquired in CZTSe-based solar cells. This type of synapses represents an entirely novel research opportunity for ultra-low energy computing.

SESSION EL21.13: Virtual Session
Session Chairs: Iuliana Radu and Subhash Shinde
Thursday Morning, April 27, 2023
EL21-virtual

8:00 AM *EL21.13.01
Interface Engineering toward Future Low-Energy and Scalable Ferroelectric Memory I-Ting Wang, Hsin-Hui Huang, Chui-Yi Chiu, Chen-Yi Cho, Tzu-Yao Lin and Tuo-Hung Hou; National Yang Ming Chiao Tung University, Taiwan

Differing from most nonvolatile memory (NVM) solutions, such as RRAM, PCRAM, STT-MRAM, SOT-MRAM, etc, the switching of a ferroelectric (FE) memory is driven by the electric field rather than the electric current. Its low operating current allows extremely low switching energy and also a compact cell size by reducing the dimension of the access transistor. The promising FE properties of thin Hafnium-Zirconium oxide (HZO) by atomic layer deposition suggest the possibility of achieving a low operating voltage, which is also critical for embedded memory in the logic process. However, some open questions remain for FE memory that might require fundamental material and physical understanding and innovative solutions. First, the thickness and area scalability of FE capacitors that satisfy the strict requirements at the advanced logic nodes remain to be explored. Second, the endurance of FE capacitors is limited by the fatigue-breakdown dilemma. Without robust endurance, the application space of FE memories with the destructive-read feature is limited. Third, the destructive-read feature is also not desirable for performing energy-efficient in-memory computing. One of the nondestructive-read FE memories is the ferroelectric tunnel junction (FTJ). However, the low on-off current ratio and the low read current of FTJ remain problematic. We analyze these challenges from both theoretical and experimental perspectives. We found that the interfaces between FE and metal electrodes play a major critical role in improving these issues. These understandings would facilitate the development of future low-energy and scalable ferroelectric memory.

8:30 AM EL21.13.02
GeOx-Ge Quantum Dot Assembly for Multistate Spatial Wavefunction Switched (SWS) Field Effect Transistors Raja Hari Gudlavalleti[1], Abdulmajeed Almalki[1], Pik-Yiu Chan[1], Ronald LaComb[1], John Chandy[1], Evan Heller[2] and Faquir Jain[1]; [1]University of Connecticut, United States; [2]Synopsys Inc., United States

Abstract:
This paper presents a novel twin-drain Ge quantum dot (QD) spatial wavefunction switched (SWS) field-effect transistor (FET) which demonstrates

multistate within a single device. [1-3]. An array of individually cladded quantum dots forms a quantum dot superlattice (QDSL) which exhibits discrete mini-energy bands that have very narrow density of states (DOS) separated by 0.3-0.4 eV. The QDSL serves as: (i) single/multiple transport channel, (ii) quantum dot gate on tunnel oxide, (iii) multiple drain SWS FET. The nanodevices create multiple intermediate logic states in addition to ON and OFF states [4]. The gate voltage determines the threshold for each of the intermediate states. The threshold voltage depends on size of the QD (core and cladding region thickness), gate dielectric thickness and constant. Jain et. al., experimentally demonstrated Si and Ge QD based three- and four-state state FET devices [4-6].

Prior work [1] demonstrated carrier wavefunction switching from lower quantum dot channel to upper quantum dot channel in a multistate SWSFET using SiOx-cladded Si QDs. Ge QDs exhibiting more energy mini-bands will provide additional multiple states and hence versatile multibit processing. We describe processing of a twin-drain SWSFET having four layers of GeOx-cladded Ge QDs self-assembled in the channel region. The upper two QD layers act as the transport channel from source S to drain D_1 and the lower two QD layers act as the transport channel from source, S to drain, D_2. The gate voltage, V_G, determines the spatial location of the charges in the upper or lower quantum-wells/-dots in the channel region. This property of the device allows it to encode logic levels at each threshold level of the device for the multivalued logic operation. The location of electrons in lower, upper, both and none encodes the logic states (01), (10), (11) and (00), respectively, which provides a 4-state/2-bit FET operation. In this method, a colloidal solution of cladded Ge QDs is prepared [7] and self-assembled at room temperature. The device sample with Ge dots is annealed at 350 C. The size of the Ge QDs is ~3-4nm with ~0.5 nm GeOx cladding. The experimental characteristics shows multiple state in the FET devices at room temperature.

The low temperature Ge QD preparation and demonstration of multistate within the single device at room temperature operation achieve reduced device count. Further, these novel FETs can be integrated with QD-NVRAMS with CMOS compatible processing. This integration serves as a hardware platform for distributed computing and artificial intelligence applications.

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8:35 AM EL21.13.03

Optimization of Materials and Interfaces for Low Power Analog Conductive Metal Oxide/HfO2 ReRAM Artificial Synapses Donato F. Falcone, Youri Popoff, Tommaso Stecconi, Valeria Bragaglia, Marilyne Sousa, Folkert Horst, Antonio La Porta and Bert Offrein; IBM Research - Europe, Switzerland

The energy required for the training and inference of complex neural networks on standard CMOS technology based on von-Neumann architecture has been growing tremendously. In particular, the data exchange between memory and the processing units is power-hungry, causing inefficiency and performance mitigation. Specialized neuromorphic hardware based on analog memristors are a promising and more energy efficient alternative. When organized in crossbar arrays, memristive technologies such as ReRAM or PCMs [1] can be used to perform vector-matrix multiplications (VMMs), the most energy-expensive operation in AI’s tasks, in the analog domain, by exploiting Ohm’s and Kirchhoff’s law. Such two-terminal technologies are scalable and can be densely integrated in the Back end of the line (BEOL) of existing CMOS technology, to create a high performing synaptic analog signal processing accelerator.

Metal/Insulator/Metal Redox-based Resistive Switching Random Access Memories (Ti/HfO_2 ReRAM), exploiting filamentary conduction, are emerging as a leading option for memristors due to the compatibility with and ease of integration in CMOS technology. Nonetheless, the electro-chemical reactions at the interface between Ti and HfO_2 tend to result in an abrupt and stochastic rather than analog and symmetric switching characteristics, hindering their suitability for applications in AI analog accelerator units [1].

A promising and innovative concept of ReRAM device was proposed in [2], replacing the Ti layer by an engineered Conductive Metal Oxide (CMO), resulting in a Metal/CMO/Insulator/Metal type ReRAM device. The CMO/HfO_2 ReRAM shows superior characteristics such as gradual, linear and symmetric conductance update, large number of states, good retention and reproducibility of the switching characteristics. Nevertheless, the main limitation of CMO/HfO_2 stack with respect to Ti/HfO_2 is the increased voltage required to perform the electro-forming (V_{foming} up to 5.5V in [2]), which represents a critical challenge for combining this technology with modern CMOS technology.

In this work, we optimized the Metal/CMO/Insulator/Metal ReRAM technology. By properly engineering the stack, we reduced the forming voltage below 3.3V without compromising all the superior electrical characteristics of the CMO based ReRAM technology. The material-stack characterization by means of TEM and EDS, as well as the DC and pulsed electrical characterization of the devices will be presented. Furthermore, by controlling the forming process of CMO/HfO_2 ReRAM, two operative switching regimes are found, with kΩ and MΩ range resistive levels. Through impedance spectroscopy experiments and finite elements simulations, we established equivalent electrical circuit models and provided a physical understanding of the optimized CMO/HfO_2 ReRAM in pristine state, after forming, in the high resistive state (HRS) and in low resistive state (LRS), explaining the importance of the CMO layer in the resistive switching behavior.

The granular switching properties and CMOS compatibility of the CMO/ReRAM devices are promising for large-scale integration of this technology for future neural network training and inference.

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8:50 AM EL21.13.04

Impact of Post-Annealing Time Duration on the Structural, Optical and Resistive Switching Properties of RF Sputtered β-Ga_2O_3 Thin Films Asma

O. Al Ghaithi, Inas Taha, Sumayya M. Ansari and Haila Aldosari; United Arab Emirates university, United Arab Emirates

Wide bandgap semiconductor gallium oxide (Ga_2O_3) recently began garnering increasing scientific interest owing to its large bandgap of 4.7−4.9 eV. The exceptional thermochemical stability of β-Ga_2O_3 makes it an intriguing material for several applications, including high-power electronic devices, solar-blind UV photodetectors, light-emitting diodes, photocatalysts, transparent conducting oxides, and chemical sensors. This presentation will discuss the impact of post-annealing time on the structural and optical properties of radio-frequency (RF) magnetron-sputtered amorphous Ga_2O_3thin films. 100 nm thick amorphous Ga_2O_3 thin films were deposited on p-type (100) silicon substrates and post-annealed in a tube furnace at 1000 °C under an argon (Ar) atmosphere for different time intervals: 1, 2, and 7 h. Various characterization techniques were used in this investigation, including grazing-incidence X-ray diffraction (GIXRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectrometry (EDS), and UV-visible- NIR spectrophotometry. GIXRD scans showed that the as-deposited Ga_2O_3 thin films were amorphous. In contrast, all post-annealed thin films were polycrystalline β-Ga_2O_3, exhibiting a monoclinic crystal structure with a C2/m space group and dominant (400) orientation. In addition, the degree of crystallinity and grain size increased upon increasing the annealing time. Cross-sectional TEM of 7 h annealed Ga_2O_3 thin film revealed interplanar distances of 2.93 Å and 2.88 Å, which correspond to the d-spacing of (400) and (002) planes of the β-Ga_2O_3, respectively. Moreover, no solid-state reaction occurred between the underlying Si substrate and the Ga_2O_3 layer. All the Ga_2O_3 thin films exhibit very high transmittance in the UV and visible ranges. The optical bandgap of the as-deposited Ga_2O_3 film is 4.45 eV, which increased after the post-annealing treatment. Finally, we developed a 100 nm Ag/20 nm Ga_2O_3/Si memristive system. The current–voltage (I–V) characteristics of Ag/Ga_2O_3/Si memristor under positive and negative bias voltages have provided valuable information on the ON and OFF states of the device and the corresponding resistive switching mechanism.

9:05 AM *EL21.13.05
Spin Dynamics in Antiferromagnets and Applications Shaloo Rakheja[1], Arun Parthasarathy[2] and Ankit Shukla[1]; [1]University of Illinois at Urbana-Champaign, United States; [2]New York University, United States

Antiferromagnetic materials have ordered spin moments that alternate between individual atomic sites, which gives them a vanishing macroscopic magnetic signature and relative immunity against perturbations from external magnetic fields. Because of their strong exchange interaction, antiferromagnets are expected to have terahertz scale magnetization dynamics, which is nearly three orders of magnitude faster compared to their ferromagnetic counterparts. Although antiferromagnets represent the overwhelming majority of magnetically ordered materials, traditionally, they have played a secondary role to ferromagnets, which are used as active elements in commercial spintronic devices like magnetic sensors and non-volatile magnetic memory. This is in part due to the difficulty associated with the electrical detection and manipulation of the order parameter in antiferromagnetic thin films. Thus, research dedicated toward understanding the antiferromagnet's material properties and electrically driven spin dynamics is necessary to harness their full potential.

We focus on the physics and modeling of spin dynamics in thin films of two unique antiferromagnets: Cr_2O_3, which is a single-phase magnetoelectric insulator and Mn_3Sn, a Weyl semi-metal. These antiferromagnetic materials and their heterostructures can overcome the central challenge of manipulating and reading the antiferromagnet's order parameter via microelectronics compatible circuitry, thus allowing us to develop antiferromagnetic spintronics along a similar route as ferromagnetic spintronics.

The principle of using Cr_2O_3 to generate a reversible exchange bias in a proximal ferromagnet for non-volatile memory operation has been experimentally demonstrated. A ferromagnet-free memory cell using Cr_2O_3 has also been experimentally reported. However, in these experiments, the actual dynamics of magnetoelectric switching in Cr_2O_3 are overlooked, even though it is important to establish whether multi-domain effects play a role. Here, we present models that describe the timescale of various domain switching mechanisms in thin films of Cr_2O_3 including nucleation, domain wall propagation, and coherent rotation. By assessing our theory against measurement data, we confirm that the switching in experimental samples is dominated by domain wall propagation, which limits the write delay of the memory cells to >10s of nanoseconds. We also show that ultrafast switching at terahertz speeds is limited by the low dielectric breakdown and high magnetic anisotropy energy, which could be mitigated via strain engineering or substitutional alloying.

Mn_3Sn is a hexagonal Weyl semi-metallic antiferromagnet in which the combination of exchange coupling and Dzyaloshinskii-Moriya interaction (DMI) stabilizes an anti-chiral 120-degrees spin structure below the Neel temperature of 420K. The combination of three sublattices having two-fold single-ion anisotropy renders the system six-fold anisotropy symmetric. Mn_3Sn displays large magneto-transport responses despite having a vanishingly small magnetic moment. In our research, we model the spin torque driven chiral spin rotation in Mn_3Sn and obtain an analytic relationship between the input spin current and the oscillation frequency of the order parameter. Using an anomalous Hall readout, we quantify the measured output voltage signal in the sample resulting from the spin rotation and correlate theory with recent experimental reports. We demonstrate the feasibility of this material platform to implement nano-oscillators whose frequency can be tuned from the megahertz to the near-terahertz regime. We also briefly discuss the use of Mn_3Sn heterostructures to emulate an artificial neuron in hardware for energy-efficient brain-inspired computing.

Our work provides valuable insight into the performance of antiferromagnetic heterostructures for applications in ultralow-power nonvolatile memory and enabling a beyond von Neumann computing paradigm.

9:35 AM EL21.03.03
Electro-Opto-Coupled Phenomenon in Mott-Material Towards Energy Efficient and Ultrafast Neuromorphic Processing Hyungtak Seo, Mohit Kumar, Seokwon Lim and Jisu Kim; Ajou Univ, Korea (the Republic of)

Functional quantum materials have the potential to generate new paradigms for programmable nanoelectronics, data processing, and even beyond. This can be accomplished through the downsizing of device sizes and the improvement of energy efficiency. Consequently, unlike conventional electronics, the fabrication of a novel technology that combines precisely regulated charge transfer and multilevel memory storage in a single nanoscale device requires the use of basic electronics.
In this talk, I will discuss how spatially confined (nano-to-micrometer) vanadium oxide (VO_2) nanochannels designed by local probe lithography enable a wide variety of nanoelectronics in a single device, including regulated current conductors (on/off ratio > 10^4), ultrafast (~32 ns) volatile switches, and multilevel (> 6) nonvolatile memory storage. In addition, probabilistic adaptation and classification of input patterns using multiterminal nanodevices combined on a single platform to take advantage of the in-material probabilistic computing made possible by the IMT's stochastic yet controllable nature will be shown.
Further, I will discuss the monolithic integration of the Mott material on photosensitive silicon and demonstrate the superlinear photoresponse (exponent >18) with an ultralow dark current of 4.46 pA and how it can be implemented for intensity-selective near-sensor night vision processing even with noisy inputs. The results shown in this talk reveal a conceptually new kind of programable nonvolatile nanoelectronics and will pave the way for the creation of high-performance photodetectors with potential uses, such as in night vision, pattern recognition, and neuromorphic processing.

9:50 AM EL21.12.05

Abstract Presented (ON-DEMAND ONLY) Exploring Bioinspired Ultra-Low Power and Opto-Induced Bio-Voltage High-Speed Memristor
Dhananjay D. Kumbhar, Navaj B. Mullani and Jun Hong Park; Gyeongsang National University, Korea (the Republic of)

The memristor is a top-notch choice for neuromorphic computing and nonvolatile memory, with potential for neuromorphic devices including high data integration density, ultrafast speed, and ultralow power consumption. Recently developed fast and energy-efficient artificial neuromorphic systems are in great need of low-power memristors, as previously described device amplitude is considerably greater than in the biological counterpart. Here we demonstrated an Opto-induced filament-based memristor using Sb_2S_3 by a novel vapor transfer deposition method for the memory applications, demonstrating excellent parameters such as a super low turn ON potential of ≈ 9 mV and a switching speed as high as 600ns, including high retention and high endurance with ON/OFF ratio of $0.3x10^3$. The ultralow-power and high-speed switching of Sb_2S_3 are associated with the lower activation energy for Ag ion migration and the presence of Sulphur vacancies. Therefore, the present optically configurable Sb_2S_3 memristors can provide a milestone to develop a single-chip-based bio-inspired computing system, converging with sensory functions.

SYMPOSIUM

April 11 - April 28, 2023

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SESSION EN01.01: 2D and 3D Electrodes
Session Chairs: Husam Alshareef and Sonia Dsoke
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2001

10:30 AM *EN01.01.01
Electrochemistry Under Confinement in Capacitive Materials for Energy Storage Applications Patrice Simon[1,2]; [1]Universite Paul Sabatier, France; [2]French Academy of Sciences, France

This presentation will give an overview of the research work achieved on capacitive 3-Dimmensional porous carbon and high-rate 2-D redox (pseudocapacitive) materials, and will show the challenges/limitations associated with the development of these materials. Starting with porous carbons [1,2], we will present the state-of-the art of the fundamental of ion adsorption mechanism in porous carbons and its practical applications. Moving from double layer to high rate redox materials, we will show how the control of the electrodes structure can help in preparing high power rate electrodes using 2-Dimensional MXene materials [3-5]. We will show how the electrolyte ion partial desolvation observed when confined in nanopores (porous carbons) or in interlayer spacing (2D materials) can result in a continuous transition from EDL formation to typical intercalation-type battery process [5]. A last part will be dedicated to the operando tracking of the ionic and electronic percolations in supercapacitor and battery electrodes using an in-plane AC impedance spectroscopy technique.

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11:00 AM *EN01.01.02

Nano-Engineering of 2D Materials for Electrochemical Energy Storage Frederic Favier[1,2]; [1]Centre National de la Recherche Scientifique, France; [2]RS2E, France

As for graphene, the main issue about 2D materials is re-stacking. This is especially true for supercapacitor electrode materials as electrode/electrolyte interface and ion transport/diffusion should be both maximized to get greater storage capabilities. Many synthetic approaches have been explored to address this issue. Starting from exfoliated materials, including graphene, MXenes, oxydes, hydroxydes… we have developed various strategies to modify the composition, structure or morphology of the layers before re-assembling them in materials with enhanced electrochemical performances.[1-4] To illustrate our progress in the field, three different approaches will be presented in this paper.

The first approach is on the synthesis of graphene-like carbide-derived carbons produced by chlorination of SiC nanosheets obtained by the magnesio-thermal reduction of a silica/graphene oxide nanocomposite. The resulting microporosity in the graphene sheets was shown to strongly improve the rate capability of the prepared electrode material.

Electrostatic stacking of layers of opposite surface charges could also be used to associate Faradaic layered double hydroxides (LDHs), for energy density, to a more stable and powerful pseudocapacitive MnO$_2$. The electrochemical performances of the resulting electrode material were assigned to synergistic effects from distinct but complementary intrinsic behaviors together with the specific morphology of the composite material.

Expanded Ti$_3$C$_2$ MXene obtained by using MgO nanoparticles as hard templates displayed an open morphology based on crumpled layers. The corresponding electrode material delivered up to 180 F.g^{-1} of capacitance at 1 A.g^{-1} over five thousand charge-discharge cycles in KOH electrolyte. On the other hand, an MXene foam prepared by decomposing an MXene-urea composite at 550°C, showed numerous macropores on the surface layer and a complex open 3D inner-architecture. Thanks to this foamy structure allowing in and through plane ion diffusion, a capacitance of 203 F.g^{-1} at 5 A.g^{-1} current density, 99 % of which was retained after five thousand cycles.

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11:30 AM *EN01.01.03
Charge Storage in 3D Architected Electrodes Meets 3D Bode Analysis Debra R. Rolison[1], Jesse S. Ko[2], Megan Sassin[1], Zachary G. Neale[3,1], Ryan DeBlock[3,1] and Jeffrey Long[1]; [1]U.S. Naval Research Laboratory, United States; [2]Johns Hopkins University Applied Physics Laboratory, United States; [3]NRC-NRL Postdoctoral Associate, United States

Electrochemical energy storage relies on multiple mechanisms to store electron/ion charge in redox active materials. Using traditional voltammetric techniques to deconvolve superimposed coulombic/temporal information can be complicated when one mechanism doesn't dominate, a common outcome with high surface-area nanomaterials that amplify capacitive-flavored storage. Impedance spectroscopy can provide deeper insight into mixed charge-storage mechanisms. Mirroring the work of Bai and Conway, which tracked pseudoinductive effects as a function of both frequency and potential,[1,2] we similarly track the colors of capacitance in a protocol we designate '3D Bode Analysis.' This impedance variant can distinguish double-layer response, pseudocapacitance, and battery-like faradaic reactions at device-relevant electrodes, particularly architected electrode structures.[3–6] Using high surface-area carbon nanofoam papers (400–500 m^2 g^{-1}) painted with 10 nm–thick MnO*x*, we used 3D Bode analysis to identify the respective potential windows for pseudocapacitance and battery-like reactions for LiMnO$_4$ and the electroprecipitation/dissolution reactions that underlie energy storage in Zn-ion cells. The 3D Bode analysis can also evaluate the positive effects of carbothermal shock to improve the double-layer response of graphene oxide–carbon nanotube composites.[7] These studies highlight another electroanalytical approach to understand the complex electrochemical response of advanced electrochemical materials.

References

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SESSION EN01.02: Theory and Characterization
Session Chairs: Veronica Augustyn and Thierry Brousse
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2001

1:30 PM *EN01.02.01
UV-vis Spectroscopy Technique for *In Situ* Monitoring Redox Processes in Electrochemical Energy Storage Danzhen Zhang[1], Ruocun (John) Wang[1], Xuehang Wang[1,2] and Yury Gogotsi[1]; [1]Drexel University, United States; [2]Delft University of Technology, Netherlands

Understanding energy storage mechanisms in electrochemical energy storage devices lays the foundations for improving their energy and power density.

Herein, we introduce a simple and easily accessible *in situ* ultraviolet-visible (UV-Vis) spectroscopy method to distinguish battery-type, pseudocapacitive, and electrical double-layer charge storage processes, on example of Ti_3C_2Tx MXene in aqueous acidic and neutral electrolyte and lithium titanium oxide in organic electrolyte. We found a correlation between the evolution of UV-Vis spectra and the charge storage mechanism. Further, we successfully tested the methodology to distinguish non-Faradaic charge storage in Ti_3C_2Tx MXene in water-in-salt electrolyte and Faradaic charge storage in battery materials, where all of these materials had well-defined peaks in cyclic voltammograms. *In situ* UV-Vis spectroscopy is an effective method to track changes in oxidation state and determine the charge storage mechanism. It effectively supplements electrochemical characterization, providing a fast and inexpensive first-line technique for monitoring redox activity in electrochemical systems.

2:00 PM *EN01.02.02
Ti and Nb-Based Oxides as Negative Electrode Materials for High Power Batteries Olivier Crosnier[1], Etienne Le Calvez[1], Eric Gautron[1], Nicolas Dupre[1], Bruce S. Dunn[2], Laurent Pilon[2] and Thierry Brousse[1]; [1]CNRS - IMN, France; [2]University of California, Los Angeles, United States

Today, one of the main challenges of lithium-ion batteries is to have the ability to charge faster and to provide high power during longer periods, thus allowing a larger development of intermittent electric power sources [1]. The actual negative electrode materials (graphite and silicon mainly) cannot sustain such high rate capabilities. In this work, we are therefore investigated some materials of the plentiful family of niobium-based oxides. A presentation of old and interesting structures will be briefly reviewed. As an example, the case of $KTiNbO_5$ will be discussed and proposed as efficient negative electrode materials for next generation of lithium ion batteries.
The layered $KTiNbO_5$ with a two-dimensional framework represents a playground to produce a large range of closely related phases.[2] The protonated $HTiNbO_5$ analogue is obtained by ion exchange in acidic solution and it preserves a layered structure with a smaller interlayer distance. After dehydration of $HTiNbO_5$ at 400°C, the so-obtained $Ti_2Nb_2O_9$ phase displays a 2D arrangement with empty channels unlike tunnels of $H(K)TiNbO_5$.
In this work, all the synthesized phases were studied as negative electrode materials in lithium-ion batteries. Tested in 1M $LiPF_6$ in EC/DMC between 1.0V and 3.0V vs Li/Li^+, these phases have shown different electrochemical behaviors. When $HTiNbO_5$ exhibits a typical plateau during the charge/discharge experiment corresponding to a biphasic phenomenon, lithiation of $Ti_2Nb_2O_9$ is governed by a solid—solution mechanism. For a better understanding of the charge storage mechanism, we have combined electrochemical experiments with *in situ* XRD measurements. We have shown that multielectron redox and corner/edge sharing system of Ti/Nb octaedra are at the origin of an interesting capacity of more than 100 $mAh.g^{-1}$ at a rate of 0.2 $A.g^{-1}$. A good observed cyclability (< 500 cycles) is in accordance with *in situ* XRD results showing a reversible behavior of the structure during cycling. Another synthesis method, using *Chimie Douce* techniques, leads to nanoparticules for both $HTiNbO_5$ and $Ti_2Nb_2O_9$ and allows an increase of the electrochemical performance of these materials.

References :

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2:30 PM EN01.02.03
Unification of Bulk Storage and Supercapacitive Storage Chuanlian Xiao, Robert Usiskin and Joachim Maier; Max Planck Institute for Solid State Research, Germany

In typical insertion electrodes for batteries, the capacity is determined by bulk storage within the electroactive particles, which is comparatively well investigated and understood. In contrast, supercapacitor electrodes are dominated by interfacial storage at interfaces, which is well addressed experimentally. However the charge carrier chemistry (defect chemistry) especially in the latter case is not taken seriously. Consequently a bridge between the two important fields is absent. Following and extending our quantitative concept of job-sharing storage [1], a generalized description that includes bulk and space charge storage (electrochemical and supercapacitive storage) is possible. In other words the treatment of defect chemistry as a function of the degree of storage as well as of position is key to a unification [2].

The experimental part of our research uses TiO_2 thin films. The precise measurement of the storage capacity of titania films as a function of thickness allows us to deconvolute bulk and interfacial contributions. We discuss the results in terms of bulk and space charge capacitance. The generalized treatment that comprises both contributions shows also how the ratio of both varies with the degree of storage. We expect this work to provide a better understanding of energy and power densities of storage devices which becomes particularly important for nanoionic systems [2].

References

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2:45 PM EN01.02.04
Supercapacitor Degradation: Understanding the Mechanisms of Cycling-Induced Deterioration and Failure of a Pseudocapacitor Katrina Mazloomian, Hector Lancaster, Chris Howard, Paul Shearing and Tom Miller; University College London, United Kingdom

Supercapacitors (SCs) have generated widespread interest in the field of energy storage because of their unique characteristics of high-power density, good reversibility and rapid rate of charge/discharge.[1] Their degradation, however, has traditionally been overlooked owing to their widely accepted reputation of having a long lifetime and an excellent cycle stability which has hindered the development of high-performance, next-generation systems.

SC degradation has thus far mainly been studied from an impedance perspective and mathematically modeled in numerous RC (resistor-capacitor) circuit configurations.[2–4] Studies such as this, however, do not account for variables such as dynamic voltage fluctuations and other deviations from ideality that inevitably occur in realistic use. More importantly, they do not actually explain why the supercapacitor is degrading; whether through chemical changes, mechanical stress, poor device engineering, or other mechanisms.

In this work, we utilize a multiscale characterization approach that pairs electrochemical analysis with X-ray computed tomography and complimentary spectroscopic, microscopic and diffraction analysis to reveal the modes of degradation in commercial SCs over their full charge/discharge cycle lifetime. Importantly, while the pseudocapacitor system studied was rated for long lifetimes of up to 100,000 cycles, it was found to suffer from extreme degradation linked to severe material degradation at the cathode after only 2000 cycles.

These findings therefore provide new insights into the aging processes of pseudocapacitors and highlight how essential it is to develop an in-depth knowledge of supercapacitor degradation before these devices become even more widely utilized in commercial applications.

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3:00 PM BREAK

SESSION EN01.03: Hybrid Devices
Session Chairs: Veronica Augustyn and Thierry Brousse
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2001

3:30 PM *EN01.03.01
Novel Insertion Concepts For Hybrid Electrochemical Capacitors Krzysztof Fic[1,2], Adam Mackowiak[1], Pawel Jezowski[1], Yukiko Matsui[2], Kazunari Soeda[2] and Masashi Ishikawa[2]; [1]Poznan University of Technology, Poland; [2]Kansai University, Japan

The world is looking for the perfect energy storage and conversion system. Two energy storage technologies are currently the most popular - electric double-layer capacitors (EDLCs) and lithium-ion batteries (LIBs). On the one hand, EDLCs cannot (and are not obliged to) compete with Li-based technology in terms of energy density; this feature is quite often sought as the reason for the limited commercialization of EDLCs. On the other hand, LIBs have shorter lifespan and lower power values comparing to EDLCs. Therefore, it seems reasonable to merge both technologies into one compact device, called a hybrid lithium-ion capacitor (LIC). The hybridization of energy storage mechanisms allows for acquiring higher energy density values than EDLCs while maintaining high specific power and a great number of charge/discharge cycles. The major problem occurring during LICs assembling is the pre-lithiation stage. Auxiliary metallic lithium electrode is one of the solutions – in fact, this approach was encouraging; however, after the pre-lithiation process, the metallic lithium electrode should be entirely utilized or removed and become replaced by a carbon electrode. This raises technical and safety issues because the exchange requires an inert environment. Another approach uses composite materials as positive electrodes, allowing full intercalation of lithium into graphite structure.
Nonetheless, after the pre-lithiation process, the dead mass of the composite stays in the system and deteriorates the efficiency. A different method of pre-lithiation using lithium from electrolyte was presented by Beguin et al. In this approach, the main problem identified was the consumption of lithium ions from the electrolyte and the diminished electrolytic conductivity of the solution.

In our work, we propose another concept that allows for full intercalation of the negative electrode without an auxiliary electrode or less-conductive composite on the positive side. In principle, the redox-active lithium salt dissolved in 1 mol L^{-1} $LiPF_6$ in EC:DMC electrolyte served as a charge-balancer. Thus, additional Li^+ in the redox agent structure made the Li^+ concentration in the electrolyte non-affected. Full electrochemical tests, including cyclic voltammetry, galvanostatic charge/discharge and impedance spectroscopy, constant power discharge were carried out. In further studies, optimal LIC operating conditions, i.e., voltage (2.2 – 4.2 V) and current density (0.2 A g^{-1}), were determined. The system has also been compared with commercial products.

Both, redox and non-redox processes occurring on both electrodes were identified. The capacitor's cycle life and the effect of the addition of inorganic salt on the conductivity were also investigated. Furthermore, detailed analysis has been conducted using operando mass spectrometry coupled with gas chromatography, SEM/EDS, XRD, Raman and FTIR spectroscopy.

4:00 PM *EN01.03.02
Roll-to-Roll Electrode Processing Towards the Development of a 100 F Lithium-Ion Capacitor María Arnaiz[1], Maria Canal[1], Daniel Carriazo[1,2], Aitor Villaverde[1] and Jon Ajuria[1]; [1]Centre for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Spain; [2]Ikerbasque, Basque Foundation for Science, Spain

Due to the advantage of combining both capacitive and faradaic charge storage mechanisms, lithium-ion capacitors (LICs) are regarded as a promising energy storage technology for many applications requiring high-power and high-energy. However, the lack of an internal source of lithium ions demands a pre-lithiation strategy for the viability of the technology. Many alternatives have shown their potential at the laboratory scale to achieve full pre-lithiation of the device, enhancing both energy and cycle life of the system. Dilithium squarate is one of those candidates. However, certain aspects are relevant to bring those strategies to real life. Thus, we aim to demonstrate this strategy at a pilot line level, by fabricating electrodes incorporating the sacrificial salt by roll-to-roll processing in a semi-automated electrode coater equipment. Moreover, to ensure a good response of the fabricated LICs under high current pulses, reducing the resistance of the cell is of high importance, and optimization of electrode processing becomes crucial at this point. In this work, the relevant aspects of the slurry formulation and roll-to-roll coating parameters of a hard carbon-based negative electrode and an activated carbon-dilithium squarate composite as positive electrode will be described. The different nature of the materials involved in both electrodes require to adapt the viscosity of the slurry, and the coating and drying parameters accordingly to ensure their correct mechanical properties. The quality of the slurry formulations is validated by the absence of agglomerates and appropriate viscosity, while the quality of final electrodes is validated by x-sectional SEM images and peeling tests. To conclude, 100 F multilayer LIC pouch cells have been fabricated. Their electrochemical characterization shows a device with low internal resistance, high capacitance, and good cycle life, confirming the good quality of the electrodes fabricated by means of roll-to-roll process.

4:30 PM EN01.03.03
An Oxygen-Rich Porous Carbon Cathode for Zinc-Ion Capacitors Jian Yin, Wenli Zhang and Husam N. Alshareef; King Abdullah University of Science and Technology, Saudi Arabia

Aqueous electrochemical zinc ion capacitors (ZICs) are promising next-generation energy storage devices based on their battery-capacitor intermediate energy densities, superior cycling stability, high safety, and inexpensive raw materials. Zn is an identical anode for aqueous energy storage systems for a high theoretical gravimetric capacity of 823 mAh g^{-1} and a low redox potential of −0.76 V (vs standard hydrogen electrode). Compared with the battery-type Zn anodes, the capacitive-type porous carbon cathode shows low capacitances. Developing porous carbon cathodes with high capacitances are required to achieve the high energy densities of ZICs. Herein, an oxygen-rich porous carbon cathode is proposed for ZICs with a high capacitance contributed by pseudocapacitances of hydrogen adsorption and oxygen redox reaction. The hydrogen adsorption capacity contribution is maximized by enlarging the working potential window with an optimized electrolyte. The oxygen pseudocapacitance is enhanced by a molecular-level oxygen doping strategy.

The oxygen-rich porous carbon was prepared from the direct pyrolysis of pyromellitic acid tetra-potassium salt. An optimized 3 mol L^{-1} $Zn(ClO_4)_2$ electrolyte is used to achieve a wide working potential window of 0-2.4 V. By enlarging the working window from 0.5-1.5 V to 0-1.9 V, two redox reactions show up on the porous carbon cathode, which is different from previous pure EDLC behavior. Two redox reactions are identified as reversible hydrogen adsorption during discharge and oxygen redox reactions during charge processes by studying the ex-situ characterizations. As capacitance is a synergic effect of EDLC and pseudocapacitance, we achieve an optimized porous carbon cathode by exploring the function of carbonization temperatures on the specific capacitances. The assembled ZIC delivers a high capacitance of 340.7 F g^{-1}, an energy density of 104.8 Wh kg^{-1}, and a power density of 48.8 kW kg^{-1}. For full cell assembly, we develop an interlayer coating strategy to prevent dendrite growth and achieve a stable cycling performance over 30,000 cycles. The viability of the pouch cell is verified by a high areal capacity of 4.7 mAh cm^{-2} at 6 mA cm^{-2} using a high mass loading of 0.96 g of the cathode.

4:45 PM EN01.03.04
Pseudocapacitive Energy Storage in $Ti_3C_2T_x$ MXene in a Wide Temperature Range Ruocun (John) Wang[1,2], Mark Anayee[1,2], Teng Zhang[1,2] and Yury Gogotsi[1,2]; [1]A.J. Drexel Nanomaterials Institute, United States; [2]Drexel University, United States

Pseudocapacitors have the potential to achieve high energy and high power density simultaneously, a holy grail for electrochemical energy storage. However, one obstacle facing pseudocapacitors is their shorter lifetime compared to commercial supercapacitors using the double-layer charge storage mechanism. In MXene-based pseudocapacitors, this concern is pronounced particularly at high temperatures due to the limited stability of the active material in contact with aqueous solutions, which can lead to oxidation and hydrolysis. This work shows that $Ti_3C_2T_x$ MXene thin-film electrodes in 5 M H_2SO_4 possess excellent rate capabilities from -50 °C to 70 °C but also a sufficient lifetime at 70 °C using a float test holding at -0.9 V vs. Hg/Hg_2SO_4 reference electrode. Post-mortem characterization using X-ray photoelectron spectroscopy, Raman spectroscopy, and scanning electron microscopy with energy dispersive X-ray spectroscopy showed no signs of oxidation in the bulk of the film. This work suggests sufficient electrochemical stability of $Ti_3C_2T_x$ MXene as a negative electrode in protic aqueous electrolytes across a wide temperature range, making it promising for pseudocapacitor energy storage.

SESSION EN01.04: Poster Session
Session Chairs: Thierry Brousse and Sonia Dsoke
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN01.04.01
Facile Synthesis Route of Various Porous Transition Metal Hydroxides for Pseudocapacitor using Poly(4-vinyl pyridine) Gyeongwon Ha and Jinkon Kim; Pohang University of Science and Technology, Korea (the Republic of)

Transition metal hydroxides are widely used in electrochemical fields because of their low cost and many advantages. In particular, porous transition metal hydroxides are attracting attention because their large surface area compensates for the disadvantage of poor electrical conductivity. Herein, we suggest facile synthesis of porous transition metal hydroxide using poly(4-vinyl pyridine) (P4VP) homopolymer by polymer-precursor method. To synthesis the metal hydroxide, we used a cyanide metal precursor present in the form of a metal hydroxide anion in an aqueous solution and coordinated it with P4VP. However, the cyanide precursor prevents the protonation of P4VP because it makes the aqueous solution basic. Therefore, in order to maintain the pH so that P4VP can be sufficiently protonated, a buffer solution that pH is not easily changed by the external environment was used. At the same time, porous transition metal hydroxide can be obtained when P4VP film was immersed in a precursor-buffer solution by inducing a nanoscale phase separation and by selective removing of P4VP through O_2 RIE. Using this prepared porous transition metal hydroxides, we compared pseudocapacitive properties of the fabricated structures depending on pH of solution. As a result, the porous metal hydroxide structure with the best efficiency among them showed satisfactory specific capacitance without optimization.

5:00 PM EN01.04.03
Ionic-liquid Gated Electrochemical Carbon Nanotube Transistor with High On-Off Ratio for Gas Sensing Peisheng He[1,2], Alexander Abelson[2], Jenny Zhou[2], Steven F. Buchsbaum[2], Liwei Lin[1] and Eric R. Meshot[2]; [1]University of California, Berkeley, United States; [2]Lawrence Livermore National Laboratory, United States

Carbon nanotubes (CNTs) hold great promise as gas sensing platform due to their large surface area-to-volume ratio for applications ranging from environmental to disease diagnostics. Notably, extremely low detection limit (ppb range) and room temperature operation has been realized for various gas molecules with semiconducting single-walled CNTs (SWCNTs)-based field-effect transistors. However, intrinsic CNT suffers from poor selectivity and thus functionalization with chemical selectors is required. To this end, we proposed a SWCNT-based field-effect transistor with ionic liquids (ILs) as both gating electrolyte and chemical functionalization layer for selective gas sensing. Replacing gate dielectrics in conventional transistors, ILs enable efficient gating of channel by forming an ultra-thin electric double layer (EDL) around the SWCNTs at low voltage, without restricting access to the CNT surface for analyte detection. Meanwhile, ILs are highly attractive chemical selectors for gas sensing since their chemical functions, such as gas solubility/selectivity and affinity for water, are variable depending on the combination of the cations and anions. In addition, ILs exhibit good environmental durability due to non-volatile behavior, wide electrochemical potential, and temperature stability. We have fabricated electrolyte-gated CNT transistors coated with different ILs. High on/off ratio (10^6~10^7) has been achieved with low operation voltage (gate voltage ~1V). Transfer characteristics were studied under various gases (N_2, O_2, NH_3, etc.) exhibiting different response, which could open up new avenues toward miniaturized electronic noses with high sensitivity and selectivity, while the material selection of CNTs and ILs is compatible with future flexible device integration.

5:00 PM EN01.04.04
Synthesis and Characteristics of CNT Grown Activated Carbon Using Ni Catalyst and Melamine to Prepare High Performance Flow-Electrode Dong Gyeong Kim, Donghyun Kim, Haeun Seo, Hyeryang Choi, Haeun Kim and SeungCheol Yang; Changwon National University, Korea (the Republic of)

Flow-electrode capacitive mixing (F-CapMix) is novel renewable energy technology generating electricity by using salinity difference between salt water and fresh water and ion adsorption/desorption on active materials in flow-electrode. To enhance performance of F-CapMix, charge percolation and electron transfer between active materials in the flow-electrode should be improved. In present work, we synthesized carbon nanotube (CNT) grown activated carbon (AC) for achieving efficient charge percolation and electron transport between AC particles in the flow-electrode. For this work, AC particles were impregnated with the solution including Ni catalyst. After filtering of AC suspension, wet AC particles was heat-treated under an inert condition at 300 celsius to form Ni seed on the surface of AC particles. After that, melamine was mixed with the AC particles, and heat treatment of the mixture was carried out under reduction condition at 700 celsius. Through SEM analysis, it was confirmed that CNTs on the surface of AC particles were successfully grown. The synthesized CNT grown AC was additionally analyzed with various tools, such as XPS, Raman, etc. We will evaluate F-CapMix performance with the flow-electrode made by using the CNT grown AC.

5:00 PM EN01.04.05
Thermal Modeling of a Supercapacitor Based on Calorimetric Measurement Chee-Burm Shin and Dongcheul Lee; Ajou University, Korea (the Republic of)

Supercapacitors have the potential to meet the high pulse power capability of the energy-storage systems for automotive applications. In the high pulse power operations for automotive applications, a large amount of heat is produced inside a supercapacitor cell. Because the lifetime and performance of a supercapacitor depend strongly on temperature, it is important to accurately predict the thermal behaviors of a supercapacitor for its efficient and reliable system integration from an application perspective. Modeling of the thermal behaviors of a supercapacitor can serve a valuable role when optimizing the design of future cells and the thermal management system for automotive applications.
In this work, the rate of heat generation of the supercapacitor cell during charge and discharge is measured with a large, custom-made calorimeter, because most commercial calorimeters are manufactured for testing small cells. Then, based on this measurement data, a three-dimensional modeling is carried-out to investigate the effects of the operating and ambient conditions on the thermal behavior of a 2.7 V/3500 F supercapacitor cell for a 42-V automotive electrical system. The results show that the temperature of the supercapacitor cell increases during the first 50 cycles after which it reaches a periodic steady-state value that increases with increasing ambient temperature.

5:00 PM EN01.04.06
Electrical Performance of MnO_2-Biochar Composite Electrodes as a Function of Initial Biochar Concentration Thomas Sadowski[1,2], Max Martone[1,2], Vanessa Adamski[1,2], Kaleb Roman[1,2], Jules Scanley[1,2], Rahul Singhal[3,2] and Christine Broadbridge[1,2]; [1]Southern Connecticut State University, United States; [2]Connecticut State Colleges and Universities Center for Nanotechnology, United States; [3]Central Connecticut State University, United States

The demand to diversify the global energy portfolio to include more renewable sources has illustrated an acute and critical need for advancements in energy storage technology to mediate their inherent intermittent nature. Hybrid supercapacitors offer such a solution for a wide range of commercial and infrastructural energy applications, with great potential for fabrication utilizing cost-effective and environmentally benign materials. Previous studies have identified electrodes composed of biochar alongside MnO_2 (for non-Faradaic and Faradaic charge storage, respectively) as great potential candidates that fit this sustainability-driven profile. In this study, the performance of pine-based biochar-MnO_2 hybrid electrodes, synthesized via a one-pot method of varying initial biochar concentrations, was investigated. The electrode surface area was quantified by BET surface analysis and the structure and composition using x-ray diffraction. The supercapacitive performances were investigated using cyclic voltammetry ranging from 3-200 mVs^{-1} as well as galvanostatic charge-discharge tests at 0.5, 1.0, and 2.0 A/g. This data along with scanning and transmission electron microscopy data provide preliminary insights on the structure-property-performance relationship for this composite materials system.

5:00 PM EN01.04.07
Hybrid Microsupercapacitor based on $Ti_3C_2T_x$ Mxene and Covalent Organic Frameworks Yusuf Khan, Jehad K. El-Demellawi, Yongjiu Lei, Vinayak S. Kale, Osama Shekhah, Mohamed Eddaoudi and Husam N. Alshareef; King Abdullah University of Science and Technology, Saudi Arabia

The construction of flexible, portable, and in-plane hybrid micro-supercapacitors has high demand in emerging electronic applications like energy storage, sensors, and portable devices. Here we report an in-plane hybrid supercapacitor based on a covalent organic framework as a positive electrode and $Ti_3C_2T_x$ Mxene as a negative electrode. Both these two different electrode materials are deposited on three-dimensional laser-scribed graphene current collectors fabricated by a laser-based process. The designed hybrid supercapacitor achieved promising initial electrochemical performance because of the two-dimensional Mxene and periodic porous COF, whose structures provide better active sites for charge storage and favorable ions movement. The prepared hybrid supercapacitor shows a high areal capacitance of 110 mF/cm^2, a wide potential window of 1.5 V with an energy density of 34.4 mWh/cm^2. Further optimization of the materials and devices is ongoing. The results so far seem encouraging for utilizing such devices in miniaturized energy storage devices and sensors.

5:00 PM EN01.04.08
Titanium Oxynitride Thin Films and Nanowires for Ultra-High Capacitance Supercapacitor Applications Panupong Jaipan[1], Schuyler Shi[2], Ram K. Gupta[3], David A. Muller[2] and Dhananjay Kumar[1]; [1]North Carolina Agricultural and Technical State University, United States; [2]Cornell University, United States; [3]Pittsburg State University, United States

The present research is aimed at the development of titanium-based transition metal oxynitrides, TiN_xO_y (TiNO), for electrochemical supercapacitor and solar water-splitting applications. The advantages of TiNO over other transition metal oxides are associated with the less electronegative and more polarizable characteristics of nitrogen relative to that of oxygen. The synthesis of high-quality multifunctional 2-dimensional (2D) TiNO thin films and 1-dimensional (1D) TiNO nanowires has been accomplished using a non-clean room-specific pulsed laser deposition method. The electrochemical supercapacitor measurements on the TiNO system using cyclic voltammetry have shown that the specific capacitance values for the TiNO nanowire samples (2,725 $mF.cm^{-2}$) are nearly six times more than that of the TiNO thin film samples (400 $mF.cm^{-2}$). The supercapacitor values are amongst the highest values reported for the recently top-tier nanoscale electrode materials. Furthermore, due to the pseudocapacitive-type behavior, the charge-ion transfer in the TiNO nanowire system is more rapid than in electrical double-layer capacitor-behavior materials. Therefore, TiNO nanowires have a high potential for usage as electrode material in lithium-ion batteries, enhancing the anode's conductivity in diverse phases of the charge-discharge cycle and the capacity of a battery with a larger specific capacitance.

5:00 PM EN01.04.09
Long-Lifespan Anode-Free Lithium Metal Batteries by Ag/Conjugated Polymer Wetting Agent Inducing Interfacial Fluorination Seonmi Pyo, Jinil Cho, Heejun Yun, Heebae Kim and Youn Sang Kim; Seoul National Unive, Korea (the Republic of)

Li metal batteries (LMBs) have emerged as a promising energy storage technology for high-energy-density rechargeable batteries. Since the Li metal anode (LMA) has an ultrahigh theoretical specific capacity (3862 mAh g^{-1}) and the lowest negative electrochemical potential (-3.040 V vs. SHE), its employment ensures higher energy density beyond commercial Li-ion batteries (LIBs) with the limited energy density of less than 250 Wh kg^{-1} at the cell level. In this

respect, anode-free LMBs (AFLMBs) with no Li excess is considered the ultimate system to achieve a dramatic increase in energy density (>500 Wh kg^{-1}), in which all the active Li sources are stored in a fully lithiated cathode. In addition, the anode-free design significantly reduces cost and simplifies the manufacturing process compared with traditional LMBs. However, LMA suffers from low coulombic efficiency (CE), rapid capacity fading, and safety hazards, which come from the Li dendrite growth and continuous formation and breakage of solid electrolyte interphase (SEI) during Li plating/stripping processes. Therefore, such uncontrollable interfacial reactions should be seriously addressed, especially in AFLMBs without excess Li inventory to compensate for the loss of active Li sources. Recently, many strategies have been reported to control the interfacial chemistry between Li and electrolyte as well as between Li and current collector (i.e. modification of current collector, electrolyte design, optimization of cycling protocols). Among them, studies about employing lithiopilic wetting agents on the current collector confirm an effective way to stabilize Li plating behavior, which can achieve a favorable life span. In particular, wetting agents show outstanding effects on guiding homogeneous Li deposition and thus suppressing dendritic Li growth by lowering the Li nucleation barrier. However, the critical problem of sequentially irreversible capacity loss before a stable SEI formation still remains, which is a fatal obstacle in no excess Li cells.
Herein, we introduced Ag nanoparticles incorporated p-doped conjugated polymer (Ag-PCP) wetting agent simultaneously to regulate the Li nucleation and promote a rapid stabilization of SEI at the early stage, and further prolong the life span of AFLMBs. Furthermore, we investigate interfacial fluorinated mechanism of the Ag-PCP chains to efficiently control SEI chemistry related to the LiF formation. The Ag-PCP wetting agent is fabricated by a simple one-step synthesis because of the electrostatic interaction between oppositely charged Ag cation and dopant. Critically, the PCP chain with the delocalized π-electron system induces an interfacial fluorinated reaction with F anions derived from TFSI$^-$ decomposition, and thus the F-doped PCP promotes the formation of LiF-rich SEI. Also, the presence of lithiophilic Ag nanoparticles on the PCP wetting agent act as both Li nucleation seeds and polymer chain modifiers about the structural rearrangement and closer packing of the Ag-PCP chains, thus providing both uniform Li nucleation and continuous conductive channel, resulting in an increase of LiF ratio in the SEI. The LiF-rich SEI facilitates Li ion diffusion, which effectively suppresses the Li dendrite growth and the depletion of the Li reservoir. Benefiting from the synergistic effect Ag-Li alloying process and interfacial fluorination, the Ag-PCP wetting agent optimizes Li deposition behavior and a favorable SEI chemistry, leading to superior cycling performances. Consequently, the Ag-PCP/Cu half-cell shows quite stable voltage profiles with low polarization (≈17 mV) over 300 cycles, even at a high current density/areal capacity of 3mA cm^{-2}/3mAh cm^{-2}. Moreover, the anode-free $LiFePO_4$ (LFP) full cell achieves superior cycling stability with a high capacity retention of 72% (Li inventory retention rate 99.8%) at 1C-rate after 200 cycles. This strategy contributes to the applicability of interfacial stabilization for long-life AFLMBs.

SESSION EN01.05: Pseudocapacitive and High Power Battery Electrodes
Session Chairs: Krzysztof Fic and Francesca Soavi
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2001

8:30 AM *EN01.05.01
Identifying New Directions for Pseudocapacitive Materials Bruce S. Dunn[1], Patricia McNeil[1], Bintao Hu[1] and Qiulong Wei[2,1]; [1]University of California, Los Angeles, United States; [2]Xiamen University, China

The prospect of developing energy storage materials with the energy density of batteries and the power density and cycle life of electrical double-layer capacitors is an exciting direction which is of great interest for mobile power applications. To achieve these properties, our research has focused on pseudocapacitive materials in which ion insertion induces reversible redox reactions at or near the surface of an electrode material. For the most part, studies on pseudocapacitive materials have focused on crystalline solids where crystallographic pathways, such as open channels or sparsely occupied planes, lead to high ion mobility. Although amorphous materials may not have long-range crystallographic considerations, they do offer other interesting features such as a more open framework which can enable percolation pathways and facilitate ion transport. Our studies on sodium-ion insertion into amorphous VO_2 (a-VO_2) showed that the charge storage properties of the amorphous material were significantly better than the crystalline counterpart. The present paper reviews our recent work on amorphous systems and underscores their promise as energy storage materials. Our studies on lithium-ion insertion into reduced amorphous transition metal oxides, a-WO_2 and a-MoO_2, show that these materials exhibit box-like cyclic voltammograms and linear galvanostatic profiles. This voltage profile is reminiscent of an electrical double layer capacitor, except that with a-WO_2 and a-MoO_2, there are redox reactions which increase the specific capacity significantly. Our initial studies indicate that a-WO_2 exhibits 120 mAh/g (1-electron redox) while a-MoO_2 supports 1.3 electron redox, leading to over 280 mAh/g. A related direction has involved the effect of nanostructuring. In this study, the sodiation of nanoparticles of anatase TiO_2 produces amorphous layers of 3 to 5 nm thick. As a result, 10 nm particles of TiO_2 become completely amorphous and exhibit pseudocapacitive signatures as redox reactions occur throughout the particle. These materials exhibit specific capacities for sodium which are on the order of 200 mAh/g at high rates. Taken together, these studies suggest that short-range order should be considered a key factor in achieving charge storage.

9:00 AM *EN01.05.02
Boosting the Pseudocapacitive Behavior of MnO_2 with a Pinch on PGM Oxides Wataru Sugimoto[1], Yuta Takemura[1], Ryota Saito[1], Annga Hermawan[1], Keisuke Muramatsu[1], Daisuke Takimoto[2] and Sho Hideshima[3]; [1]Shinshu University, Japan; [2]University of the Ryukus, Japan; [3]Tokyo City University, Japan

Various polymorphs and morphologies of manganese dioxide and related materials have been studied as pseudocapacitive materials for aqueous supercapacitors. While the surface and near surface-confied redox processes affords high specific activity, a fairly large amount of conducting additive, typically 30 to 50 wt% acetylene black, needs to be added in order to achieve high rate charge storage. Since the conducting additive is characterized by low surface area and electrochemical inertness, the carbon additive generally does not contribute much to the specific capacitance, leading to decrease in total energy density of the cell in terms of both mass and volume. Polymeric binders such as PTFE and PVdF are also necessary to fabricate rigid electrodes with good contact.
As an alternative to these typical conductive binders and polymer binders, we have studied the possibility of using RuO_2 nanosheets as a novel inorganic binder with both high electronic conductivity and polymeric properties and excellent pseudocapacitive properties. RuO_2 nanosheets are highly conductive (comparable to activated carbon), possess characteristics as macroanion, are extremely stable within the water electrolysis potential, and shows high redox activity.
As an example, the effect of adding a small amount of RuO_2 nanosheets to MnO_2 particles (primary particle size ~200 nm) was studied.[1] A large synergetic effect was observed where the specific capacitance per MnO_2 mass exhibited a maximum value at low content; i.e. x=10-20, or 10-20 mol% of RuO_2. The increase in the specific capacitance is suggested to be associated with the decrease in charge transfer resistance of MnO_2 as a result of the RuO_2 nanosheets sufficiently working as a conductive additive to MnO_2. The amount of RuO_2 in terms of mass is 13 wt% for x=20, which is much lower than the amount generally used for conductive carbon additives despite the much higher formula weight of RuO_2 (133.07 g mol^{-1}) compared to carbon (12.01 g mol^{-1}). As

another example, the case of an all nanosheet (ns) composite, MnO_2(ns)-RuO_2(ns), with different electrode mass loading was studied. At low mass loading the conducitivy is sufficient enough so only a small synergetic effect is observed. However at high mass loadings, RuO_2(ns) acts as an active binder similar to the case of MnO_2 particles. The difference in nanoparticles versus nanosheets will also be discussed in detail in the presentation.
In another case, the effect of doping birnessite MnO2 with Ir was studied by synthesizing a new solid solution $K_{0.2}(Mn,Ir)O_2.xH_2O$.[2] Two important effects of Ir doping was found. First, the overall capacitance increased from 37 F g^{-1} for pristine birnessite to 64 F g^{-1} for 10% Ir doped birnessite, which is due to the increase in the Mn^{4+}/Mn^{3+} redox-related charge. Second, a decrease in peak-to-peak difference was observed, which indicates an improvement in the charge-transfer kinetics with Ir substitution. This uncommon behavior is attributed to a strong electronic interaction between the host Mn ion and the dopant Ir ion.

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9:30 AM EN01.05.03
The Role of Defects Created by Implanted Ions on the Electrochemical Behavior of Pseudocapacitive Thin Film Electrodes Etienne Le Calvez[1], Allan Lebreton[1], Bukola Jolayemi[2], Jérémy Barbé[1], Camille Douard[1], Olivier Crosnier[1], Dmitri Yarekha[2], Kevin Robert[2], Gaetan Buvat[2], Pascal Roussel[3], Christophe Lethien[2] and Thierry Brousse[1]; [1]Nantes Université/CNRS, France; [2]IEMN, France; [3]UCCS, France

The pseudocapacitive behavior of RuO_2 electrode was initially described as a peculiar behavior in $HClO_4$ aqueous electrolyte. Since then, pseudocapacitive materials have been the topic of extensive investigations. Their rectangular shape cyclic voltammograms (CVs) are the signature of capacitive-like electrochemical behavior due to specific fast and reversible Faradaic surface and sub-surface reactions as it has also been demonstrated for MnO_2, $MnFe_2O_4$, $FeWO_4$ or VN electrodes among others. Experimental evidences plead for charge transfer at the surface of the active material particles involving transition metal redox couples. Many parameters seem to influence the extend of charge storage in pseudocapacitive electrodes: the amount of electroactive cations in the pristine material, the structural defects such as vacancies, the specific surface area, the particle size and shape, and many more, which makes it difficult to determine their individual influence. One way to overcome the presence of intrinsic defects in pseudocapacitive materials is to intentionally introduce them. This can be done by several means, including the use of ion implantation. The amount and nature od introduced defects can be tuned by playing on the dose of implanted ions and the implantation energy. Although such technique is common in microelectronic, it has rarely been applied to electrode materials for supercapacitors.
In this communication, different pseudocapacitive materials were deposited as thin films and further implanted with different cations using different energies. Some clues about the influence of the defects introduced upon ions implantation will be given with regards to microstructural/structural/electrochemical changes. Such investigation technique opens the way for unveiling the role of defects on the charge storage mechanism of pseudocapacitive materials.

9:45 AM EN01.05.04
Pseudocapacitive Responses for Systems with Two Transition Metals—$M_3Nb_2O_{14}$ (M = Mo, W) Bronze Phase Materials Yunkai Luo[1], Etienne Le Calvez[2], Yucheng Zhou[1], Eric Gautron[2], Eric Quarez[2], Molleigh Preefer[3], Olivier Crosnier[2], Johanna N. Weker[3], Laurent Pilon[1], Thierry Brousse[2] and Bruce S. Dunn[1]; [1]University of California, Los Angeles, United States; [2]Nantes Université, France; [3]SLAC National Accelerator Laboratory, United States

Recently, bronze phase materials have gained attention as high-rate lithium-ion battery anode materials. Their large tunnels and open framework are attractive for lithium-ion diffusion and high-rate performance, while the presence of two transition metals, such as W and Nb, provide a means to achieve high energy density from multi-electron redox. In this paper we report on the structure and electrochemical properties of two different bronze phase compositions having the same stoichiometry: $W_3Nb_2O_{14}$ and $Mo_3Nb_2O_{14}$. It is significant to note that both bronze phase materials exhibit pseudocapacitive characteristics. This includes a box-like characteristic in cyclic voltammetry (CV) experiments and nearly linear voltage-capacity curves from galvanostatic (GV) experiments. The CV results for $W_3Nb_2O_{14}$ were used to determine the b-value from the relationship between current (I) and sweep rate (v):= ab^v The peak located around 2.1V versus Li/Li+ shows a value of 0.85 and the peak around 1.7V vs Li/Li+ shows value of 0.95, which suggests a surface-controlled redox reaction. XPS measurements indicate that both transition metals are undergoing redox reactions. The lithium capacity for the $W_3Nb_2O_{14}$ bronze phase at C/5 is the theoretical value of 139 mAh/g corresponding to a 5 electrons redox process. In contrast to the stable behavior of $W_3Nb_2O_{14}$ bronze, the $Mo_3Nb_2O_{14}$ bronze phase undergoes an irreversible structural rearrangement upon cycling. Although the CV is initially box-like, the CV permanently becomes a broad peak shape when the scan rate is above 0.5mV/s. $Mo_3Nb_2O_{14}$ exhibits 220 mAh/g at C/5 and thus achieves multi-electron redox (1 Li per transition metal = 192mAh/g), but the capacity retention is worse than that of $W_3Nb_2O_{14}$. The change in CV shape is attributed to an irreversible structural rearrangement. XPS measurements indicate that although the Nb returns to the 5+ state on oxidation, the Mo oxidation state does not return to 6+, suggesting that lithium is trapped in the structure and leads to increased overpotential during cycling. Our results indicate that pseudocapacitive behavior is not limited to systems with a single transition metal ion. The results for both $W_3Nb_2O_{14}$ and $Mo_3Nb_2O_{14}$ bronzes show that pseudocapacitive responses can be achieved in systems where two transition metal ions undergo redox reactions.

10:00 AM BREAK

10:30 AM *EN01.05.05
Fast and High Capacitive Electrode Materials for Asymmetric Supercapacitors Masashi Ishikawa; Kansai University, Japan

Lithium ion capacitors (LICs) are unique energy storage devices that combine the high power technology of conventional EDLCs with the high energy density characteristics of lithium ion batteries. An important technology in LICs is lithium pre-dope to a carbon negative electrode (NE), but how the depth of charge by pre-dope affects the charging and discharging performance of LICs is not well understood so far. In this study, pitch-coated graphite (PCG), which suppresses self-discharge, was used as NE. Noting that PCG has several stage structures, the objective of this study is to investigate the effects of NE utilization conditions (utilization stages and cycle utilization capacity) on the cycling behavior of LICs. In other words, we will report the effect of different utilizing stages with controlled depth of charge by pre-doping on the cycle behavior.
A four-terminal aluminum laminate cell was used with activated carbon as the positive electrode material, PCG as NE, Li metal foil as the counter electrode and reference electrode for pre-doping, and 1.2 M $LiPF_6$ /EC : PC : DEC (3 : 1 : 4 v/v/v) as the electrolyte. Pre-doping and cycling tests were performed according to planned negative electrode utilization conditions. Pre-doping was performed up to a certain utilizing stage in a high-temperature environment, and the cycle test was conducted at room temperature for 500 cycles under constant current conditions at 5C.
First, we found that the smaller the cycle capacity, the more stable the cycle behavior is, and that there is obvious Li loss in the early cycles, which does not affect the cycle stability regardless of the NE utilization conditions. We observed the change in electrode potential (potential swing) for three cycle test conditions with a cycle capacity range of 150 mAh g^{-1} at different utilizing stages. When the cycling is centered on “dilute stage II”, the utilization stage shifts to a shallower direction with cycling, and the NE potential increases and degrades. It is considered that Li is continuously lost from the NE during cycling. When we utilize “stage II” as the utilizing stage, compared to the previous result, the NE potential does not change with cycling and shows stable cycling behavior. When we utilize “stage I”, although there is a concern about an increase in the resistance of the NE because the electrode potential falls

below 0 V vs. Li / Li$^+$ during charging, the cycle behavior looks stable. From these results, we considere that the utilizing stage has a significant impact on the cycle characteristics. Based on the above, we will extensively discuss the influence of the utilizing stage on the cycle behavior.

11:00 AM EN01.05.07

Metal-Phosphates-Based Materials for Hybrid Supercapacitors Qiang Fu and Sonia Dsoke; Karlsruhe Institute of Technology, Germany

Battery materials provide higher capacity than double-layer ones. However, most part of high-capacity materials suffers from intrinsic kinetics problems, due to phase transitions, slow solid diffusion and low electronic conductivity, which makes them often unsuitable for high-power devices [1]. Some of the strategies to improve the kinetics are to coat the particles with a thin carbon layer (to enhance the electronic conductivity), to reduce the particles (to shorten the solid ionic diffusion) or to tune the structure by metal doping with the aim of suppressing phase transitions [2, 3].
Metal phosphates, with the advantages of abundance, environmental friendliness and low cost are emerging as promising faradaic electrode materials. Herein we will present strategies to convert the battery-like features of materials such as $M_3V_2(PO_4)_3$ (M=Li, Na, K) to pseudocapacitive-like ones by suppressing their phase transitions [4].

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Acknowledgments

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11:15 AM EN01.05.08

Towards Flexible and Ultra-Stable Pseudo-Supercapacitors based on Nanocomposite "Silicon Nanowires/Nanometric Alumina/Conducting Polymer" Marc Dietrich[1], Pascal Gentile[1], Mathieu Deschanel[2], Cristina Iojoiu[3], Fannie Alloin[3] and Said Sadki[2]; [1]CEA Grenoble, France; [2]UGA, France; [3]CNRS, France

With the increase in the use of embedded wearable technologies: the pseudo-capacitive storage, or asymmetric systems, flexible all-solid state supercapacitors raised considerable attention in recent years with their many advantages and ease of use, including the ability to have systems that are small in size, light in weight, easy to handle and usable over wide temperature ranges.
In this context, we realized high-performance electrochemical energy storage microdevices based on nanocomposites electrodes (silicon nanowires / nanometric dielectric / conductive polymer or transition metal oxide) within aqueous electrolyte and all-solid electrolyte. This processed nanocomposite electrode is a major improvement in energy density and durability of devices: that becomes possible thanks to the Atomic Layer Deposition (ALD) technique and the homogeneous growth of Alumina layers [1, 2]. The nanocomposite is realised in three successive steps:
i) Doped Silicon nanowires (SiNWs) growth by Chemical Vapor Deposition (CVD) through a Vapor-Liquid-Solid (VLS) process [3-4].
ii) Deposition of a 3nm nanometric alumina layer deposited by ALD to chemically protect[5].
iii) Conductive Polymers coating to add a new faradic energy storage mechanism to our capacitive system, deposited (PEDOT-PSS) by drop-casting on the SiNWs, or by electropolymerization of EDOT directly on the nanostructures [6,7].
With SiNWs and nanometric (3-5 nm) layers of alumina, we obtained cyclability greater than 2 million cycles and retentions of capacities close to 100%. With the nanocomposite electrodes (SiNWs / Al_2O_3 / Conductive Polymers), the gravimetric performances proved to be excellent with a loan capacity retention of 95% over 500 000 cycles for an initial gravimetric capacity 8.5 F.g^{-1} and 11 mF.cm^{-2} and specific energies and powers of 8.2 mJ.cm^{-2} and of 4.1 mW.cm^{-2}. Such cycling stability for a polymer-based nanocomposite in aqueous media combined with first-order electrochemical storage performance is unprecedented in the literature [6]. We used also second way to deposit conductive polymer on our nanostructures, by electropolymerization in aqueous media of EDOT monomers, using micellar media and forming small aggregates targeted on our SiNWs, exhibiting a capacitance of 4.75 mF.cm^{-2}. For these flexible applications, we changed our standard substrates (silicon <111>) for growing SiNWs on carbon fiber cloth or carbon felts. For our all-solid component, we use a polymer electrolyte. Our solid-state electrolyte was obtained by bi-functionalization on polysiloxane with trimethylammonium and a crosslinkable function, i.e. methyldiallylammonium groups. The crosslinking is done in-situ by heating the sandwich device at 80° C for 48 hours. The good interface property between the polymer electrolyte and the protected SiNWs allows a very long cycling stability for a cell potential of 3 V, that was observed with galvanostatic cycling of the device.
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11:30 AM EN01.05.09

Electrochemical Capacitance in Hydrous Oxides Veronica Augustyn; North Carolina State University, United States

Abstract not available.

SESSION EN01.06: Electrolytes and Emerging Concepts

Session Chairs: Majid Beidaghi and Jayan Thomas
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2001

1:30 PM PANEL DISCUSSION

2:00 PM *EN01.06.02

On the Use of Protic Ionic Liquids as Electrolytes for RuO_2 Microsupercapacitors Dominic Rochefort[1], Jensheer Shamsudeen Seenath[1,2] and David Pech[2]; [1]University of Montreal, Canada; [2]Centre National de la Recherche Scientifique, France

Ionic liquids are very appealing electrolytes for electrochemical capacitors. Being organic molecules in nature (at least for the vast majority), they offer immense possibilities for structural modifications to adjust their properties (viscosity, electrochemical stability window, melting point, etc.) or to add a functionality to do chemical reactions. With a careful design, such modifications can be made while keeping the original properties of the ionic liquid which make them attractive as functional electrolytes to improve energy storage devices.

Protic ionic liquids (PIL) are obtained by the proton transfer reaction between Bronsted acids and bases to generate the cations and anions of the ionic liquid. In contrast, aprotic ionic liquids like those based on imidazolium, pyrrolidinium and ammonium cations are formed by the quaternization of a nitrogen by alkylation. As a result, PIL are often less viscous since, for an equivalent structure, the N-H leads to fewer interactions than a N-alkyl. This, combined to straightforward synthesis, explain the interest in PIL. PIL can also be seen as functional ILs when considering their ability to exchange protons with an electrode material, allowing to carry out proton-coupled reactions that are usually restricted to aqueous electrolytes. Relevant to this presentation is their ability to transfer protons with metal oxide electrodes for pseusocapacitive energy storage. The focus of this contribution will be on the use of the protic ionic liquid triethylammonium bis(trifluoromethanesulfonyl)imide (TEAH-TFSI) to improve the energy density of RuO_2 microsupercapacitors. These electrochemical capacitors are fabricated by photolithography and are expected to find application in microelectronic devices to power sensors and data transmission for the Internet-of-Things. This first demonstration of the use of PILs for metal oxides microsupercapacitors showed an extended cell voltage up to 2 V with an energy density 4 times higher than what was obtained in a conventional H_2SO_4 electrolyte. The presentation will include results with several other PIL and propose approaches to improve cycling stability using PIL-based ionogels.

2:30 PM EN01.06.03

Lignin Activated Carbon and Green Electrolyte as Sustainable Components for EDLCs Devices Elisabetta Petri, Monica Giovannucci, Federico Poli, Alessandro Brilloni and Francesca Soavi; Alma Mater Studiorum University of Bologna, Italy

Activated carbon-based Electrical double-layer capacitors (EDLCs) are the preferential choice given their unique combination of chemical inertia, electrochemical stability, conductivity, and specific surface area, together with the possibility to highly tune the textural properties of these materials in terms of surface moieties and pores size distributions [1]. To improve sustainability and reduce CO_2 footprint of the production of activated carbons, the pyrolysis of real bio-waste derived from local resources enables their valorization as well as the disengaging from fossil-derived resources.
For practical purposes, to enable an effective scale-up, biomass sources must be abundant and cheap [2]. Lignin stands out because it is the third most abundant natural polymer and one of the major wastes of anaerobic digestion processes and pulp and paper making industries [3]. The exponentially growing market of Electrical double-layer capacitors (EDLCs) requires the substitution of flammable, volatile, and toxic electrolytes with less dangerous and sustainable ones. The main limitation which is hindering the promises held by aqueous electrolytes is the low maximum cell voltage if compared to the organic ones. Therefore, the investigation of novel green electrolytes, such as DES and WiSE [4, 5], featuring an improved stability window compared to conventional aqueous electrolytes is critical to increasing the energy density of aqueous-based EDLCs.

Here we report a systematic study to scale up the production of Lignin Activated Carbon (LAC) generated by a one-step carbonization route starting from a real lignin waste, using $KHCO_3$ as a mild activating agent [3]. Different process pathways have been explored and the effect of the process parameter on the textural and chemical-physical and electrochemical properties of the activated carbon are analyzed and discussed.
Moreover, the optimized upscaled LAC produced and novel green electrolyte, have been exploited to produce an electrochemical characterize lab-scale EDLCs prototypes featuring 1.7 V of maximum cell voltage.

Acknowledgments
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2:45 PM EN01.06.04

Acetate-based Water-in-Salt Electrolytes for Electrochemical Energy Storage Mona Amiri and Daniel Belanger; Univ of Montreal-Quebec, Canada

Aqueous electrolytes are widely used in electrochemical technologies. Recently, superconcentrated aqueous electrolytes, also called water-in-salt electrolytes, have attracted much attention for electrochemical energy storage systems. These superconcentrated electrolytes can have salt/water weight ratio higher than 1. They are also characterized by a much wider electrochemical stability window, in comparison to low concentration electrolytes. In this talk, the physicochemical properties of highly concentrated aqueous electrolytes based on acetate salts will be presented. For example, the nature of ions-water and ions-ions interactions of the electrolytes will be discussed. The electrochemical behavior of these electrolytes in electrochemical energy storage will be presented and their advantages as well as limitations will be discussed.

3:00 PM BREAK

3:30 PM EN01.06.05

Electrochemically Modulated Interaction of MXenes with Microwaves Danzhen Zhang[1], Meikang Han[1,2], Christopher E. Shuck[1], Bernard McBride[1], Teng Zhang[1], Ruocun (John) Wang[1], Kateryna Shevchuk[1] and Yury Gogotsi[1]; [1]Drexel University, United States; [2]Fudan University, China

Controlling the reflection and absorption of incident electromagnetic waves at gigahertz frequencies in thin films remains a fundamental challenge. The ability to dynamically depress electromagnetic wave jamming is significant for protecting electronic devices but lacking in conventional electromagnetic interference (EMI) shielding materials. MXenes, as a large family of two-dimensional transition metal carbides and nitrides, have shown a broad range of EMI shielding performance as well as different energy storage mechanisms from electric-double-layer capacitance to pseudocapacitive behavior. Herein, we report a method for active control of electromagnetic wave interactions with various MXene films, including $Ti_3C_2T_x$, Ti_2CT_x, V_2CT_x, $V_4C_3T_x$ and

$Nb_4C_3T_x$, leading to EMI shields with unprecedented bidirectional modulation of shielding capability. The reversible tunability of EMI shielding effectiveness was achieved by electrochemically driven ion insertion/desertion and charge transfer in MXene layers with different electrolytes, accompanied by expansion and shrinkage of layer spacing. An EMI shielding 'switch' was demonstrated through electrochemical oxidation of MXene films. Our results offer opportunities to develop smart EMI protection with active modulation, which is different from conventional 'static' shielding and can adapt to demanding environments.

3:45 PM EN01.06.06
Surface Electrochemistry of Capacitive Deionization and Development of Highly Stable Cabon Electrodes Jin Soo Kang; Seoul National University, Korea (the Republic of)

Capacitive deionization (CDI), whose operation principle mimics that of the supercapacitor, has received a broad attention as a promising method for desalination. In CDI, removal of salt takes place by adsorption of Na^+ and Cl^- on charged electrode surfaces. In order to maximize the desalination capacity, activated carbon electrodes with large surface area have been widely used as electrode materials. Meanwhile, during the operation, carbon undergoes significant oxidative degradation and the CDI performance decreases to a significant extent, even leading to an inverted operation with a very low capacity. In this study, surface electrochemistry of activated carbon electrodes, which include the interactions with water and dissolved oxygen, are thoroughly investigated to understand the environment where the activated carbon electrodes are placed in CDI operation. Then based on the findings, design strategy of electrode materials and the newly developed heteroatom-doped activated carbon electrodes will be presented. Moreover, utilizing the inversion behavior of activated carbon electrodes in electrochemical desalination will be suggested as an intrinsic solution to addresses the stability issues of activated carbons.

4:00 PM DISCUSSION TIME

4:15 PM EN01.06.08
High-Performance Novel Multifunctional Structural Supercapacitors for Electrical Energy Storage Applications Atif Javaid[1,2,1], Ahmet Emre[1,1] and Nicholas A. Kotov[1,1,1]; [1]University of Michigan, United States; [2]University of Engineering and Technology, Pakistan

Carbon fiber (CF) reinforced epoxy composites are playing a significant role in a wide variety of civil and military applications because of their outstanding properties, ease of fabrication, low shrinkage after curing, and good thermal resistance. Currently, the focus is on the development of smaller, smarter, and more efficient materials that can perform multiple functions simultaneously1, including a function of structural material as well as exhibit at least one additional performance-linked function. Our goal is to create a structural material that simultaneously stores electrical energy within itself, by acting as a supercapacitor. Any load-bearing device, requiring electrical energy, can be fabricated using the structural supercapacitor concept [1-3]. This can be imagined by considering a mobile phone, without a heavy energy storage device installed, extracting the required energy from the outer casing, or cutting the weight of the heavy energy storage devices that a soldier must carry for powering up various electronic gadgets, as the lightweight structural supercapacitor can easily fit under the soldier uniform. Herein, we demonstrate a way to improve the electrochemical performances of the structural supercapacitors by impregnating modified diglycidylether of bisphenol-A epoxy polymer electrolyte into two iron selenide hedgehog particles [4] deposited carbon fabric (CF) electrodes, separated by a novel aramid nanofiber membrane separator [5,6], using vacuum bagging technique. The deposition of high surface area iron selenide hedgehog particles4 on CF mats is an effective process to improve the charge storage capacity of the electrodes and can be used in structural supercapacitors which can offer a different direction to the electric vehicle industries. Electrochemical and mechanical properties of the structural supercapacitors are investigated by chronoamperometry, cyclic voltammetry, impedance spectroscopy, chronocoulometry, dynamic mechanical thermal analysis, and in-plane shear testing, respectively. The fabricated structural supercapacitors, produced in this way, exhibit excellent multifunctional performance in capacitance and energy/power densities and exhibit a long cycle life with improved mechanical properties. Thus, this study has demonstrated that the deposition of iron selenide hedgehog particles on the surface of carbon fabrics as well as using aramid nanofiber membrane as a separator, are novel and easy approaches to improving the multifunctionality of structural supercapacitors that could be exploited in various applications including portable electronics, electric cars, and unmanned aerial vehicles (UAVs). This development of the novel concept potentially could have significant mass and/or volume efficiencies for applications that utilize both structural components and energy storage devices.

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SESSION EN01.07: Emerging Concepts
Session Chairs: María Arnaiz and Olivier Crosnier
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2001

8:30 AM *EN01.07.01
Energy Storing Structural Body Panels for EVs Jayan Thomas[1], Deepak Pandey[1], Kowsik Sambath Kumar[1], Leaford Henderson[1] and Luke Roberson[2]; [1]University of Central Florida, United States; [2]Kennedy Space Center, United States

As the global appetite for clean energy is growing like never before, energy storage devices like hybrid supercapacitors are attracting considerable attention. As electric vehicles (EVs) are becoming more and more popular, they face many challenges, including limited charge capacity and long charging times. This presentation discusses how we addressed some of these challenges by developing an electrified carbon fiber reinforced polymer (e-CFRP) composite that stores electrical energy and function as a load-bearing structural component to make EV's body panel. The carbon fiber mat electrode is developed by vertically attaching graphene sheets on carbon fibers. A high-strength multilayer e-CFRP composite is fabricated using an alternate layer patterning configuration of epoxy and gel electrolyte. The e-CFRP so developed delivered an areal energy density of > 0.31 mWh cm^{-2} at 0.3mm thickness and a high tensile strength of 518 MPa and a bending strength of 477 MPa. The e-CFRP panel is used to run a toy car to demonstrate its potential application in EVs. The energy harvested by an integrated solar cell is stored in the e-CFRP and used to power an IoT device to demonstrate its application in communication satellites.

9:00 AM *EN01.07.02
Carbon Capture with High Mass Loading Supercapacitor Electrodes from Biomass Waste. Muhammad Bilal, Jiajie Li and Kai M. Landskron; Lehigh Univ, United States

Supercapacitive Swing Adsorption (SSA) is a carbon capture technique that achieves selective, and reversible CO_2 adsorption through capacitive charge and discharge of activated carbon electrodes in aqueous electrolytes. We report SSA with garlic roots-derived activated carbon achieving a record adsorption capacity of 312 mmol/kg at a low energy consumption of 72 kJ/mol and high mass loadings (>30 mg/cm^2) at 1 V. The activated carbons are inexpensively prepared in a one-step process using potassium carbonate, and air as activators. The adsorption capacity further increases with increasing voltage. Up to a voltage of 1.4 V there is only minor increase in energy consumption, and a sorption capacity of 524 mmol/kg at an energy consumption of 130 kJ/mol can be achieved. The volumetric sorption capacity is also enhanced, and reaches values of 85.7 mol.m^{-3} at 1.0 V, and 126 mol.m^{-3} at 1.4 V. Cycle stability for at least 130 h is demonstrated.

9:30 AM EN01.07.03
Supercapacitors for Improved RFBs Performance in Hybrid Systems Monica Giovannucci, Elisabetta Petri, Federico Poli, Alessandro Brilloni and Francesca Soavi; Alma Mater Studiorum University of Bologna, Italy

Modern energy grids must rely on renewable energy sources, such as solar and wind, which are characterized by high fluctuations in power. In view of the increased exploitation of intermittent renewable energy sources, modern grids need to adapt and necessitate more dynamic energy storage systems.

Nowadays, vanadium redox flow batteries (VRFB) are the most diffuse and established technology for stationary storage thanks to the ability of to decouple energy and power design [1]. However, this type of battery still suffers of low power peak and are not able to fulfill the demand for intermittent renewable energy source connected to the grid. Supercapacitors are electrochemical storage devices that can deliver and absorb high power peaks.

Hybrid energy storage systems (HESS) in which high-power redox flow batteries and supercapacitors work together are promising solution for applications having frequent high peak-to-average power demand. Hybridization of Energy Storage Systems (ESS) will also lead to more efficient storage systems, with longer lifetimes and with the ability to operate on all time-scale applications, from seconds to days [2].

Here we report on the hybridization of a HP-VRFB with commercial Supercapacitors (SC) by a direct parallel connection of the two devices that aims at improving the overall energy efficiency at high power rates. At first, the power and energy response of the HP-VRFB cell and SC single cell has been tested under the same discharge protocols and has been, then, compared to the hybrid assembled system.
Overall, our study highlights that the direct connection of the HP-VRFB cell with the SC makes it possible to extend the range of currents by a factor of 5. The direct connection showed also beneficial effects in terms of delivered energy under a power pulse that increased by 46%. In addition, the discharge curve of the SC was modified by the presence of the HP-VRFB, a phenomenon that we defined as an apparent capacitance increase [3]. This study is the base of future research in which green materials for high power supercapacitors and high power semi-solid electrodes for VRFB will be embedded in the hybrid system.

Acknowledgments
This work was supported by the European Union within the Horizon 2020 Research and Innovation Program 2020-2023 (Grant No. 963550 HyFlow project https://hyflow-h2020.eu/); CO_2CARBON - EIT RawMaterials Project Agreement n° 21081; and MIAMI Project 2022-2025 - Italian Minister for Ecological Transition, MiTE.
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9:45 AM DISCUSSION TIME

10:00 AM BREAK

10:30 AM *EN01.07.05
Green Hybrid Supercapacitive Systems Francesca Soavi, Elisabetta Petri, Monica Giovannucci, Federico Poli and Alessandro Brilloni; University of Bologna, Italy

Electrical double layer capacitors (EDLCs) are key energy storage systems for applications having frequent high peak-to-average power demand, from portable to stationary applications and e-mobility. They are also considered systems of choice to design different hybrid energy technologies, where they are connected to batteries, fuel cells or ambient energy harvesters to improve the overall power performance and reliability.
A unique feature of EDLCs is that, unlike batteries, they store energy electrostatically within a wide operational voltage range, limited only by the electrochemical stability window of the electrolyte. This dynamic response makes EDLCs easily connectable, at single cell level, with a wide range of energy harvesters/storage units including those operating at low and variable voltage, like solar cells, piezoelectric generators, and microbial fuel cells.

Depending on the defined end-use, the hybrid energy storage/conversion systems should be properly sized and designed with attention to the sustainability of materials and manufacturing processes. Specifically, the storage unit has to be tailored, both to meet the device design requirements (flexibility, thickness, size) and the electric behavior of the harvester. In addition, today, EDLCs cannot be considered as totally green. Greener component options are biochar electrodes obtained by the pyrolysis of bio-derived-waste that will enable the exploitation of ubiquitous and scalable raw materials within a circular economy approach. Electrode and membrane manufacturing by water-processable polymers is also a valuable approach, as well as novel electrolyte formulations, including ionic-liquids and water in salt electrolytes (WiSE) could solve most of the criticality of today EDLC organic solvent-based electrolytes.

Here, we report about different activities that target the design of hybrid systems, where EDLCs are designed taking into account the electric characteristics of the energy harvesters parallel connected and and manufactured by exploiting sustainable components. The main achievements obtained within the HyFLOW UE project, that targets the development of an environmentally friendly hybrid storage unit based on vanadium redox fow batteries and supercapacitors will be reported. We will discuss about the different approaches that should be followed for hybrid systems, based on different harvesters like solar cells, piezoelectric generators, or microbial fuel cells, where EDLCs play a key role in improving the output power quality and efficiency. We will also propose a semi-empirical method for proper supercapacitor sizing and component selection.

Acknowledgments
This work was supported by the European Union within the Horizon 2020 Research and Innovation Program 2020-2023 (Grant No. 963550 HyFlow project https://hyflow-h2020.eu/) and by NATO Science for Peace and Security Programme, under grant agreement G5772.

11:00 AM EN01.07.06
The Effect of Particle Motion on Charging Behavior Observed in a Microfluidic Flow Capacitor Brandon Stacks, Deyu Li, Kelsey B. Hatzell and Haoxiang Luo; Vanderbilt University, United States

Electrochemical flow capacitors (EFCs) are promising energy storage devices because of their large storage capacity, low fatigue rates, and fast charge/discharge rates. These devices employ the electric double layer of high-surface-area porous carbon particles in a flowable slurry, i.e., a 'flowable electrode', to store ionic charges from an electrolyte solution. In the charging process, continuous electrical paths between carbon particles and the stationary electrode have to be established in the flowing slurry. The slurry can then be pumped into storage reservoirs. To extract the stored electricity, the flow is reversed, and the stored charges can be released to the electrodes again relying on particle-electrode and particle-particle interactions. Therefore, the flow characteristics of the carbon slurry and the particle interactions could play an important role in the charging and discharging performance of the device. Despite this, there are very few studies that directly observe the particle motion inside the charging channels. Most studies consider the EFC from an electrochemical perspective, so slurry components, such as electrolyte selection, carbon particle porosity, and carbon loading percentages, are tested to achieve the best possible charging performance. This approach however does not allow the researcher to probe the effect of slurry flow characteristics on charging performance. To address this issue, we have developed a microfluidic electrochemical flow capacitor (MEFC) that is compatible with optical imaging. The device is fabricated using transparent indium tin oxide (ITO) electrodes, a transparent polycarbonate track etch (PCTE) separator membrane, and polydimethylsiloxane (PDMS) channels for the slurry to flow through. This platform allows us to investigate the influence of various slurry flow behaviors on the charging performance of the flowable electrode during the operation of the device using an inverted microscope with a high-speed camera. We have used this setup to directly observe the effect of slurry flow rate on the particle-electrode and particle-particle interactions and consequently the charging/discharging performance. We will report on the fabrication of the MEFC, the experimental setup, and the charging/discharging results under different slurry flow rates.

11:15 AM EN01.07.07
Ni/Co Bimetallic Flower-Like Metal-Organic Frameworks with Enhanced Performance for High-Power Energy Storage Applications Ilias Ntoukas[1], Alexander Roberts[1], Rong Lan[1], Chiara Milanese[2] and Evangelos Gkanas[1]; [1]Coventry University, United Kingdom; [2]University of Pavia, Italy

Metal-Organic Frameworks (MOFs) are compounds consisting of metal ions coordinated to organic ligands to form crystalline porous structures by self-assembly. They have emerged as a class of crystalline materials with high surface area and porosity, tuneable pore size and functionalized surface. Due to the metal nodes in the framework, they provide redox centres facilitating faradaic reactions, and due to their crystalline porous structure they provide easier access for electrolyte diffusion. Thus, they own great electrochemical properties, making them ideal for electrode materials for supercapacitors.
However, most reported MOFs own an insulating nature which is a major drawback for their electrochemical applications. A common method to solve this restriction is to incorporate another metallic element to enhance the properties of the electrode material.
Nickel materials demonstrate high specific capacitance and exhibit promising electrochemical properties as electrode materials for supercapacitors, but they own low rate capability and cycle life, which is attributed to their poor structural stability during the fast charge-discharge process. With the addition of another metal ion such as Co^{2+} into the structure, more active sites and improved conductivity can be obtained, while stabilizing the Ni species. The partial substitution of the second metal ions in the inorganic nodes will provide synergistic effects for the bimetallic framework. The ratio between the metals can also be adjusted to tune the physiochemical properties of MOFs.
For all these reasons, bimetallic Ni/Co MOFs are promising materials for electrodes in energy storage applications. Currently, Activated Carbon (AC) is used as electrode material for supercapacitors due to its high conductivity, large number of micropores and high surface area. However, the micropore structure of activated carbon limits pore accessibility and ion diffusion, thus reducing the capacitance and energy density. Transition metal oxides are also used as electrode materials for supercapacitors due to their metal centres, which provide faradaic redox reactions, and their low cost. Though, their poor conductivity leads to a low specific capacitance and causes structural destruction of the materials, thus decreasing the stability of the system.
In this study, using terephthalic and trimesic acid as the linkers, binary Ni/Co MOFs (Ni:Co = 4:1, 3:1, 2:1, 1:1) have been synthesized utilizing a solvothermal method. Various parameters that affect the structure and properties of MOFs such as time, temperature, ligands, Ni/Co ratio, and additives have been investigated. The main focus is on the effect of Co ions that substitute the Ni ones in the framework, how they affect the structure's stability and the electrochemical properties of the bimetallic Ni/Co MOFs.
These materials have been structurally characterised by SEM, EDX, XRD, XPS, FTIR, TGA, BET and TEM. The morphology consists of 2D interlayered nanosheets with smooth surface that assemble to form 3D microflower-like crystalline structures. The addition of Co^{2+} leads to a more dense, hierarchical and spherical morphology. The phase of these materials is also identified by Rietveld analysis and is: $Ni_2(OH)_2(C_8H_4O_4)$ *(CCDC no. 985792).* The addition of Co^{2+} does not alter the framework but only provides stability.
Moreover, these materials have been electrochemically tested by CV, GCD, EIS and cycling measurements. A large specific capacitance of 1503 F/g at 1A/g has been achieved with 70% retention after 3000 cycles. Finally, asymmetric coin cells using these materials and Activated Carbon (AC) have been developed and tested for their capacitance and cycle life.
In conclusion, Ni/Co MOFs have been synthesized and the effect of Co^{2+} in the framework has been investigated. The incorporation of Co^{2+} provides stability and advanced electrochemical properties, making these materials promising candidates as electrode materials for supercapacitors.

11:30 AM DISCUSSION TIME

11:45 AM EN01.07.09
High-Voltage Hybrid Electrolytes for Fast Charging Devices Jeng-Yu Lin; Tunghai University, Taiwan

Developing high-voltage electrolytes to extend the cell voltage has been regarded as an efficient strategy to increase the energy density of supercapacitors (SCs) since energy density is proportional to the square of the cell voltage. Recently, deep eutectic solvent (DES), as an ionic liquid analog, has been regarded as a green liquid media and novel alternative for non-aqueous type electrolytes for SCs due to its unique features of non-flammability, low cost, wide ESW, low vapor pressure, biodegradability, renewability, and compositional tunability. Unfortunately, due to the strong molecular interaction of DES, it shows high viscosity and low ionic conductivity behavior, resulting in a diminished capacitive performance at high current densities.
To overcome these issues, a novel hybrid DES electrolyte was developed by simply introducing the appropriate amount of water and acetonitrile co-solvents. The as-fabricated symmetric SC device using the optimized DES hybrid electrolyte showed an impressive cell voltage of 2.2 V and delivered a high energy density of 21.4 Wh kg^{-1} at the power density of 1100 W kg^{-1}, and also achieved excellent capacity retention of 86.8% after 120-h floating test. As a consequence, this work should definitely enlarge the application of the DES electrolyte systems consisting of water/acetonitrile towards high-

performance energy storage devices.

SESSION EN01.08: Microsupercapacitors and Applications
Session Chairs: Maria Lukatskaya and Dominic Rochefort
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2001

1:45 PM *EN01.08.01
Latest Advances in Sputtered Nitride Films as High Performance Pseudocapacitive Electrodes for Solid-State Micro-Supercapacitors Christophe Lethien[1,2], Thierry Brousse[3], Bruce S. Dunn[4] and Pascal Roussel[5]; [1]IEMN - RS2E, France; [2]Institut Universitaire de France, France; [3]Institut des Matériaux Jean Rouxel, France; [4]University California Los Angeles, United States; [5]Unité de Catalyse et de Chimie du Solide, France

Micro-supercapacitors[1–3] (MSC) are a new class of miniaturized electrochemical capacitors which could be used to power the next generation of Internet of Things (IoT) devices. Despite the fact that the 1st RuO_2 // LIPON // RuO_2 MSC was proposed[4] twenty years ago by Yoon *et al*, there is still no commercially available MSC. Nevertheless, this promising technology with high power capabilities is fully complementary to solid-state lithium-based micro-batteries[5,6] (storing and delivering high energy densities) and could be combined in a single unit to power autonomous IoT devices. In that context, the development of advanced MSC at the production level is mandatory for the future. The lack of Off-The-Shelf MSC is due to two technological bottlenecks. The first limitation is that of achieving the deposition of thin or thick films electrodes at the wafer level by methods which are compatible with clean room environment: carbon-based electrodes[7,8] or pseudocapacitive oxide/nitride films[9–13] deposited by magnetron sputtering methods seem to be attractive solutions to achieve high performance electrodes using mass production compatible techniques. The second limitation deals with the development of solid electrolytes whose high ionic conductivities occur within the small footprint restricted to the area of the MSC (~ mm^2). Ionogel technology[14,15] combined with photopatternable[16,17] capabilities is the best candidate to fulfil this requirement.
This presentation will focus on the recent advances that we made to remove these two technological barriers in order to upscale the MSC technology from lab to market. The latest results that were obtained on vanadium nitride and ruthenium nitride films will be detailed.

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2:15 PM EN01.08.02
Synthesis of 2D/2D $MoS_2/Ti_3C_2T_x$ MXene Heterostructure for High Performance Supercapacitor Thi Kim Anh Nguyen and Ruey-An Doong; National Tsing Hua University, Taiwan

Although a number of strategies have been boosted on 2D-$Ti_3C_2T_x$ Mxene as electrode material for supercapacitors, the re-stacking nanomellar and instability in structure have always inhibited its practical application. The development of 2D/2D heterostructures of Mxene with another 2D material has been proposed to combine the collective advantages of each 2D constructive and expose enhanced electrochemical performance. In this research, a rationally designed electrode 2D/2D heterostructure of 2D-MoS_2 decorated 2D-$Ti_3C_2T_x$ ($MoS_2/Ti_3C_2T_x$) was constructed by a benign hydrothermal etching method. The physicochemical characteristics of as-prepared $MoS_2/Ti_3C_2T_x$ were thoroughly in-depth investigated and the electrochemical storage mechanisms were clearly interpreted. The superior electrochemical performance and excellent long-term durability of the as-obtained $MoS_2/Ti_3C_2T_x$ are observed, which is attributed to not only the extensive ion storage site from a synergistically nanomellar effect in 3D interconnected networks but also the ultrafast electron transport channel resulting from the immobilization/bonding between 2D-MoS_2 and $Ti_3C_2T_x$ MXene. This study gives a new archetype to realize the real applications of 2D/2D heterostructures for electrochemical energy storage devices with high energy and power densities.

2:30 PM BREAK

3:30 PM *EN01.08.03
The Impact of Synthesis Conditions and Heterostructuring on the Capacitive Performance of MXenes Majid Beidaghi; Auburn University, United States

2D MXenes have shown promise for various applications due to their unique physical and chemical properties. The high electrical conductivity, 2D and layered structure, and rich surface chemistry of MXenes have sparked great interest in their properties as electrode materials for energy storage devices. MXenes are particularly of high interest because they can store charge in the bulk of the electrode through ultrafast intercalation of ions and fast and reversible redox reactions. The main focus of this talk is our recent studies on tuning the synthesis conditions to improve the capacitive performance of MXene electrodes. Particularly, the role of defects introduced during the MXene synthesis on the electrochemical properties will be discussed. Also, our recent work on the assembly of MXene heterostructures with improved capacitive performance will be presented, and the chemical and electrochemical stability of defected and heterostructured MXenes will be discussed. Finally, the current gaps in the knowledge about the electrochemical properties of

MXenes and some of the future research directions in this area will be summarized

4:00 PM EN01.08.04
Three-dimensional $Ti_3C_2T_x$ MXene-Prussian Blue Hybrid Microsupercapacitors by Water Lift-Off Lithography Yongjiu Lei, Wenli Zhao and Husam N. Alshareef; King Abdullah University of Science and Technology, Saudi Arabia

The accelerating development of miniaturized portable and wearable electronic devices is a significant emerging application for compatible microscale power systems. On-chip microsupercapacitors (MSCs) are promising micropower candidates, which typically exhibit high-power delivery, fast rate capability, and extended lifetime. Herein, we demonstrate an in-plane hybrid microsupercapacitor with a high areal energy density by employing battery-type CuFe-Prussian blue analogue (CuFe-PBA) as the positive electrode, and pseudocapacitive titanium carbide MXene ($Ti_3C_2T_x$) as the negative electrode. A three-dimensional (3D) lignin laser-induced graphene electrode was prepared as the substrate by a simple water-based lift-off lithography method. Thanks to the excellent match of the two types of high-rate performance materials in proton-based electrolytes and the numerous electrochemically active sites, the designed device achieved excellent electrochemical performance, even when using a gel electrolyte. In particular, the device delivers a high areal capacitance of 198 mF cm^{-2}, a wide potential window (1.6 V), an ultrahigh rate performance (75.8 mF cm^{-2} retained even at a practical/high current density of 100 mA cm^{-2}), and a competitive energy density of 70.5 and 27.6 μWh cm^{-2} at the power densities 0.74 and 52 mW cm^{-2}, respectively. The hybrid microsupercapacitor is fabricated using scalable thin-film microfabrication methods, which opens a new avenue for miniaturized and highly integrated micropower sources in future portable and wireless devices.

4:15 PM EN01.08.05
Fully-Printed, High-Temperature Microsupercapacitor Arrays Enabled by Hexagonal Boron Nitride Ionogel Electrolytes Lindsay Chaney[1], Woo Jin Hyun[1,2], Maryam Khalaj[1], Janan Hui[1] and Mark C. Hersam[1,1]; [1]Northwestern University, United States; [2]Guangdong Technion–Israel Institute of Technology, China

Abstract: Rising demand for portable electronics and sensors for the Internet of Things continues to drive innovations in the energy storage sector. In order for these devices to run remotely, they must be able to self-sufficiently store their own energy and thus require compact, integrated power sources. Microsupercapacitors are an excellent option due to their exceptionally long cycle lives and their rapid energy delivery and uptake. Additionally, their planar device architecture is easily integrated with all components of a wireless device, allowing for streamlined manufacturing directly on a single substrate. In this work, we demonstrate fully screen-printed, flexible microsupercapacitor arrays via rapid deposition of a high-temperature hexagonal boron nitride (hBN) ionogel electrolyte. The hBN ionogel can be printed onto large-area (~100 cm^2) graphene-based microsupercapacitor arrays within seconds, enabling mass-manufacturing. The devices have an areal capacitance of 0.92 mF cm^{-2}, which rivals the best graphene-based devices to date. In addition, unlike incumbent polymer-based electrolytes, hBN ionogel electrolytes exhibit stable cycling at high temperatures up to 180°C. Elevated operating temperatures result in an increase in power density and enable self-powered, remote devices to be deployed in harsh, high-temperature environments such as underground exploration, aviation, and electric vehicles. This combination of high-performance functionality in harsh conditions and a scalable fabrication strategy significantly expands the application space for microsupercapacitors.

4:30 PM EN01.08.06
Giant Energy Storage Microsupercapacitors via Electrostatic Negative Capacitance Suraj Cheema[1], Nirmaan Shanker[1], Shang-Lin Hsu[1], Mohamed Mohamed[2] and Sayeef Salahuddin[1,3]; [1]University of California, Berkeley, United States; [2]Massachusetts Institute of Technology, United States; [3]Lawrence Berkeley National Laboratory, United States

Dielectric electrostatic capacitors, although they lag behind their electrochemical counterparts in energy storage, are better suited for integrated on-chip energy storage. Here we report record-high electrostatic energy storage density (ESD) and power density (PD) in back-end-of-the-line (BEOL)-compatible HfO_2-ZrO_2 (HZO)-based thin films on silicon [1]. Until now, the promise of ultrathin (anti)ferroelectricity in HZO on silicon has mostly motivated low-power computing applications [2]. However, the same features which make HZO so promising for computing – (anti)ferroelectric order down to the ultrathin regime [3,4], high permittivity via negative capacitance (NC) [2], inherently large breakdown field, conformal growth by ALD [1-4] – are also appealing for energy storage. First, to increase its intrinsic energy storage, atomic-layer-deposited antiferroelectric HZO films were engineered near its field-driven ferroelectric phase transition to exhibit amplified charge storage via the NC effect [5], which enhanced its volumetric ESD beyond the best known BEOL-compatible dielectrics (120 J/cm^3). Second, to increase the overall stored energy, amorphous-templated HZO-Al_2O_3 superlattices overcame the conventional thickness limitations of HZO-based (anti)ferroelectricity to scale-up its high storage antiferroelectric NC behavior (100-nm regime). Third, to increase storage-per-footprint, the superlattices were conformally integrated into three-dimensional (3D) capacitors to boost its areal ESD (PD) to 9-times (180-times) the best-known 3D electrostatic capacitors: 80 mJ/cm^2 (300 kW/cm^2). Notably, this ESD value exceeds that of most state-of-the-art electrochemical microsupercapacitors and is only ~ 1 order of magnitude away from commercial Li-ion microbatteries, despite boasting over 8 orders of magnitude larger PD. Therefore, this work leverages NC ferroic engineering, superlattice thickness scaling, and 3D integration to overcome the traditional capacity-speed (ESD-PD) trade-off spanning the electrostatic-to-electrochemical energy storage hierarchy. Furthermore, this work demonstrates that HfO_2-ZrO_2 can serve as the functional material system across all technologies required for energy-efficient autonomous electronics, including on-chip microsupercapacitors [1] as well as computing units [2]. Therefore, these results establish a pathway for co-designed microelectronics in which computing and energy technologies are monolithically-integrated and synergistically-operated towards enhanced energy-efficiency and sustainability.

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4:45 PM EN01.08.07
Liquid Metal-Based Stretchable All-Solid-State Supercapacitor Adit Gupta, Jian Lv and Pooi See Lee; Nanyang Technological University, Singapore

The components of wearable electronics should be flexible and stretchable in order for the electronics to demonstrate mechanical stability against deformation caused by human motions without experiencing performance degradation. For achieving a fully autonomous system, energy storage devices used to power the active devices on wearable electronics should be able to endure deformation along with other components. Stretchable supercapacitors (SSCs) are viewed as viable power sources for wearable electronics because of their advantages of high-power density, high cyclic stability, and superior safety. At present, SSCs are typically prepared by loading or coating the active materials on the stretchable substrate composed of the conductive filler and the polymer elastic matrix (acting as a current collector). Unfortunately, they suffer from delamination between the stretchable electrode and active material while causing exposure of noncontributing volume/mass of elastic substrate during mechanical deformation. Here, we develop an intrinsically stretchable electrode by sedimenting the conductive and electrochemical active liquid metal microparticles (Eutectic Gallium Indium alloy, EGaIn) in the stretchable conductive matrix. A similar polymer matrix is used to prepare ionogel to improve the electrolyte and electrode compatibility. An all-solid-state energy storage device is constructed by UV curing the ionogel in between the two liquid metal-based electrode. This strategy of utilizing liquid metal microparticles as the active material provides an added advantage of retaining mechanical conductivity and conserving the amount of active material present on the surface of the electrode during stretching. The liquid metal-based electrode has high conductivity, attaining a high stretchability with ~900% strain, and provides a continuous conductive network due to the flow of liquid metal during mechanical strain. Through this strategy, we are not only able to improve the mechanical and electrochemical performance during mechanical deformation but also prevent the leaching of liquid metal to produce a stable system. Our work on liquid metal-based electrodes with ionogel electrolyte is a viable path for creating next-generation high-performance, stretchable energy storage devices.

SESSION EN01.09: Virtual Session
Session Chairs: Husam Alshareef and Veronica Augustyn
Wednesday Afternoon, April 26, 2023
EN01-virtual

9:00 PM EN01.09.02
Template-Free Ethylene Glycol-Assisted Etching Method to Increase the Porosity of Metal-Organic Framework Derived Carbons for Supercapacitors Ruijing Xin[1], Yusuke Yamauchi[1,2] and Yusuf V. Kaneti[1]; [1]University of Queensland, Australia; [2]National Institute for Materials Science, Japan

Metal-organic frameworks (MOFs) have drawn great interests as both carbon sources and self-templates for creating carbon materials with intrinsic porosity, tuneable chemical and physical properties and high surface area. Hard or soft template methods have been primarily used in the fabrication of hierarchical porous carbons. The template-based approaches, however, require uniform combination of the carbon sources with templates and post-synthetic template removal, making the fabrication procedures costly and complex. Herein, we demonstrate a facile template-free etching strategy for enlarging the micropores in bimetallic zeolitic imidazolate framework (ZIF) particles into mesopores at room temperature. Hierarchical porous bimetallic ZIF particles (etched $Zn_{33}Co_{67}$-ZIF) exhibiting both micropores and mesopores have been successfully prepared while maintaining the framework integrity using the ethylene glycol-assisted aqueous etching method. After pyrolysis, the etched $Zn_{33}Co_{67}$-ZIF particles are transformed into cobalt- and nitrogen-doped hierarchical porous carbon (i.e., etched $Zn_{33}Co_{67}$-C) particles with increased mesoporosity. The etched bimetallic carbon (etched $Zn_{33}Co_{67}$-C) displays 1.6- and 14.8- times higher specific capacitance at a high scan rate of 100 mV s^{-1} than unetched bimetallic carbon ($Zn_{33}Co_{67}$-C) and Zn-only carbon (Zn-C), respectively as electrochemical double layer supercapacitor electrode materials. Additionally, the etched $Zn_{33}Co_{67}$-C exhibits good electrochemical stability after 5,000 cycles. The presented ethylene glycol-assisted aqueous etching process provides an useful method for enlarging the porosity of MOFs, and their corresponding porous carbon materials and improve their supercapacitor performance.

9:15 PM EN01.09.03
Improving Electrochemical Performance of Polyaniline-Derived Activated Carbon in Different Electrolytes for Energy Storage Devices K.A.U. Madhushani, A.A.P.R. Perera, Wang Lin and Ram K. Gupta; Pittsburg State University, United States

The development of efficient energy storage devices can be introduced as a sustainable route for storing energy for long-term purposes. Among those, supercapacitors have attracted remarkable attention in recent research and commercial activities. Herein, several techniques have been used to improve the performance of the polyaniline-derived carbon material. Through the combined process of carbonization and activation process, the surface area and porosity of the electrode material are increased, leading to better electrochemical performance of the energy storage devices. Also, this can be significantly improved by selecting the best active electrolytes. Therefore, it is essential to find the best combination of electrodes and suitable electrolytes for the fabrication of supercapacitors to achieve higher chemical performances. The electrochemical performance of activated polyaniline using various ratios of KOH as an activating agent (1:0.5, 1:1, and 1:2 wt./wt.) was studied. The electrode derived using a 1:1 ratio showed better capacitive performances in an aqueous electrolyte. A symmetrical coin-cell supercapacitor based on 1:1 activated polyaniline was further tested in an aqueous electrolyte (6M KOH) and two organic electrolytes ($TEATFB_4$ in acetonitrile and PMPyrr-TFSI). The supercapacitor based on aqueous electrolyte exhibited a high specific capacitance of 137 F/g at 1 A/g, which is much higher than that of 88 F/g and 86 F/g from $TEATFB_4$ and PMPyrr-TFSI, respectively. However, the energy and power density of these two organic electrolyte systems illustrated superior values compared to those of the aqueous electrolyte system. The highest energy and power density were owned by PMPyrr-TFSI, which was 182 Wh/kg and 1953 W/kg at 1 A/g, respectively. Our research focuses on developing an energy storage device based on the superior electrode that can be used for the fabrication of commercial supercapacitors.

SESSION EN01.10: On-Demand Session
Friday Morning, April 28, 2023
EN01-virtual

April 11 - April 27, 2023

Symposium Organizers
Eric Colegrove, National Renewable Energy Laboratory
Jessica de Wild, imec
Byungha Shin, Korea Advanced Institute of Science and Technology
Colin Wolden, Colorado School of Mines

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* Invited Paper
\+ Distinguished Invited

SESSION EN02.01: CdTe I
Session Chairs: Eric Colegrove and Randy Ellingson
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2002

10:30 AM *EN02.01.01
Defects in Arsenic doped CdSeTe Absorbers and their Impact to Current Collection Efficiency Mariana I. Bertoni; Arizona State University, United States

Copper and arsenic have been used as primary dopants in CdSeTe photovoltaic absorbers. However, both atomic species suffer from very low dopant activation. Arsenic concentration in these devices are on the order of 10^{16} cm^{-3}, which makes it notoriously difficult to correlate nanoscale distributions to the local charge transport properties. To measure and correlate these properties, measurement techniques require high sensitivity to elemental concentration, large penetration depth, and operando compatibility. In this work, we use nanoscale X-ray microscopy to correlate chemical distribution – structure – electrical properties through X-ray Fluorescence, X-ray Absorption Near edge spectroscopy, and X-ray Beam Induced Current at a pixel-to-pixel level (50-120nm).
Our cross-section studies unveil the segregation of As and the transition of the maximum charge-collection efficiency from the back interface to the front interface as a function of processing conditions, which is correlated to the balance of acceptors and donors, and thus the activation of the dopants. We will show linear combination fitting of XANES and the presence of active species as well as inactive species through the absorber.

11:00 AM EN02.01.02
Cd(Se,Te) Densification to Moderate As Diffusion in Thin-Film PV Devices Brian Good[1,2], Eric Colegrove[2] and Matthew Reese[2]; [1]University of Illinois at Chicago, United States; [2]National Renewable Energy Laboratory, United States

Arsenic doping is a significant topic of interest in CdTe solar cells. Carrier concentrations have far surpassed those achieved with copper, and stability has also improved. However, challenges remain in reducing the V_{oc} deficit in devices. Arsenic is known to self-compensate in CdTe, which can lead to low dopant activation levels and associated voltage fluctuations that contribute to losses. Additionally, SIMS has shown significant As accumulation near the front interface, likely leading to reduced activation levels in the Se-rich region. Our modeling has demonstrated that deep levels near the interface can drastically reduce device performance. Furthermore it suggested that reduced doping near the interface can improve V_{oc} and thus a quasi- p-i-n structure was proposed where the intrinsic layer would be only a few hundred nm thick in the Se-rich region. In practice, an intrinsic layer is difficult to achieve when dopant diffusion is performed afterwards. However, reduction of the As accumulation would be ideal. In this work, we explore methods of accomplishing this through anneals on evaporated Cd(Se,Te) prior to vapor transport deposited (VTD) CdTe:As.
Our absorber preparation involves the evaporation of an undoped Cd(Se,Te) layer, followed by a thicker VTD layer of CdTe:As. Arsenic is introduced *in situ* and diffuses throughout the absorber. Since As readily diffuses along grain boundaries, we believe the small Cd(Se,Te) grains allow significant As accumulation in the evaporated layer. While $CdCl_2$ is known to increase grain size, its formation of a eutectic phase also can massively increase As diffusion rates. We have demonstrated that anneals over CdTe powder help remove voids and create more compact VTD films. We hypothesized that performing similar anneals on the undoped layer may reduce two potential pathways for As diffusion. First, it can reduce the prevalence of grain boundaries and inhibit excessive As diffusion near the interface. Second, Se vacancies, which can contribute to diffusion and recombination, may be filled in. If these are able to sufficiently reduce As pileup, it should yield a higher V_{oc} due to less near-interface compensation.
Anneals were performed with various temperatures and ambients, as well as with both CdTe and Cd(Se,Te) powder, the latter as an effort to inhibit possible Se loss in the film. The effects of hydrogen and oxygen incorporation were explored, with hydrogen expected to reduce undesired oxidation. Following these anneals, films were $CdCl_2$ annealed to obtain measurable lifetime via time resolved photoluminescence (TRPL). The highest lifetime was observed with CdTe powder in a nitrogen-only ambient at 575°C. Microscopy on annealed films showed substantive grain growth prior to $CdCl_2$ treatments, with higher temperatures yielding larger grains.
In addition to material studies of the undoped evaporated material, equivalent films were processed into devices, including VTD CdTe:As and subsequent densification and $CdCl_2$ anneals. J-V measurements showed slightly increased V_{oc} for devices with annealed Cd(Se,Te) layers compared to those without the anneal. SIMS measurements showed that As content decreased approximately one order of magnitude within ~200 nm of the front interface, a 2-3 order of magnitude decrease compared to films without the pre-VTD anneal.
Combining material characterization with device performance, we see improved V_{oc} correlated with lower near-interface As concentration and larger Cd(Se,Te) grains. The pre-VTD anneals therefore had the desired result. Ongoing work involves strategies to remove unintentional oxidation during this anneal, as well as further reducing the As content near the interface to increase the observed effect on V_{oc}. Hydrogen anneals and thicker undoped layers, respectively, are being explored for these purposes. Through this work, we hope to provide a method to reduce near-interface compensation in As-doped CdTe devices.

11:15 AM *EN02.01.03
The Implications of Metal Saturated Growth for As Doped CdTe and CdSeTe Solar Cells Stuart J. Irvine[1], Ochai Oklobia[1], Dan Lamb[1], Stephen Jones[1], Dingyuan Lu[2] and Gang Xiong[2]; [1]Swansea University, United Kingdom; [2]First Solar Inc., United States

The drive for 25% CdSeTe solar cells depends on effective acceptor doping above 1x10^{16} cm^{-3} which can be achieved using group V doping. However, the incorporation of a Group V dopant onto the Group VI site is highly compensated with associated deep level defects. Until recently this has resulted in no discernable improvement in V_{oc} compared with much lower acceptor concentrations achieved with Cu doping. The increase in acceptor concentration leads to a reduction of the depletion width from over 1 μm to 0.2 μm. Recombination within the depletion region leads to a reduction in V_{oc}. It has become clear that high acceptor concentration CdTe and CdSeTe solar cells are less tolerant towards defects close to the front emitter. In this talk the Group V doping of CdTe will be reviewed and recent results presented on the influence of metal saturated conditions on doping with As. Using metal organic chemical vapour deposition (MOCVD) it has been possible to create a wide range of different thermodynamic conditions. In this study we have explored metal saturated growth that has led to an improvement in V_{oc} close to 900 mV. The role of the front interface will be considered as this becomes more influential in achieving high V_{oc} for high acceptor concentrations. We have used a combinatorial approach to track V_{oc} with the Group II and Group VI precursor ratio and acceptor concentration. Approaches to unlock the true potential of Group V doped CdSeTe solar cells using doped emitters with V_{oc}>1 V will be discussed.

11:45 AM EN02.01.04
Deep Level Transient Spectroscopy of Inorganic Thin Film Solar Cells Jon Major; University of Liverpool, United Kingdom

Deep level transient spectroscopy (DLTS) is capable of resolving electrically active defect levels within semiconductors. The technique works by temperature dependant analyis of capacitance transients which occur as trap states within the band gap are depopulated. DLTS allows the energetic poisition of defect levels within the bandgap to be determine, alongside estimates for the capture cross section and density of such defect level. It evolved from analysis single crystal materials such as silicon and gallium arseninde but is also able to resolve defect levels present within polycrystalline thin films. For thin film solar cells this can provide useful information on native and extrinsic defect and/or doping levels aiding the development of new processes. This presentation will demonstrate the capability of the techqiue to determine the defect content inorganic thin film materials such as in emerging antimony chalcogenide materials Sb_2Se_3 and Sb_2S_3, as well as the impact of alloying and group V doping in CdTe via analysis of $CdSe_{1-x}Te_x$ and CdTe:As solar cells. We will also demonstrate the links between device performance and deep level defect content and show how this measurment approach can be used to inform device process development.

SESSION EN02.02: Modeling I
Session Chairs: Eric Colegrove and Marco Nardone
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2002

1:30 PM *EN02.02.01
Modeling and AI-Guided Understanding of CdTe-Based Photovoltaics Maria K. Chan; Argonne National Laboratory, United States

CdTe-based PV devices are currently the only commercially viable alternative to Si. Significant mysteries remain as to the effects of grain boundaries on device performance, and the local environment of dopants and how it relates to activation. In this talk, we will discuss characterization-informed first principles and atomistic modeling of grain boundaries and impurities in CdTe and related systems. The use of x-ray absorption near edge spectra (XANES) and scanning transmission electron microscopy (STEM), in particular, gives unprecedented atomic-level information and the interpretation of XANES and STEM data benefits from AI/ML and modeling.

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2:00 PM EN02.02.02
First-Principles Understanding of NiO and TeO_2-Based Back Passivation Layers in CdTe PV Anthony P. Nicholson[1,2], Stephan Lany[2] and Walajabad Sampath[1]; [1]Colorado State University, United States; [2]National Renewable Energy Laboratory, United States

There is progressive interest toward fundamentally understanding the roles attributed to passivated back contact layers in thin-film semiconductor PV. Within the cadmium telluride PV community, special emphasis is given to a back passivation layer capable of reducing back interface recombination losses while ensuring carrier selectivity and the possibility for bifaciality. Transparent thin-film oxide layers such as NiO_x or TeO_x may offer a viable solution for back passivation layers in CdTe PV. However, atomic scale effects for NiO_x and TeO_x in relation to possible defect interactions during copper and/or chloride-based treatments as well as energy band alignment of the absorber/passivating oxide interfaces are not well understood. The current work uses a first-principles computational approach based on density functional theory to investigate the electronic structures of NiO and TeO_2 bulk layers in the presence of relevant defects along with the formation of pristine interfacial morphologies when either oxide layer is in contact with the absorber layer in CdTe PV. For the bulk defect studies, defect pair interactions are evaluated to determine avenues of dopability and/or compensation that may affect bulk carrier transport within the oxide thin-film layers. Additionally, an atomic-scale perspective of the pristine absorber/oxide interface structures is given with respect to plane orientation, termination layer, and associated surface reconstruction to give insight on how NiO and TeO_2 differ in band alignment features influencing charge transport at the back interface. Details from the first-principles-based computational study provide further insight on the mechanisms inherent to passivating oxide layers that could potentially lead to benefits in CdTe thin-film PV device performance.

2:15 PM EN02.02.03
Impact of Defects on Solar Cell Performance in Low-Dimensional Selenium Seán R. Kavanagh[1,2], Alp Samli[1], Aron Walsh[2] and David O. Scanlon[1]; [1]University College London, United Kingdom; [2]Imperial College London, United Kingdom

Low-dimensional trigonal selenium (Se) was the first material to exhibit the photovoltaic effect and has recently experienced a renaissance in research interest as a candidate solar cell absorber, due to its desirable properties (suitable band gap, high earth abundance, low temperature processing), potential implementation in silicon tandem cells and *'simple' elemental chemistry*. Though cell efficiencies have improved much since its initial application in 1883, Se still lags behind leading technologies such as silicon and lead-halide perovskites, with the fundamental limitations (doping density, defect-mediated recombination, intrinsic Urbach tailing…) remaining unclear.

In this work, we use hybrid density functional theory to investigate the electronic properties, band alignment and defect chemistry of Se, in order to shed light on the key limiting factors for solar cells. We find the crystal dimensionality to dictate the energies of intrinsic defects (vacancies and interstitials) in this system and their impact on electronic properties. In doing so, we identify key deleterious impurities for performance and important considerations for the experimental fabrication of high-efficiency selenium solar cells, as well as establishing an outlook for the attainable performance of Se solar cells based off the fundamental intrinsic limitations.

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2:30 PM EN02.02.04
Designing Nanostructured Ferroelectric Films: Geometry, Polarization and Electronic Properties of the $BaTiO_3$/Hematite Interface from First Principles Jorge Ontaneda[1], Ricardo Grau-Crespo[2], Keith T. Butler[1] and Joe Briscoe[1]; [1]Queen Mary University of London, United Kingdom; [2]University of Reading, United Kingdom

By coupling together a junction-based photovoltaic system and a bulk photovoltaic effect-based material in a nanocomposite thin film device, the well-known limitations[1–3] of both technologies could be overcome. This idea relies on the proven ability of ferroelectrics to influence coupled materials, such as photocatalysts and organic photovoltaics. By using the recently-developed Electronic Lattice Strain procedure,[4] we identified the $BaTiO_3$/hematite interface as a promising candidate for the proposed device. Screening was performed in terms of epitaxially-compatible interfaces (to minimize defects) and appropriate band alignment (to minimize charge transfer). To gain insights into the geometry, polarization and electronic properties of the aforementioned system, Density Functional Theory (DFT) modelling is employed. To this purpose, we assume the $BaTiO_3$ (110) surface as substrate on which the hematite (100) surface grows epitaxially strained to it. Within the supercell approach, we are required to employ 5×5 surface unit cells of $BaTiO_3$ (110) and 4×2 units of hematite (100) to reproduce the minimally strained interface (~2.6%).

Our preliminary tests show that GGA-PBE functional with a Hubbard-type correction to the Ti 3*d* orbitals, where $U_{\mathrm{eff}} = 2.6$ eV, can reproduce the spontaneous polarization in $BaTiO_3$. However, the bandgap is still poorly described: ~30% off with respect to experimental value. In the case of hematite, where $U_{\mathrm{eff}} = 3.5$ eV is applied to the Fe 3*d* orbitals, the bandgap is in excellent agreement with experimental reports. Even though bandgaps can be accurately described by DFT via hybrid functionals, such as HSE06, their application for the above heterojunction is impractical due to the size of the interface model which consists of 855 atoms.

In order to estimate a proper offset from the $BaTiO_3$/hematite heterojunction, we will employ bulk HSE06 values to correct the band alignments of this interface, which is computed with the PBE+*U* method. Our scheme is tested with heterojunctions that can be tackled with the HSE06 hybrid functional, ranging from covalent to ionic solids. This scheme might allow us to model not only this complex epitaxially-compatibles interface, but also other heterojunction for novel devices.

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2:45 PM EN02.02.05
Bulk Photovoltaic Effect in Ferroelectric Vertically Aligned Nanocomposites Emanuele Palladino[1], Subhajit Pal[1], Muireann A. de Hora[2], Judith MacManus-Driscoll[2] and Joe Briscoe[1]; [1]Queen Mary University of London, United Kingdom; [2]University of Cambridge, United Kingdom

Exploiting physical and electrical properties of polar materials is currently an area of substantial research interest, with the scope to create multifunctional materials that aim to solve the challenges of the next decades in the fields of renewable energy, transportation, and quantum computing to name a few. Among these, ferroelectric materials whose spontaneous polarisation can be switched by an applied electric field, are known to generate currents without the need of a heterojunction as required for traditional semiconductors. The phenomenon is known as the bulk photovoltaic effect (BPVE), and it results in large photovoltages well above the bandgap which have the potential to surpass the Shockley-Quessier (S-Q) limit for single junction devices[1,2]. However, the high photovoltage is limited by the conductivity which combined with the intrinsic wide band gap results in unremarkable efficiencies below 1%[3,4]. Different approaches have been adopted to overcome this limitation like ionic doping, heterostructures or localized surface plasmons resonances (LSPR)[5]. Here we report the use of a two-phase nanocomposite approach coupling a ferroelectric with a narrow band gap material that allows us to exploit the built-in voltage of the former with the high absorption and conductivity of the latter. Epitaxial nanocomposites thin films of $BaTiO_3$:Sm_2O_3 and $BaTiO_3$:MgO were fabricated via pulsed laser deposition (PLD) and the secondary phase was etched away and replaced with α-Fe_2O_3 phase. The combination of atomic force microscopy allowed us to assess the electrical properties of the films, the presence of BPVE and how these are affected by strain in vertically aligned nanocomposites (VANs).
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3:00 PM BREAK

SESSION EN02.03: Tandem I
Session Chairs: Philip Schulz and Byungha Shin
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2002

3:30 PM *EN02.03.01
Flexible Kesterite Solar Cells—Optoelectronic Characteristics Implied by Mechanical Deformation William Jo; Ewha Womans University, Korea (the Republic of)

We will present recent progress of photovoltaic devices using chalcogen-based compounds: kesterites and chalcopyrites. Kesterite $Cu_2ZnSn(S,Se)_4$ (CZTSSe), promising earth-abundant materials for thin film solar cells, has been widely studied and active research efforts raise the efficiency of flexible kesterite solar cells close to 12%. To fabricate the robust and highly efficient flexible thin film solar cells, understanding the changes in device properties under mechanical stress is crucial. In this study, transport of photogenerated carriers with mechanical stress was characterized. CZTSSe samples with and without Na deposited on flexible Mo foil were prepared and solar cell parameters after the mechanical bending were measured. Degradation of open-circuit voltage (V_{OC}) was varied by the direction of mechanical bending and the existence of Na elements. Photo-assisted Kelvin probe force microscopy was utilized to characterize the transport of photogenerated carriers, and it was found that the magnitude of surface photovoltage changed under mechanical bending state. It refers the degradation of local V_{OC} and transport of the photogenerated carriers was limited with mechanical stress resulting in decrease of V_{OC} of devices. In addition, CZTSSe sample with Na doping showed the larger SPV under bending than sample without Na which suggest the passivation of defects and prevention of damage from bending. To quantify the disorder in energy band structure under mechanical bending, Urbach energy was obtained from absorption coefficient function. Attribution of Na in transport of photogenerated carriers will be investigated to clarify the robust carrier transport under mechanical stress compared to the CZTSSe without Na.

4:00 PM EN02.03.02
Characterization of Ag Alloyed CuInSe Solar Cells Using Bias-Dependent Admittance Spectroscopy Jessica de Wild, Jonathan Parion, Romain Scaffidi, Guy Brammertz and Bart Vermang; imec, Belgium

The well-known Shockley-Queisser limit for single junction solar cells can be overcome using multiple solar cells with different band gaps on top of each other. In the case of a tandem solar cell, the ideal band gap of the bottom cell is about 1 eV, of the top cell about 1.7 eV and efficiencies of 42% can be achieved theoretically.[1] As bottom cell often Si is used, which has a band gap of 1.12 eV. For a full thin film tandem structure, which could be suitable for flexible or light weight applications, $Cu(In,Ga)Se_2$ (CIGS) can also be used. The band gap of CIGS varies between 1.0 and 1.6 eV depending on the Ga/In ratio. Optimal performance of CIGS solar cells is achieved with about 30% Ga and using Ga gradients at the front and the back. The band gap is then around 1.2 eV, thus above the ideal value for a bottom cell. Without Ga in the absorber layer the band gap will be reduced to 1 eV, but also the quality of the absorber layer and its interfaces are less optimal without the Ga gradients. When low band gap CIGS (low or without Ga) will be used as bottom cell, other methods to increase the absorber quality and its interface with the buffer layer need to be investigated. For this purpose, we explore incorporation of small amount of Ag in the absorber layer (ACIS) to improve the bulk properties, and stoichiometric growth in combination with InSe on the surface to improve the buffer/absorber interface.
CIS layers were grown by a 3-stage process on Mo with or without a 10 nm Ag layer. When Ag is added in the CIS absorber, the efficiency of the ACIS solar cell increases about 2% absolute, mainly due to an increased fill factor. Depositing InSe on top of a stoichiometric CIS layer, increases the Voc by 50-60 mV. The efficiency increases about 1% absolute compared to the copper poor CIS. When depositing InSe on a stoichiometric ACIS absorber layer, the solar cell performance deteriorates. The cell is completely shunted, and Voc, FF and Jsc are reduced.
The various solar cells are then further analysed using bias-dependent admittance spectroscopy. The data of these measurements is presented in a so-called CVf-map, and with SCAPS modelling the CVf-maps may be analysed.[2, 3] At first the difference between ACIS and CIS is analysed. Minor differences in the CVf-maps are observed between ACIS and CIS. The CVF-map of ACIS looks slightly cleaner in a larger bias and frequency range, but in general they are very similar, indicating that there are no large differences in the absorber or at the interfaces. The 'cleaner' CVf-map for ACIS, corroborates with the higher FF measured for ACIS. When InSe is deposited on a stoichiometric CIS sample, the apparent doping is much higher, which could explain the increase in Voc measured for this kind of structure. When InSe is deposited on a stoichiometric ACIS sample, the apparent doping still increases but a defect signature is seen at 0V bias voltage which seems to be responsible for the deterioration of the performance.
Temperature dependent CVf measurements are further performed to allow for disentanglement of the various features that are seen in the CVf maps. Using SCAPS modelling, CVf maps and low-temperature data, a model is proposed on why the ACIS absorber layer has such a different response when InSe is deposited and how this can be improved.

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4:15 PM EN02.03.03
Semi-Monolithic Integration of Chalcopyrite Solar Cells into Multijunction Devices Kai C. Outlaw-Spruell[1], Christopher P. Muzzillo[2], Kai Zhu[2] and Nicolas Gaillard[1]; [1]University of Hawaii, United States; [2]National Renewable Energy Laboratory, United States

Monolithic integration, the process by which solid-state devices are made by sequentially depositing layers of materials on top of each other, is used in all commercial thin film-based technology. This process is so foundational nowadays that it is difficult to imagine any other way to create high-efficiency solid-state devices. In the context of photovoltaics (PV), monolithically-integrated multi-junction (MJ) cells have demonstrated their capability in overcoming the thermodynamic efficiency limits of single-junction (SJ) devices, as well as being a practical solution to create devices with sufficient photovoltage for direct solar-to-hydrogen (STH) conversion.Despite its wide acceptance, however, monolithic integration presents major limitations in process compatibility, restricting materials selection and synthesis to a sub-set of compatible systems while limiting the adoption of emerging promising candidates.

The strategy we present in this communication, further referred to as *semi-monolithic* integration, relies on the exfoliation and bonding at room temperature of independently processed, substrate-grown SJ devices to create a whole thin film-based MJ device. By design, this scheme allows successive integration of thermally, chemically and/or mechanically incompatible material classes onto a single substrate without compromising state-of-the art SJ fabrication processes. First, we report on whole chalcopyrite-based semi-monolithic MJ devices comprised of 1.85 eV ordered vacancy compound (OVC) $CuGa_3Se_5$ and 1.13 eV $Cu(In,Ga)Se_2$ sub-cells. Our process takes advantage of the weak out of plane van-der Waals forces in the $MoSe_2$ layer which naturally forms at the $Cu(In,Ga)Se_2$/Mo interface. Both chalcopyrite cells were successively transferred and bonded onto a single rigid FTO host substrate at room temperature using transparent conductive composites (TCC). A champion $CuGa_3Se_5$/CIGSe MJ device showed power conversion efficiency of 5.04% with open-circuit voltage (Voc), short-circuit current density and fill factor of 1.24 V, 7.19 mA/cm^2, and 56.7%, respectively. Following this successful proof-of-concept demonstration, we constructed the world’s first whole-chalcopyrite triple junction MJ device comprising 1.13 eV and 1.44 eV $Cu(In,Ga)Se_2$ and 1.85 eV $CuGa_3Se_5$ sub-cells. The device exhibited a V_{OC} of 1.85 V and was capable to splitting water with an STH efficiency of 3% in a PV-electrolysis configuration.

4:30 PM EN02.03.04

Approaching 24% Flexible All-perovskite Monolithic Tandem Solar Cells Enabled by Reducing V_{OC}-deficit in Wide-bandgap Subcell Huagui Lai[1], Jincheng Luo[2], Yannick Zwirner[1], Selina Olthof[3], Alexander Wieczorek[1], Fangyuan Ye[4], Quentin Jeangros[5,6], Xinxing Yin[7], Fatima Akhundova[8], Tianshu Ma[9], Rui He[2], Radha K. Kothandaraman[1], Xinyu Chin[5,6], Evgeniia Gilshtein[1], André Müller[1], Changlei Wang[9], Jarla Thiesbrummel[10], Sebastian Siol[1], José M. Prieto[11,8], Thomas Unold[8], Martin Stolterfoht[4], Cong Chen[2], Ayodhya N. Tiwari[1], Dewei Zhao[2] and Fan Fu[1]; [1]Empa-Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [2]Sichuan University, China; [3]University of Cologne, Germany; [4]University of Potsdam, Germany; [5]École Polytechnique Fédérale de Lausanne, Switzerland; [6]Sustainable Energy Center, Centre Suisse d’Electronique et de Microtechnique, Switzerland; [7]Jiaxing University, China; [8]Helmholtz-Zentrum Berlin, Germany; [9]Soochow University, China; [10]University of Oxford, United Kingdom; [11]Humboldt-Universität zu Berlin, Germany

Tandem solar cells (TSCs) are one approach to exceeding the efficiency limits of single-junction solar cells by making better use of the solar spectrum with multiple junctions. Among various types of perovskite-based TSCs. All-perovskite TSCs are of particularly attractive for building- and vehicle-integrated photovoltaics, or space energy areas as they can be fabricated on flexible and lightweight substrates with a very high power-to-weight ratio. However, the efficiency of flexible all-perovskite tandems is lagging far behind their rigid counterparts primarily due to the challenges in developing efficient wide-bandgap (WBG) perovskite solar cells (PSCs) on the flexible substrates as well as their low open-circuit voltage (V_{OC}). Firstly, the relatively rougher surface of the flexible substrate poses a certain difficulty in the deposition of a uniform layers through solution processing. Moreover, the WBG PSCs suffer from a larger V_{OC}-deficit (E_g-V_{OC}) when compared with narrow-bandgap (NBG) PSCs, which has been constantly reported to be >550 mV. To construct a high-performance flexible all-perovskite TSC, there is an urgent need to develop high-quality WBG PSC based on flexible substrates with a reduced V_{OC}-deficit.

Here, we first developed a modified spin-coating protocol of [2-(9H-carbazol-9-yl)ethyl] phosphonic acid (2PACz) on flexible ITO substrate. Long resting time together with multiple spin-coating ensure the deposition of a uniform 2PACz layer, which serves as a lossless hole selective contact and allows the subsequent uniform growth of a 1.77 eV WBG perovskite. This translates to ~40 mV gain in V_{OC} of the devices compared to those based on poly-triarylamine. To further reduce the V_{OC}-deficit, we employed a post-deposition treatment (PDT) on the perovskite surface with 2-thiopheneethylammonium chloride (TEACl), which suppresses both the bulk and interfacial recombination, boosting the V_{OC} of the flexible NIR-transparent WBG PSC by ~100 mV. We identified an accumulation of TEA^+ on the surface of perovskite, which widens the surface band structure and reduces the interfacial recombination by realizing a better band alignment between perovskite and electron transport layer. In addition, we found that Cl^- tends to diffuse more into the bulk perovskite, which could be helpful for reducing the non-radiative in the bulk. Based on this, we achieved a high V_{OC} of 1.29 V and 15.1%-efficient NIR-transparent WBG (1.77 eV) PSCs grown on flexible substrates. The high V_{OC} corresponds to a record low V_{OC}-deficit of 480 mV for perovskite with a bandgap around 1.80 eV. In conjunction with flexible NBG (1.24 eV) PSCs, a 23.8% monolithic flexible all-perovskite TSC (0.09 cm^2) with a superior V_{OC} of 2.1 V is achieved, which is on par with the V_{OC} reported on the 28% all-perovskite tandems grown on the rigid substrate. Moreover, a 23.6% efficiency was also realized on a larger area device (1.04 cm^2), which is close to that of the small device and shows a great upscaling potential of the flexible monolithic TSC.

In summary, our work provides a holistic and effective approach to improve the performance (V_{OC} in particular) of flexible NIR-transparent WBG PSC and all-perovskite monolithic TSC. The understanding of the passivation mechanism of TEACl PDT sheds new light on the future work in targeted choice of passivation reagent for the perovskite solar cells. Further reducing the V_{OC}-deficit within the WBG and NBG subcells will be the key for reaching a 30% efficiency in flexible monolithic all-perovskite TSCs.

4:45 PM EN02.03.05

Chemical and Electronic Properties of the $Mg_xZn_{1-x}O/CuGa_3Se_5$ Interface with a Cd^{2+}-Treatment Mary Blankenship[1], Brooklynne Jacobellis[1], Dirk Hauschild[1,2,2], Lothar Weinhardt[1,2,2], Imran Khan[3], Christopher P. Muzzillo[3], Andriy Zakutayev[3], Nicolas Gaillard[4] and Clemens Heske[1,2,2]; [1]University of Nevada, Las Vegas, United States; [2]Karlsruhe Institute of Technology, Germany; [3]National Renewable Energy Laboratory, United States; [4]University of Hawai‘i at Mānoa, United States

Ordered-vacancy wide band gap $CuGa_3Se_5$ is a promising candidate as absorber material for the top cell in tandem solar cells as well as in photoelectrochemical water-splitting devices. For wide band gap absorber materials, it is increasingly important to also use a wide band gap buffer layer to avoid absorption losses. Instead of the traditionally used CdS buffer layer, a conductive oxide $Mg_xZn_{1-x}O$ (MZO) was thus chosen in this study, deposited by RF sputtering on the absorber. To further improve the interface properties, a Cd^{2+} partial electrolyte treatment (CdPE) can be applied to the $CuGa_3Se_5$ surface prior to MZO layer deposition. Further optimization of the interface requires a more detailed understanding of the chemical and electronic properties at the MZO/absorber interface, such as the band edge positions, band gaps at the interface and, in particular, the band alignment.

In this contribution, we investigate the $CuGa_3Se_5$ absorber after CdPE, as well as its interface with the MZO layer using a toolchest of electron spectroscopies, including laboratory-based x-ray and UV photoelectron spectroscopy (XPS and UPS), x-ray-excited Auger electron spectroscopy (XAES), and inverse photoemission spectroscopy (IPES). With this combination of techniques, a detailed electronic and chemical picture of the interface is painted and will be discussed in view of its impact on the performance of $CuGa_3Se_5$ solar devices.

SESSION EN02.04: Poster Session I
Session Chairs: Gizem Birant and Eric Colegrove
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN02.04.01
Structural Flexibility of Photovolatic Materials—The Key to High Efficient Solar Cells Susan Schorr[1,2]; [1]Helmholtz-Zentrum Berlin, Germany; [2]Freie Universität Berlin, Germany

Photovoltaics (PV) based on crystalline silicon wafers has developed into a mature technology for the conversion of sunlight into electrical energy. Thin film PV is an emerging alternative technology because of short energy payback time and minimum use of high purity materials, addressing the urgent need for cost-competitive renewable energy technologies.
Compound semiconductors with a high absorption coefficient are the most advanced and most efficient absorber materials in thin film PV technologies. Highly efficient devices are based on absorber layers out of ternary or quaternary chalcogenides or hybrid halide perovskites.
Record efficiencies are reached with solar cells based on $Cu(In,Ga)Se_2$ (CIGSe) $Cu_2ZnSn(S,Se)_4$ (CZTSSe) and $(Cs,MA,FA)Pb(I,Br)_3$ absorbers (power conversion efficiency of 23.3%, 13.0% and 25.5% respectively [1]). CIGSe crystallizes in the chalcopyrite-type structure, whereas CZTSSe adopts the kesterite-type structure. Both compounds (and silicon as well) belong to the adamantine family [2] which is characterized by a 3D network of corner sharing tetrahedra. $(Cs,MA,FA)Pb(I,Br)_3$ (MA-methyl-ammonium, FA-formamidinium) crystallizes in the perovskite-type structure, characterized by a 3D network of corner sharing octahedra. In this sense chalcogenide materials are based on common building blocks: an A_2B_2X-tetrahedron in ternary $A^IB^{III}X_2$ and an A_2BCX-tetrahedron in quaternary $A^I_2B^{II}C^{IV}X_4$ chalcogenide semiconductors. The parent structure of the adamantines is the diamond-type. In binary, ternary and quaternary adamantines the metals are ordered on defined cation sites which led to typical superstructures with lowered symmetry. The parent structure (aristotype) of ABX_3 perovskites is the cubic perovskite-type structure in which the B cations are octahedrally coordinated by the anions. Thus, the PbX_6-octahedra are the building blocks of hybrid halide perovskites. Tilting and distortions of the octahedra led to structures with lowered symmetry (Bärnighausen tree [3]), but all these crystal structures are named perovskite structure which leads to confusion sometimes [4]. IN the chalcogenide compounds it is a tilting and distortion of the tetrahedra which led to crystal structures with lower symmetry (e. g. wurtz-stannite structure).
The success of CIGSe, CZTSSe and $(Cs,MA,FA)Pb(I,Br)_3$ as PV material has to do with their overall structural flexibility. In the tetrahedrally coordinated chalcogenides this flexibility originates from the propensity of the crystal structure to stabilize intrinsic point defects as vacancies, anti-sites, and interstitials. Deviations from the stoichiometric composition led to the formation of such intrinsic point defects without dramatic structural changes, but with significant influence on the electrical and optical properties of the material [5,6]. On the other hand, hybrid halide perovskites were shown to have a high defect tolerance. Here the flexibility of the crystal structure gives remarkable positional freedom of the molecular cation and ionic movement.
The presentation will give an overview of the basic building block principle of these compound semiconductors, the flexibility of the crystal structure and the resulting effect on the optoelectronic materials properties.
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[2] B. Pamplin, Progr. Crystal Growth Charact. 3 (1981) 179
[3] H. Bärnighausen, Commun. Math. Chem. 9 (1980) 139
[4] J. Breternitz, S. Schorr, Adv. Energy Mater *8* (2018) 1802366
[5] S. Schorr, G. Gurieva (p.123); A. Lafond et al. (p.93) in: Crystallography in Materials Science, ed. by S. Schorr and C. Weidenthaler, De Gruyter, 2021
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5:00 PM EN02.04.03
Role of CdTe Deposition Temperature in the Fabrication and Optimization of Sputtered CdTe Solar Cells Mohammed Alaani[1], Prakash Koirala[1], Nikolas Podraza[1], Stephen K. O'Leary[2] and Robert W. Collins[1]; [1]The University of Toledo, United States; [2]University of British Columbia, Canada

Thin film CdTe solar cells have been fabricated through RF magnetron sputtering on soda lime glass substrates coated with transparent conducting oxide layers. The performance of such devices is expected to be sensitive to the CdTe absorber layer deposition parameters, such as the target power, which controls the flux of depositing species, gas pressure, which controls the energetic bombardment of the growing film, and deposition temperature, which controls the surface diffusion of the depositing species. Recent studies of the Urbach absorption tails of both sputtered and close space sublimated CdTe applied in solar cells have suggested that the broader band tails found in the sputtered form of CdTe provides a route for photogenerated carrier recombination [1]. Such broader band tails appear to be associated with smaller grains and residual stresses that exist even after an optimized $CdCl_2$ thermal treatment. These results motivates the study of sputtered CdTe solar cells prepared with absorbers fabricated at elevated temperatures in order to explore the role of deposition temperature in controlling the grain size, Urbach tail breadth, and band tail recombination for both as-deposited and $CdCl_2$ treated materials. The $CdCl_2$ treatment may play the dominant role, however, compared to deposition temperature, in controlling the CdTe grain size and the resulting optoelectronic properties. Although the effect of the $CdCl_2$ treatment on the quality of CdTe films and devices has been studied extensively, few studies have investigated the role of the as-deposited material properties which in the case of low temperature sputtered CdTe are more strongly modified by the treatment [1]. In this work, we have fabricated CdS/CdTe solar cell devices on 15 cm x 15 cm TEC-15/HRT glass substrates in the superstrate configuration with the CdTe deposition temperatures varied from 150 to 330 °C. The structural and the optical characteristics of the as-deposited and treated CdTe materials are investigated using X-ray diffraction, scanning electron microscopy, photothermal deflection spectroscopy, and spectroscopic ellipsometry (SE) in order to compare the impact of deposition temperature and the $CdCl_2$ treatment on the CdTe film structure and optoelectronic properties. Mapping spectroscopic ellipsometry (M-SE) in conjunction with specialized calibration procedures have been applied to optimize the window layer and back contact layer thicknesses independently for each deposition temperature [2]. In this process, it has been found that at the low sputtering pressures an appreciable thickness of the CdS window layer evaporates prior to the CdTe sputter deposition at the elevated temperature, and this possibly unrecognized effect has a significant influence on solar cell process optimization at elevated temperatures.

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5:00 PM EN02.04.04
A Pathway to Enhance the Photovoltages in CdTe and Other Polycrystalline Mosaic Solar Cells Steluta A. Dinca and Eric A. Schiff; Syracuse University, United States

Polycrystalline "mosaic" semiconductors as used in current state of the art solar cells have grain boundaries that primarily extend throughout the cell's thickness. Extensive work done in the impact of grain boundaries on the photovoltaic properties of cadmium telluride (CdTe) and other mosaic cells suggests that grain boundaries dominate the recombination of photocarriers, and thus largely determine the open-circuit voltage of such cells. Further, CdTe solar cells, one of the important commercial cells, have now achieved laboratory power conversion efficiencies above 20%. A better understanding of how this was achieved may guide research to improve efficiencies in this class of polycrystalline cells.

The work reported here illustrates a potential route to enhance the open-circuit voltage of polycrystalline solar cells by eliminating a photocarrier recombination channel that has not, to our knowledge, been identified in earlier work. We used the semiconductor modeling software Sesame to do two-dimensional numerical calculations of the optoelectronic properties of an idealized n-CdS/p-CdTe solar cell assuming that the recombination of the carrier occurs primary at the grain boundary. We find that the electron carriers photogenerated closer to the CdS interface, but relatively distant from the grain boundary, follow a shortcut through the front CdS emitter to recombine with a hole in the CdTe absorber layer. The recombination event occurs at a “hot spot” near the intersection of the grain boundary with the CdS layer. This recombination channel reduces the open-circuit voltage in the models by about 0.05 V. Blocking the shortcut recombination channel could raise the efficiency of champion thin film CdTe cells from 21%, where it has been for several years, to 22%.

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5:00 PM EN02.04.05

Atomistic Models of In and Ga Diffusion in $Cu(In,Ga)Se_2$ Aaron S. Gehrke, David Sommer and Scott Dunham; University of Washington, United States

To improve the performance of $Cu(In,Ga)Se_2$ (CIGS) thin-film photovoltaic devices, a robust understanding of the dominant diffusion pathways of the alloy species In and Ga is needed. For example, because the bandgap of CIGS varies significantly between pure $CuInSe_2$ (CIS) and pure $CuGaSe_2$ (CGS), knowledge and control of In/Ga interdiffusion in the system is necessary to optimize the spatial bandgap tuning. This in turn is necessary to produce the highest-quality devices. Here, we identify the most probable defects and mechanisms for mediating In and Ga diffusion by reviewing previous experimental and computational literature. We determine that defect complexes comprised of In_{Cu} and Ga_{Cu} antisites and V_{Cu} vacancies are the primary drivers of diffusion. With the aid of density functional theory software packages, we calculate the binding energies and migration barriers of these complexes in bulk CIS and CGS. We find that the binding between In_{Cu}, Ga_{Cu}, and V_{Cu} defects can be modeled as simple electrostatic interactions between point charges. We also find that the migration barriers for Ga_{Cu} are much higher than those for In_{Cu}, explained by a larger lattice distortion arising during Ga_{Cu} migration than during In_{Cu} migration. Using these results, we develop rate expressions for the different atomistic processes and incorporate them into analytic models and kinetic lattice Monte Carlo (KLMC) simulations, which are employed to predict the diffusivity of In and Ga in CIS under variations in composition and temperature. The activation energy of In diffusion in CIS from our KLMC simulations is 1.24 eV, and for Ga it is 1.54 eV. We show that In diffusion is dominated by correlated hops, where most In_{Cu}-V_{Cu} exchanges quickly reverse. Consequently, very few hops contribute to net long-range diffusion. In contrast, Ga diffusion is dominated by uncorrelated hops, which show little to no memory of the previous state and move in a random walk. We develop an analytic model for In and Ga diffusion, suitable for use in a continuum simulation, and show that it predicts complex formation and diffusivity as seen in our KLMC simulations with great accuracy. We find our models produce results that match well with experiment. The methods used here are highly transferable and can be applied to understand diffusion of both native and extrinsic species in many different materials.

5:00 PM EN02.04.06

Measuring Steady-State and Time-Resolved Photoluminescence of a Thin Film CIGS Solar Cell by a Positionable, Micrometer-Sized Observation Volume Eugeny Ermilov, Volker Buschmann, Christian Oelsner, Frank Birke, Matthias Patting and Rainer Erdmann; PicoQuant GmbH, Germany

Over the years, luminescence spectroscopy has established itself as one of the fundamental methods for analyzing the photophysical properties of a variety of samples, ranging from simple organic molecules to semiconductor light-emitting materials and photovoltaic (PV) devices. The commonly used steady-state methods (i.e. excitation and emission spectroscopy) provide valuable insights into the photophysics of samples. However, such results give only a partial view of sample`s behavior after photoexcitation.

A further piece of the puzzle is often revealed by performing time-resolved luminescence spectroscopy, as it provides deeper insights into the photophysical processes occurring in the sample under investigation. It is worth to mention, that the luminescence lifetime is an intrinsic characteristic of emitting species. It indicates how long species under consideration will remain in electronically excited states before returning to ground state. Each emitting species has a characteristic luminescence lifetime, that can be influenced by its environment.

A series of spectroscopic and microscopic methods based on luminescence lifetime have been developed and provide further information, which are not accessible by steady-state experiments. Acquiring time-resolved spectroscopic data at regions of interest (ROI) of the sample can help in inferring structural-to-photophysical relationships in different materials and can give information about important photophysical processes as well as changes in the local environment of emitting species. For example, fluorescence lifetime imaging microscopy (FLIM) is a very well established imaging method in life sciences where the lifetime information is combined with spatial localization in the sample, allowing investigating biochemical or physical processes, or probing the local environment of the fluorophore. As processes commonly investigated in materials science are mostly not classical fluorescence processes, in general the term time-resolved photoluminescence (TRPL) imaging is more adequate. In materials science, TRPL imaging can be used for the characterization of key parameters like e.g. charge carrier dynamics and mobility in semiconductors. It is worth to mention, that very often these processes occur on timescales ranging from tens of picoseconds to several hundreds of nanoseconds.

Here we will demonstrate the performance of a spectrometer-microscope assembly for characterization and analysis of different materials in terms of lifetime, spectral and spatial resolution. Using a laser driver with burst capabilities enables measurements of long luminescence decays in the range of µs to ms. The benefitsof this multi-dimensional approach will be demonstrated with a series of examples reflecting a broad range of applications in materials science research.

5:00 PM EN02.04.07

Time-Resolved Photoluminescence Mapping of CIGS Devices Using a Combination of a Superconducting Nanowire Detector and a Confocal Microscope Eugeny Ermilov[1], Volker Buschmann[1], Felix Koberling[1], Jürgen Breitlow[1], Hugo Kooiman[2], Johannes W. Los[2], Jan van Willigen[2], Martin Caldarola[2], Andreas Fognini[2], Mario U. Castaneda[2], Jessica de Wild[3,4,5], Bart Vermang[3,4,5], Guy Brammertz[3,4,5] and Rainer Erdmann[1]; [1]PicoQuant GmbH, Germany; [2]Single Quantum, Netherlands; [3]Hasselt University, Belgium; [4]imec, Belgium; [5]EnergyVille, Belgium

Over the years, luminescence spectroscopy has become one of the fundamental methods for analyzing the photophysical properties of a variety of samples, ranging from organic molecules to semiconductor materials and photovoltaic (PV) devices. It is worth emphasizing that detection sensitivity is a key parameter to meet today's demands for handling weak luminescent samples and forshort measurement times in the optical evaluation of PV devices. The introduction of single-photon counting based data acquisition has proven to yield a major sensitivity increase and very high dynamic range – it is the ideal method for measuring weak photoluminescence (PL).

The commonly used steady-state luminescence spectroscopy methods provide valuable insights into the photophysics of a sample. However, such results give only a partial view of the sample’s behavior after photoexcitation. A further piece of the puzzle is often revealed by performing time-resolved luminescence spectroscopy, as it provides deeper insights into the photophysical processes occurring in the sample under investigation. An even more comprehensive picture is gained by including spatial information. Acquiring time-resolved spectroscopic data at regions of interest (ROI) in the sample can help in inferring structural-to-photophysical relationships in PV materials. Gathering such information is an important step toward the optimization of structure as well as preparation process of such materials in order to increase the performance of PV devices.

In terms of detector performance, superconducting nanowire single-photon detectors (SNSPDs) stand out due to achievable close-to-unity detection efficiency in NIR spectral range, picosecond time resolution (down to < 20 ps (FWHM)), and low dark noise (< 100 counts/s)[1,2]. SNSPDs are a rather new technology that is being used in multiple applications in the field of quantum optics, luminescence lifetime measurements, and singlet oxygen detection. The high quantum efficiency is especially important for material science applications in the NIR-range beyond 1000 nm, where other available single photon detectors have low sensitivity, high dark noise and slow time response.

In this report we demonstrate the combination of the MicroTime 100 upright confocal fluorescence lifetime microscope with the Single Quantum EOS SNSPDs as a powerful tool for photophysical research on CIGS ($Cu(InGa)Se_2$) devices, yielding spatial and temporal information on semiconductor samples studied through PL emission.

While one of the used SNSPDs had a classical single-mode fiber coupling to guide the light onto the sensor, the other detector used an internal multi-mode fiber instead[2]. We detected a significant increase in photoluminescence sensitivity of both designs compared to a standard NIR-PMT (H10330-45, Hamamatsu) as well as a several times higher sensitivity of the multi-mode fiber coupled nanowire compared to the singe-mode fiber one, in spite of comparable photon quantum efficiencies in this wavelength range for the sensor only. The increased sensitivity combined with the lower dark count rate resulted in an increase of the signal-to-noise ratio by more than 3 orders of magnitude compared to the NIR-PMT. Moreover, the very high sensitivity of the SNSPD as well as high temporal resolution (instrument response function of the overall system was below 100 ps) reveals clearly the differences in the PL decay profiles of the defect and unquenched areas of the weakly luminescent thin-film CIGS sample[3] even at low illumination levels, which is extemely difficult to resolve when using the NIR-PMT detector.

[1] https://doi.org/10.1063/5.0045990
[2] https://doi.org/10.1364/AO.58.009803
[3] https://doi.org/10.1021/acsaem.9b01370

5:00 PM EN02.04.09
Setting the Baseline for the Modelling of Kesterite Solar Cells—The Case Study of Tandem Application Axel Gon Medaille[1,2], Alex Jimenez[1,2], Alejandro Navarro[1], Sergio Giraldo[1], Kunal Tiwari[1], Marcel Placidi[1,2], Alejandro Perez-Rodriguez[2], Edgardo Saucedo[1] and Zacharie Jehl Li-Kao[1]; [1]Polytechnic University of Catalonia, Spain; [2]Institut de Recerca en Energia de Catalunya, Spain

The research on Kesterite-based solar cells is reaching a turning point. After a strong effort and record efficiencies in the early 2010s, this promising thin film photovoltaic absorber, free of toxic and critical raw materials, has seen a decade of relative stalling in terms of performance despite the continuous progress of competing technologies. Recent advances in the understanding of the bottlenecks hampering Kesterite solar cells have permitted **new efficiency records** within the past two years, finally breaking the 13% threshold. **Device modelling is bound to be instrumental** going forward and in spite of an extensive usage throughout the past decade, no realistic and quantitative representation of a Kesterite solar cell has been reported. This often leads to models relying on a partial knowledge of material and device parameters extracted from different sources, and this lack of consistency severely limits the accuracy of those models both quantitatively and qualitatively while rendering results' comparison between different laboratories almost impossible. In the meantime, low-cost tandem devices combining either inorganic thin film, perovskite and crystalline silicon cells have emerged as the next frontier for future efficient large scale photovoltaic deployment, and accurate quantitative device modelling combining electrical and optical simulation is more than ever needed to assess existing devices and predict possible improvements in future architectures.

This work reports on the modelling of Kesterite solar cells by combining SCAPS for the electrical part and the transfer matrix method for the optical part, using an in-lab developed modelling program. The objective is twofold. Firstly, **accurate and quantitative baselines based on the systematic characterization of Kesterite solar cells** fabricated at our group using a consistent experimental process are proposed. Our focus is on narrow bandgap Kesterite $Cu_2ZnSnSe_4$ (CZTSe) and wide bandgap Kesterite Cu_2ZnSnS_4 (CZTS). Specifically, we demonstrate in both cases the **simultaneous reproduction of all four photovoltaic figures of merit (voltage, current density, fill factor and efficiency) with less than 1% of relative discrepancy between the model and the experimental devices.**

Secondly, and using the aforementioned accurate modelling baselines and transfer matrix optical modelling, a case study on the potential of Kesterite solar cells in tandem devices is performed, namely for a narrow bandgap CZTSe subcell in tandem with a Perovskite top cell, and for a wide bandgap CZTS top cell in tandem with a crystalline silicon bottom cell. In each case, several material and optical improvements to the Kesterite cell are proposed and evaluated by the model with a high degree of quantitative accuracy, including bulk defect density, interface defects, bandgap engineering, doping gradient and selective contacts. It is found **that a moderate reduction in the density of Sn_{Zn} antisite defect permits to significantly enhance the efficiency of CZTSe solar cells up to 16%, which in combination with a 21% efficient Perovskite top cell allows to reach a total tandem efficiency of 30%**. In contrast, even ambitious optimizations to the wide bandgap CZTS solar cell do not permit to overcome the 26% efficiency threshold in tandem with a silicon subcell. The results from our simulation are compared with experimental values reported in the literature using Kesterite in tandem devices, allowing to assess the excellent robustness of the baseline parameters determined in this work. The complete set of material, optical and device input parameters are **openly shared**, which not only allows various research groups working on Kesterite solar cells to assess their validity, but also permits for the community to use common baselines for the numerical modelling of devices for **more consistent comparisons between research groups**.

5:00 PM EN02.04.11
Ultra-Thin Si Solar Cells with Hyperuniform Disordered Light Trapping Alexander Lambertz[1,2], Nasim Tavakoli[1], Stefan Tabernig[1], Richard Spalding[3], Anja Tiede[4], Anna Fontcuberta i Morral[4], Jorik Van de Groep[2], Marian Florescu[3] and Esther Alarcon-Llado[1]; [1]NWO-i AMOLF, Netherlands; [2]University of Amsterdam, Netherlands; [3]University of Surrey, United Kingdom; [4]EPFL, Switzerland

Mono- and multicrystalline silicon as absorbing materials in solar cells comprise about 95% of the global photovoltaics market and a total worldwide installed PV capacity of close to 3TW was reached in 2020. The benchmark efficiency of 19% for industrial modules reached in 2018 was enabled by the widespread adoption of Passivated Emitter and Rear Cell (PERC) device architecture. Typically, these cells feature 160μm-thick absorbing layers produced via the Czoralski method, which expunges up to 40% high-quality silicon as kerf loss. It has been inferred that the PERC baseline is not able to achieve the cumulative installed PV capacity target set by the IPCC of 7-10 TW by 2030 and further reduction of capital expenditure (capex) is needed. Reducing the thickness of Si-wafers for solar cells to 50μm could potentially reduce the manufacturing capex by 48%, module cost by 28%, and LCOE by 24% [1]. Thin c-silicon suffers from poor light absorption already at 100μm thickness necessitating light trapping to reach competitive efficiencies. High-performance light-trapping structures with sub-micron features, however, usually involve slow and complex manufacturing processes hindering their adoption by industry.

We present hyperuniform disordered (HUD) light-trapping structures applied to ultra-thin solar cells via substrate-conformal imprint lithography. This approach enables rapid patterning of large areas (m^2) at the nanoscale and can be performed on virtually any substrate and for any type of functional layer, such as the absorber, back-reflector, anti-reflection coating or carrier transporting layers. Correlated-disorder structures were shown to outperform periodic as well as random light trapping approaches [2] and the hyperuniform platform in addition offers engineered light scattering [3]. We developed a coupled-

mode theory (CMT) approach for estimating absorption with HUD patterns, which reduces the parameter space at low computational effort and is used as a starting point for numerical optimizations. Furthermore, we show experimentally measured absorption in ultra-thin, free-standing, hyperuniform-patterned silicon slabs of thicknesses ranging from 1-30µm and compare with simulations. Though silicon is our main candidate, also other PV materials can benefit from our approach and some of these examples will be presented.
Finally, we show the performance of ultra-thin Si solar cells before and after the application of HUD light trapping structures.
In conclusion, our work aims to further expand the success of earth-abundant silicon to ultra-thin, flexible and semi-transparent PV devices, which can be produced with kerfless bottom-up technologies at significantly reduced capex and accompanying CO_2 emissions while maintaining high power conversion efficiencies – A type of device that could literally pave all roads, roofs, walls, and windows by 2050!

Publication
N. Tavakoli et al., "Over 65% Sunlight Absorption in a 1 µm Si Slab with Hyperuniform Texture"*, ACS Photonics 2022, 9, 4, 1206–1217*, DOI: 10.1021/acsphotonics.1c01668

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5:00 PM EN02.04.12
Ultrathin Wide-Bandgap a-Si:H/oxide Transparent Photovoltaic Devices with Improved Open-Circuit Voltage via Electron Transport Layer Optimization Alex J. Lopez-Garcia[1], Gustavo Álvarez[1], Eloi R. Costals[2], Lorenzo Calvo[3], Pablo Ortega[2], Cristobal Voz[2], Joaquim Puigdollers[2], Victor Izquierdo-Roca[1] and Alejandro Perez-Rodriguez[1,3]; [1]Institut de Recerca en Energia de Catalunya, Spain; [2]Universitat Politècnica de Catalunya, Spain; [3]Universitat de Barcelona, Spain

Transparent Photovoltaic (TPV) devices open novel and unexplored pathways for the development of alternative photovoltaic technologies with a clear aim towards distributed applications, focusing on on-site generation while reducing visual impact as well as other inconveniences found in conventional PV applications. Implementation of TPV architectures can potentially allow for a wide array of applications, for example, smart windows in façades and other glazing elements such as vehicle windows, or canopies. Other examples can be the use of TPV to ubiquitously power up sensors and future IoT devices with a low-power draw. In order to deploy these applications into everyday life, it is crucial to develop the technology to be cost-effective. To do so, the pursuit of functional devices that rely on cheap, earth-abundant, stable, and non-toxic materials is of paramount importance if lab research is to be translated to industry. Additionally, the use of industrially scalable techniques is also an important requirement.
In this work, we report the development of wide-bandgap inorganic-based TPV devices that are fabricated using an ultrathin a-Si:H as a highly transparent absorber and oxide layers that are acting as carrier selective contacts and transparent electrical contacts. The basic device structure is FTO/AZO/a-Si:H/MoO_3/ITO, where FTO and ITO serve as back and front contacts while AZO is also used as electron transport layer. We will also report results on structures including V_2O_5 as hole transport material and AZO as top contact, comparing them against the reference HTL/front-contact stack, MoO_3/ITO. We will present results showing that the introduction of an intrinsic ZnO nanometric layer in-between the AZO ETL and a-Si:H leads to an overall performance increase, with the most notable improvement coming from an increased V_{oc} as compared to reference devices, as well as an increase in FF. Preliminary results show that there is an optimal thickness value for the ZnO interfacial film, and beyond this value there is a worsening of the device performance, which has been attributed to an increase in series resistance leading to poor transport in the TPV devices. This increase in PCE directly translates into an increased Light Utilization Efficiency (LUE), as the introduction of the ZnO interfacial film does not reduce Average Visible Transmittance (AVT) or Color Rendering Index (CRI) of the devices.
At the present time, spectrophotometry and J-V measurements performed in dark and under AM1.5G illumination (from the front and back sides) as well as Spectral Response measurements (under no bias as well as under light and electrical bias) have been carried out. As a preliminary result, we present devices with PCE>1% and AVT=40% (LUE>0.4%), overcoming the barrier of PCE ≤0.5% that has been observed in literature for state-of-the-art oxide-based devices. Record device efficiency achieved with these devices in our lab is PCE = 2%. We provide robust statistics showing that the process is reproducible thanks to the use of PE-CVD and ALD techniques, which allow for chemical composition tailoring and high film conformality even at the nanometric scale. These techniques are industrially scalable and could thus allow for a rapid TRL transition towards higher tiers. Ongoing characterization with XPS is also being performed. Ongoing work is exploring further optimization of the ETL via introduction of novel dipolar materials based on organic polymers: (PEI) and exploring different generations of dendrimeric molecules (PAMAM).
The work presented is of high relevance for the development of the field of inorganic thin film Transparent PV technologies, especially those working on extremely thin absorbers. It might also spark interest in thin film technologies in general that rely on advanced ETL/Active layer/HTL architectures.

This work has received funding from the European Union H2020 Framework Programme under Grant Agreement no. 826002 (Tech4Win).

5:00 PM EN02.04.13
Studies on Short-Circuit Currents of Subcells in a Compound Multijunction Solar Cell Hao Lo[1], Chia-Hua Huang[2], Chieh Lo[3], Chia-Chieh Hsu[4] and Wen Lour[4]; [1]University of Minnesota Twin Cities, United States; [2]National Dong-Hwa University, Taiwan; [3]National Taiwan University, Taiwan; [4]National Taiwan Ocean Univ, Taiwan

An InGaP compound semiconductor together with $In_xGa_{1-x}As$ related layers on a Ge substrate is one of the most popular active materials in the research of multijunction (MJ) solar cells formed by serially connecting multiple p-n junctions for its applications for power generation and space satellites. According to their energy band gaps, every p-n junction in the MJ solar cell forms an individual subcell being responsible for their own light spectrum independently. Then, an overall open-circuit voltage (V_{OC}) of the MJ solar cell is equal to the sum of V_{OC} of the individual subcell. However, an overall short-circuit current density (J_{SC}) of the MJ solar cell is determined by the subcell having the minimal J_{SC}. Thus, it is of particular importance to avoid any one of the subcells failing and producing a small J_{SC}. The conversion efficiency of the MJ solar cell cannot be improved without so-called current match. Here, a current mismatching ratio (CMMR) for the InGaP-InGaAs-Ge based solar cell is defined as:: CMRR=($|J_{SCT}$-$J_{SCM}|$)/(J_{SCT}+J_{SCM}), where J_{SCT} and J_{SCM} are the short-circuit current densities of the InGaP subcell and the InGaAs subcell, respectively. Besides, an average value of the J_{SCT} and the J_{SCM} represents a possibly optimized overall J_{SC} in the triple-junction (3J) solar cell.
In this work, a concept of J_{SC}-modulation effects was applied to optimize layers' parameters of every subcell in a MJ solar cell so that a fabricated MJ can be easily verified and theoretically simulated to achieve a high-efficiency MJ solar cell. An appropriate light spot with an adjustable power was used to change and to compensate the J_{SC} of one of the subcells in the MJ solar cell. For example, the appropriate light spot is with a wavelength of 405 nm. The one of the subcells is the InGaP subcell which is proposed to have the minimal J_{SC}. In the case, the measured overall J_{SC} will then be increased with increasing 405 nm light-spot power until it no more dominate the overall J_{SC}. Both J_{SCT} and J_{SCM} are then extracted. In experimental, the structure used to fabricate InGaP-InGaAs-Ge MJ solar cells consists of an InGaP subcell, an InGaAs subcell, and a Ge subcell. The 3J solar cell was fabricated to with a cell area of 0.25 cm^2 and a shielding ratio of 5%. To fabricate double junction (2J) solar cells having the same absorption spectrum, only 5% area of InGaP-

based layers was removed. Thus, 95% area of an InGaP-based layer remains upon the 2J solar cells to work as a short wavelength filter. Various compensated lights were employed to determine key CMMR of InGaP-InGaAs-Ge related 3J and 2J solar cells. Experimental results of using a 405 nm compensated light reveal that J_{SC}s of 9.37 mA/cm^2 and 10.28 mA/cm^2 were determined for the InGaP subcell and InGaAs subcell, respectively. Thus, the CMMR for the as-fabricated 3J solar cell is about 4.44%. The possibly best design for the J_{SCT} and/or J_{SCM} in the 3J solar cell is considered to be 9.814 mA/cm^2. An optimal conversion efficiency of 18.47% is expected. Thus, remind that a 4.44% CMRR will lead to 0.82% (18.47% - 17.65%) reduction in the conversion efficiency. Excellent agreement in evaluated properties was obtained when a 532 nm, a 638 nm, and 808 nm compensated lights were used. Another 3J solar cell fabricated with an anti-reflected coating was also evaluated. Measured results reveal that an overall J_{SC} of 13.5 mA/cm^2 is still limited by the InGaP subcell, resulting in a conversion efficiency of 27%. Together with determined J_{SC} of 15.5 mA/cm^2 for the InGaAs subcell, a possible optimum conversion efficiency of 29.11% is expected.
Finally, J_{SC}s for our 3J and 2J solar cells under multiple suns were also nondestructively evaluated. Important conclusions concerning CMMR variation and improvement in conversion efficiency will be reported.

5:00 PM EN02.04.14
Understanding the Role Thin Film Interfaces Play in Solar Cell Performance and Stability Mirra M. Rasmussen[1], Kristopher O. Davis[2], Laura S. Bruckman[1] and Ina T. Martin[1]; [1]Case Western Reserve University, United States; [2]University of Central Florida, United States

As more efficient and cost-effective photovoltaic (PV) architectures are developed, solar becomes an ever more competitive and viable replacement for fossil fuels. Full grid electrification necessitates the development of efficient, reliable, cost-effective technologies - and there is room for many different kinds of PV in this expanding market. The practical challenges and constraints of terawatt PV production have brought scalability and durability into sharp scientific focus. From a materials perspective, there are commonalities in the materials questions and challenges across different PV technologies. Whereas most PV technology is referred to by the absorber layer - e.g. silicon, or perovskite solar cells, other layers in the device are equally important to performance and durability. These layers are often composed of metal oxides, and are common across device technologies - for example, interfacial layers (such as charge transport layers, CTLs), and transparent conducting oxides (TCOs) used as electrodes.This work addresses materials oxide characterization and its relationship to materials and device performance and degradation across PV technologies.

Among the most promising PVs to date are two technologies with different levels of thin film incorporation: silicon heterojunction (SHJ) and perovskite PV. SHJ cells are part of the industrial Si PV portfolio, and perovskite cells are starting to be commercially produced after a decade of intensive research. However, there are well-known stability and cost limitations associated with each technology. Understanding the thin film materials science in these devices, and using that understanding to enhance device performance and stability is key to more reliable and cost effective electricity production.

Under practical aging conditions, careful materials-level characterization is required to understand the degradation mechanisms of these materials and the complex effects of aging on the multilayer system. This work details the effects of practical degradation challenges such as damp heat (DH) exposure and encapsulation degradation on the stability of inorganic metal oxides in both the SHJ and perovskite thin film photovoltaic architectures. For perovskite devices, $MAPbI_3$ films were deposited by spin coating onto a range of substrates and CTLs; substrates of glass and indium tin oxide (ITO) were paired with metal oxides (MOs) including MoO_X, NiO_X, and ZnO. SE and SEM were used to characterize the surface and bulk properties of the perovskite films. Results demonstrate that the underlying layers affect the rate of absorber degradation when exposed to heat and moisture.

Unencapsulated SHJ cells (a subset of which were exposed to low concentrations of acetic acid under an applied voltage) were aged under DH 85°C/85% relative humidity conditions. The contact-ITO interface was examined via optical profilometry (OP), spectroscopic ellipsometry (SE), and scanning electron microscopy (SEM). SHJ cells have interfaces unique to their architecture, namely the c-Si/a-Si:H and a-Si:H/ITO interfaces at the top of the device. Examining the degradation of unencapsulated SHJ cells and comparing those results to historical degradation profiles of encapsulated SHJ cells in addition to the simulated effects of acetic acid exposure will help to decouple the effects of encapsulation on ITO stability in this architecture. It is well known that ethylene vinyl acetate (EVA) encapsulation degrades and produces acetic acid upon exposure to heat and humidity. When under an applied voltage, even small concentrations of acetic acid can quickly corrode the contact-ITO interface, leading to decreases in efficiency and increases in series resistance of the cell. Here, XPS was used to monitor the changes in the front contact of the SHJ cells during DH and acetic acid exposure. Changes to the materials will be correlated to changes in device performance under the same aging conditions.

5:00 PM EN02.04.15
ZnS Buffer Layers: Novel Precursors for Aerosol-Assited Chemical Vapour Deposition Max Robson and Andrew Johnson; University of Bath, United Kingdom

The efficiency of thin film solar technologies continues to increase; most notably, that of copper indium gallium selenide (CIGS) which has demonstrated lab-scale conversion efficiencies comparable with crystalline silicon-based solar cells.(1) Marketing such technology also provides an alternative to cadmium telluride thin films which have unavoidably toxic properties. The same hazards can be avoided via the deployment of zinc-based buffer layer materials, in replacement of the popular cadmium sulfide. Alloys of zinc oxide and zinc sulfide, Zn(O,S), exhibit a tuneable bandgap such to facilitate alignment with respective solar absorbers. This tunability requires control of Zn/S stoichiometry whilst also exercising high uniformity during fabrication, and given the intricate nature of thin film architectures, controllable and scalable fabrication methods must be considered. In this vein, chemical vapour deposition (CVD) is a viable technique for thin film deposition as single-source precursors can afford stoichiometric control. However, given their thermal sensitivity, single-source metal chalcogenide precursors are ill-suited for conventional CVD methods requiring volatile precursors. Instead, aerosol-assisted chemical vapour deposition (AACVD) presents an attractive deposition process which circumvents this criterion by atomizing a solution of the appropriate precursor.
In this body of work, a novel single-source precursor design is explored as a basis for low-temperature deposition of metal chalcogenides via AACVD. A series of zinc thioamidate complexes is presented as potential precursors for the deposition of ZnS. Viability studies were conducted using thermogravimetric and NMR experiments. Viable precursor candidates give precedent for ZnO/ZnS co-deposition via AACVD for solar cell technology, and, more broadly, clean deposition of metal chalcogenide materials.

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5:00 PM EN02.04.16
Improvement of Interface Quality Between Chalcogenide-Based Absorption Layer and Buffer Layer for Low-Cost Thin Film Solar Cells Yong Tae Kim, Jae Yu Cho and Jaeyeong Heo; Chonnam National University, Korea (the Republic of)

Orthorhombic tin sulfide (SnS) is a promising absorber material for thin-film solar cells (TFSCs) due to its ideal optical band gap of ~1.3 eV, non-toxic and relatively earth-abundant constituents, high absorption coefficient ($\geq 10^{-5}$), and the high theoretical limit of ~32%. To date, the cell efficiency has mostly

remained below 4% for SnS TFSCs, which is fairly low compared to its theoretical limit. The improvement in the efficiency of SnS is mostly hindered because of its low heterojunction quality with the CdS buffer layer.
This work reports the study on improving the heterojunction quality at vapor-transport-deposited (VTD) SnS absorber/CdS interface via an annealing process. The highest efficiency of ~4.3% with good long-term stability was achieved by optimizing the annealing conditions for the heterojunction interface. This improved performance was primarily attributed to the reduction in interface defects of the SnS/CdS heterojunction, which can occur either during the deposition of transparent electrodes (Al-doped ZnO) or direct annealing of SnS/CdS heterojunction at 300 °C. The enhanced heterojunction interface quality is well supported by the reduced reverse saturation current density and shunt conductance of the fabricated devices measured under dark conditions. Although the SnS/CdS device exhibits an efficiency of over 4%, significant short-circuit current loss, mainly due to recombination, was revealed by quantum efficiency and optical analysis. Admittance spectroscopy analysis shows the presence of numerous defect densities of Sn and S vacancies (〉 10^{17} cm^{-3}) in the VTD-grown SnS absorber. Here, a detailed analysis of the device's performance will be presented.

5:00 PM EN02.04.18
Surface Passivation and Detrimental Heat-Induced Diffusion Effects in RbF-Treated Cu(In,Ga)Se_2 Solar Cell Absorbers Amala Elizabeth[1,2], Sudhir K. Sahoo[3], Himanshu Phirke[4], Tim Kodalle[5], Thomas D. Kühne[3], Jean-Nicolas Audinot[6], Tom Wirtz[6], Alex Redinger[4], Christian A. Kaufmann[5], Hossein Mirhosseini[3] and Harry Mönig[1,2]; [1]University of Münster, Germany; [2]Centre for Nanotechnology (CeNTech), Germany; [3]University of Paderborn, Germany; [4]Université du Luxembourg, Luxembourg; [5]PVcomB/ Helmhotz-Zentrum Berlin, Germany; [6]Luxembourg Institute of Science and Technology, Luxembourg

The remarkable efficiency improvements of Cu(In,Ga)Se_2-based chalcopyrite thin film solar cells to more than 23 % in the past few years have been largely attributed to post deposition treatments (PDTs) of the absorbers with heavy alkali metal compounds such as KF, RbF and CsF [1]. Therefore, understanding the effect of alkali PDTs on the electronic properties and defect physics of the chalcopyrite absorber surfaces are of utmost importance in view of the p/n junction formation and device optimization of such solar cells. In the present work, we adopt a combined analytical approach using scanning tunneling spectroscopy (STS) with a lateral resolution in the nanometer-regime and X-ray photoelectron spectroscopy (XPS) to compare the defect electronic properties and chemical composition of RbF-treated and non-treated Cu(In,Ga)Se_2 absorber surfaces [2]. Our STS results show that RbF PDT is effective in passivating the electronic defect levels at the absorber surface, as indicated by the low differential conductance within the bandgap. This is achieved by preventing surface oxidation and the formation of In, Ga and Se oxides on RbF-treated samples, as opposed to bare Cu(In,Ga)Se_2 surfaces. The passivating effect of RbF PDT is confirmed by ab-initio density functional theory (DFT) calculations which show that the chalcopyrite surfaces after the PDT are significantly less prone to oxidation and the incorporation of oxygen into such surfaces is energetically less favored. Furthermore, our XPS data indicate the presence of chemisorbed Rb species on the surface with a bonding configuration similar to a $RbInSe_2$ bulk compound, which is the likely cause of the observed surface passivation. A quantitative analysis of the XPS data shows that the Rb coverage is only in the sub-monolayer regime. During device fabrication, the chalcopyrite absorber usually undergoes several heating steps. Hence, to understand the effect of heat on RbF-treated samples, they were investigated before and after annealing under ultra-high vacuum conditions up to 320 °C. Our measurements indicate that there is a homogeneous distribution of Rb on the surface both before and after annealing, albeit with an increased concentration at the surface after the heat treatment. This suggests that the heat treatment leads to elemental diffusion of Rb from the bulk to the absorber surface. Additional depth-resolved magnetic sector secondary ion mass spectroscopy (SIMS) measurements highlighted that this diffusion in the bulk occurs predominantly along the grain boundaries. Annealing the samples to temperatures higher than 100 °C is found to lead to the formation of metallic Rb species on the surface, which results in a significant increase in the electronic defect levels and/or surface dipole formation as shown by STS and XPS measurements. Thus, heat-induced diffusion of Rb towards the surface effectively degrades the surface and will likely cause the deterioration of the absorber-window interface due to increased recombination losses at the p/n-junction. Our results strongly suggest that RbF PDT is a double-edged sword, where in addition to its advantageous surface passivation effect, a potential detrimental effect needs to be considered, especially during further device fabrication steps (e.g. the sputter deposition of ZnO on RbF-treated Cu(In,Ga)Se_2 thin films) at elevated temperatures.

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SESSION EN02.05: Modeling II
Session Chairs: Jessica de Wild and James Sites
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2002

8:00 AM *EN02.05.01
Quantifying V_{oc} Loss Pathways in Polycrystalline Solar Cells Marco Nardone, Eva Mulloy, Sakshi Gupta and Andrew Prostor; Bowling Green State University, United States

The power conversion efficiency of thin film photovoltaic (PV) devices has improved considerably over the past few decades, but thermodynamic limits and practical limits determined by device simulations suggest that there is yet significant room for improvement. In addition, the typically reported efficiency of champion devices represents the tail end of a wide distribution; narrowing that distribution is critical to the continued success of the thin film PV. An ongoing challenge is determining exactly where in the devices the greatest losses are occurring. Even in crystalline devices, identifying and quantifying the various loss pathways requires multiple test structures and characterization techniques. The difficulty is further exacerbated by the polycrystalline nature of thin film PV due to the presence of grain boundaries, incommensurate interfaces, a wide array of bulk deep defects, large band tails, various crystallite facets, nonuniformities, and uncertain dopant activation energies.

The goal of this work is to explore the possibility of developing a universal method for independently quantifying V_{oc} losses due to front interface, back interface, and bulk recombination mechanisms. If a universal approach is not feasible, then best practices and general guidelines will be developed. From a practical perspective, the scope of work considers determination of three key parameters: i) the effective front surface recombination velocity; ii) effective back surface recombination velocity; and iii) effective bulk lifetime. These parameters, while not exhaustive, are critical for diagnosing the regions of most significant performance losses and providing guidance for further improvement. Our approach is based on considering combinations of characterization techniques, test structures, and numerical simulations to minimize the coupling between the key parameters. Hypothesis testing of such decoupling will be done by employing numerical simulation of characterization techniques such as current-voltage as a function of temperature and intensity (JVTi), quantum efficiency (QE), capacitance-voltage (CV), time resolved photoluminescence (TRPL), and others. The role of band tails in V_{oc} loss, such as Urbach tails, will also be considered through analysis of sub-band gap features in photoluminescence (PL) data. Numerical simulations are conducted using the finite element method to solve to the semiconductor equations with time and temperature dependence and customized photogeneration scenarios. Cd(Se,Te) PV devices will be used as specific case study.

One approach considered so far employs a set of test structures, TRPL, and simulations in a sequential procedure to minimize the number of fitting parameters in each step. Three test structures are required: i) well-passivated double heterostructures (DHs) of various thicknesses (e.g. Al_2O_3/Cd(Se,Te)/Al_2O_3); ii) DHs of various thicknesses with one contact emulating the device back contact (e.g. Al_2O_3/Cd(Se,Te)/b.c); and iii) a complete device. Initial results from a thickness series of DHs quantified the front and back surface recombination velocities and the bulk lifetime. A challenge to this approach is maintaining consistent absorber properties while varying the DH thickness and between DHs and devices. Modifications to this approach and additional methods will be explored to spatially quantify recombination and identify regions of V_{oc} loss.

8:30 AM EN02.05.02

Interfacial Manipulation through Oxygen Management for 20%-Efficient Cd(Se,Te) Solar Cells Dengbing Li[1], Sabin Neupane[1], Chuanxiao Xiao[2], Manoj Jamarkattel[1], Adam Phillips[1], Michael J. Heben[1], Jonathan D. Poplawsky[3], David Cullen[3], Randy Ellingson[1] and Yanfa Yan[1]; [1]University of Toledo, United States; [2]National Renewable Energy Laboratory, United States; [3]Oak Ridge National Laboratory, United States

Bandgap gradient has been successfully applied in efficient Cu(In,Ga)Se_2 and Cu(Zn,Sn)Se_2 solar cells. However, this approach has not been realized in Cd(Se,Te) thin-film solar cells. Here, a facile strategy was proposed and demonstrated to incorporate the bandgap gradient in CdTe solar cells. The key to this achievement is proper oxygen management during the device fabrication, which is compatible to state-of-the-art CdTe production. Through oxygen management, a Cd(O,S,Se,Te) region with a gradient bandgap near the front junction can form without introducing any detrimental interface. With this bandgap gradient, the devices show significantly reduced nonradiative recombination and thereby demonstrated a record efficiency of 20.03%.

8:45 AM EN02.05.03

Minimizing Roughness Induced Optical Losses for a 4-Terminal CdTe/Si Solar Device John W. Keil[1], Bryan M. Cote[1], Vinodh Chandrasekaran[2], Andrei Los[2] and Vivian Ferry[1]; [1]University of Minnesota, United States; [2]First Solar, United States

CdTe/Si four-terminal tandem solar cells are a techno-economically advantageous option for high efficiency, low-cost photovoltaic cells. The tandem design reduces thermalization losses and can increase efficiency above commercial Si cells, and both junctions can be mass produced at relatively low cost. A four-terminal configuration provides flexibility in the electrical design of the tandem module, as the top and bottom cells avoid the current matching requirement that can limit performance. However, this configuration introduces significant optical challenges, as three high-transparency conductive layers and an insulating interlayer are required that all lead to increased parasitic absorption and reflection losses. This study uses a combination of experiments and simulations to characterize and understand CdTe roughness induced optical losses and provide strategies to increase optical coupling in the CdTe/Si four-terminal module.

The CdTe device stack is comprised of a planar front transparent conductive oxide (TCO) deposited on plate glass with a $CdSe_xTe_{1-x}$ absorber layer. A conformally grown back TCO serves as the rear electrode and adopts the roughness characteristics of the polycrystalline $CdSe_xTe_{1-x}$ absorber layer. Transmission measurements of the devices measured with UV-Vis spectrophotometry demonstrated that the sub-bandgap $CdSe_xTe_{1-x}$ module transmission was enhanced with reduced $CdSe_xTe_{1-x}$ roughness.

Surface height data from atomic force microscopy (AFM) measurements were incorporated into finite-different time-domain (FDTD) simulations of the $CdSe_xTe_{1-x}$ cell to capture the influence of roughness on the optical properties. The $CdSe_xTe_{1-x}$ transmission was modeled into air and into ethylene-vinyl acetate (EVA). The reduced index contrast by encapsulating the back TCO with EVA increases the transmission and through the $CdSe_xTe_{1-x}$ top cell by as much as 33%.

The dominant loss mechanisms preventing sub-bandgap $CdSe_xTe_{1-x}$ transmission were backscattering, reflection, front TCO absorption, and back TCO absorption. The optical losses are mitigated through decreased roughness and inclusion of the interlayer. The reflection and front TCO absorption are both controlled by the increased backscattering from the rougher back surface of the $CdSe_xTe_{1-x}$. Spatially resolved maps of the back TCO absorption show a non-uniform absorption profile with regions of light localization and absorption enhancement controlled by the surface topography. Mesoscale sized surface features create a focusing effect from constructive interference of the scattered and diffracted optical plane waves. The roughness induced regions of local absorption enhancement leads to the global enhancement of the back TCO absorption. The reduced index contrast with inclusion of the EVA does not eliminate the focusing effect but reduces the magnitude of the intensity enhancement. Simulations on an ideally flat surface indicated that planarizing eliminates the light localization and parasitic absorption enhancement.

Higher index optical coatings were also simulated to increase optical coupling in the tandem device. 1.7 and 1.9 refractive index optical coatings with finite thickness did not significantly increase the $CdSe_xTe_{1-x}$ transmission compared to just the EVA interlayer, but combining a 1.9 and 1.7 index film to create a graded index coating increased the sub-bandgap transmission by about 2% between 900 and 1000 nm.

This study describes how increased roughness and different interlayer materials influences the reflection, TCO absorption, and optical coupling in a CdTe/Si four-terminal tandem device, and demonstrates methods to mitigate losses and promote $CdSe_xTe_{1-x}$ transmission to the Si cell.

9:00 AM *EN02.05.04

Modeling Recombination Junctions for Tandem Solar Cells Johan Lauwaert; Ghent University, Belgium

Thin film solar cells of the 2nd and 3th generation with CIGS, CdTe, CZTS and perovskite based absorber layers are very promising solar cell technologies. One of the main advantages comparing to silicon technologies are the limited materials consumption and the flexibility to deposit them on a variety of surfaces including flexible substrates. Both silicon, CIGS and perovskite solar cells have nowadays already a descent efficiency. To further improve the efficiency of solar cells scientists are often investigating their potential in tandem structures. This can be tandem structures with a thin film solar cell on top of silicon but also a combination of thin film technologies.
For monolithic solar cells not only the optical quality of the junction between both cells but also electrical losses need to be minimized. Traditionally in tandems based on III-V semiconductors this is done with tunnel junctions. However for the materials used as carrier selective contact in thin film solar cells creating heavily doped layers to enhance the tunnel probability is still questionable. Therefore recombination junctions are good candidates to fulfill the task of forming a good optical and electrical contact between the two solar cells. Nonetheless traditionally in modeling potential thin film tandem solar cells the cells are modeled individually and combined as a monolithic cell by connecting both IV curves in series and adjusting the irradiation spectrum of the bottom cell. This often results in an overestimate of the performance by not including the electrical losses in the connection in between. Many TCAD simulation packages are not including the possibility to add an interface defect that allows a direct coupling between the electron and hole currents from both sides via this recombination.

In this work we developed a theoretical model for the current voltage characteristics (IV) of a recombination junction in between solar cells. Based on this IV curve the voltage loss of a tandem solar cell with known IV curves for the individual solar cells is evaluated.
We implemented the equations for such a recombination defect in DeVSim TCAD software, which allows python scripting. These TCAD simulations allow to solve the continuity equations for holes and electrons for the whole tandem structure. This software package is used to calculate the efficiency of a 1D - Perovskite CIGS solar cell. These calculations show a good correspondence with our theoretical model. Based on these TCAD simulations the impact of the recombination junction and its properties on the performance of the a CIGS – Perovskite tandem solar cell is evaluated.

9:30 AM BREAK

SESSION EN02.06: Novel and Emerging I
Session Chairs: Edgardo Saucedo Silva and Byungha Shin
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2002

10:00 AM *EN02.06.01
P-Type Doping and Phase Transformation of N-Substituted ZnSe1-xTex Thin Films Andriy Zakutayev and Sage Bauers; National Renewable Energy Laboratory, United States

N-doped ZnTe is a common p-type material with the valence band matched to CdTe absorber. The ZnSe1-xTex semiconductor alloys offer the potential to tune the valence band position to match other absorbers, however p-type doping if these materials is less explored. In addition p-type doping of these alloys would be beneficial for wide-gap absorber applications in photoelectrochemical CO2 reduction reactions for sustainable fuels.
This presentation will discuss N-doped ZnSe1-xTex thin films grown by RF sputtering from compound targets with N2 gas as a N source. Crystalline films form across a large range of growth conditions, with a p-type carrier density of p = 1e19 cm-3 and a carrier mobility of mu = 0.05 cm2/Vs determined by Hall effect, and verified by Seebeck coefficient measurements.
Surprisingly, some N-doped films there is a transformation from the usual zinc blende structure to wurtzite. Depending on the temperature and N2 flow rate during growth, wurtzite phase can be synthesized across most of the composition range, ranging from Te-rich (x ~ 0.7) to nearly pure ZnSe (x ~ 0.1). Density functional theory calculations suggest that dilute N concentrations help stabilize the wurtzite polymorph of ZnSe0.5Te0.5.
Ongoing progress towards controlling the p-type doping towards N:ZnSe1-xTex p-type contact applicaiton, and improving the charge trasnport properties of the ZnSe1-xTex alloys towards photoelectrochemical solar energy conversion, would be discussed in this presentation.

Nitrogen stabilizes the wurtzite polymorph in ZnSe1-xTe x thin films. Journal of Materials Chemistry C 2022. DOI: 10.1039/d2tc02716j

10:30 AM EN02.06.02
Examining Short-Range Order in $ZnSnN_2$-ZnO Alloys *via* STEM EELS Allison Mis[1], Celeste Melamed[1,2], Adele Tamboli[2], Raymond R. Unocic[3] and Geoffrey L. Brennecka[1]; [1]Colorado School of Mines, United States; [2]National Renewable Energy Laboratory, United States; [3]Oak Ridge National Laboratory, United States

Ternary pnictides offer a vast landscape of promising optoelectronic materials, many of which are composed of non-toxic, earth-abundant elements. Though many of these materials provide unique combinations of band gap and lattice constant compared to traditional semiconductors, making them of interest for multi-junction solar cells and other applications, their potential utility is magnified by the possibility of optical property tuning with cation ordering. This tunability could enable homoepitaxial stacks in which layers of the same material with differing degrees of ordering provide different optical properties without introducing performance-reducing crystalline defects.
One paradigm for examining cation ordering is “Short Range Order” (SRO), which examines the local bonding of the anion. For instance, in a system with the anion nearest-neighbor bonded to four cations, it is possible for those cations to be 2 of metal A and 2 of metal B, 3 A and 1 B, etc. Only some of these arrangements, or motifs, conserve the local octet rule, and the presence of octet-rule-violating motifs can strongly affect electronic and optical behavior of the material.
One system for which the SRO behavior has been examined is ZnSn(O,N). $ZnSnN_2$ has potential for application in photovoltaics, but nitride growth is often contaminated by oxygen, leading to a wurtzite $ZnSnN_2$-ZnO alloy. Computationally, it is predicted that $(ZnSnN_2)_{0.75}ZnO_{0.25}$ is capable of perfect SRO and that the ordered alloy would have a band gap ~0.3 eV above that of the disordered material at the same composition. [1]
This work expands upon previous study of $ZnSnN_2$-ZnO alloy thin films. These films were grown via RF co-sputtering and then in-situ annealed. Prior X-ray Absorption Near-Edge Structure (XANES) measurements of these films indicate differing degrees of SRO with differing in-situ anneal treatments. Prior optical measurements also show a shift in band gap similar to the shift predicted computationally. [2] In this work, cross sections of these films are examined using Scanning Transmission Electron Microscopy Energy-Dispersive Electron Spectroscopy (STEM EELS), specifically focusing on the near-edge fine structure of the oxygen and nitrogen peaks. Similarly to XANES, the near-edge structure of EELS is sensitive to bonding environment and can be related to the presence of various SRO motifs. In this work, peak shape and location is correlated to SRO.
STEM EELS provides several orders of magnitude improvement in spatial resolution over XANES, allowing for the study of SRO motif density across the film growth direction as well as across grain boundaries and other features. Here, variations in SRO among samples, as measured by EELS, are discussed and compared to XANES results, and spatial variation in SRO within each sample is assessed. Changes in anion bonding environment at grain boundaries are illustrated. This work also discusses the extraction of spatially-resolved bandgap from low-loss EELS and correlating bandgap and local SRO.
Microscopy research conducted as part of a user project at the Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.
[1] Pan, J., et al. Perfect Short-Range Ordered Alloy with Line-Compound-like Properties in the $ZnSnN_2$:ZnO System. *npj Comput Mater* 2020, 6 (1), 63.
[2] Melamed, C. L., et al. Short-Range Order Tunes Optical Properties in Long-Range Disordered $ZnSnN_2$ –ZnO Alloy. *Chem. Mater.* 2022, 34 (9), 3910–3919.

10:45 AM EN02.06.03
Quaternary Adamantine $CuAlC^{IV}X^{VI}_4$ – Crystal Growth, Structure and Properties Versus Ternary Chalcopyrite Yvonne Tomm[1], Joachim Breternitz[1] and Susan Schorr[1,2]; [1]Helmholtz-Zentrum Berlin, Germany; [2]Freie Universität Berlin, Germany

Adamantine-type compounds, including kesterites, are currently the most promising material for fully inorganic thin-film photovoltaic technology that is free of critical raw materials and thus offers sustainable solutions. To avoid indium and to find new compounds for absorber layers as well as window materials in thin film solar cells, the $A^{I}B^{III}X^{VI}_2$ chalcopyrite compound family is extended by chemical substitution to quaternary "defect adamantines" such as A^{I}-■-B^{III}-C^{IV}-X^{VI}_4 compounds. With band gap energies ranging from 1.42eV for $CuGaSnSe_4$ [1] to 2.34eV for $CuAlGeSe_4$ [1], the defect adamantines are interesting materials for photovoltaic applications.

Quaternary compounds of the Adamantine family are of type A^{I}_2-B^{II}-C^{IV}-X^{VI}_4 and A^{I}-■-B^{III}-C^{IV}-X^{VI}_4. Replacing one monovalent and one trivalent cation by one IV-valent cation in the chalcopyrite crystal structure and keeping the tetrahedral coordination, the quaternary compound A^{I}-■-B^{III}-C^{IV}-X^{VI}_4 with cation vacancies can be derived, the so called “defect adamantine”. These quaternary A^{I}-■-B^{III}-C^{IV}-X^{VI}_4 compounds crystallize in the chalcopyrite-type crystal structure (space group *I-42d*) or the cubic spinel-type structure (space group *Fd-3m*). The common feature of the cubic spinel structure and the tetragonal chalcopyrite structure is the tetrahedral coordination of the chalcogen, which is arranged in an (almost) cubic close spherical packing. In spinel, 1/8 of the tetrahedral voids are occupied by A^{I} cations and half of the octahedral voids are occupied by B^{III} and C^{IV} cations.
Starting from the ternary chalcopyrite $CuAlS_2$ and $CuAlSe_2$, we studied the group of defect adamantine with the general formula $CuAlC^{III}X^{VI}_4$ with C=Ge, Sn and X= S, Se.
Here we report on the growth of single crystals of these quaternary compounds such as $CuAlGeSe_4$, and $CuAlSnS_4$ and their structural as well as optoelectronic properties. The single crystals were grown by chemical vapor transport using iodine as a transport agent.
The evolved material and the crystals grown were characterized by X-ray diffraction (XRD) at 298K and LeBail analysis of the diffraction pattern. For $CuAlGeS_4$ and $CuAlSnS_4$, we determined the crystal structure to be the chalcopyrite-type (space group *I-42d*) and the cubic spinel structure (*Fd-3m*), respectively. The chemical composition of the crystals was determined by X-ray fluorescence.
The band gap energy was determined from the diffuse reflectance measured by UV-VIS spectroscopy.

[1] J.C. Woolley etal. Jpn.J.Appl.Phys. 19 (1980) Suppl. 19-3, 145-148

11:00 AM EN02.06.04

Role of Ligand Exchange on the Optoelectronic Properties of $NaBiS_2$ Nanocrystals Yi-Teng Huang[1], Igal Levine[2], Hannes Hempel[2], Markus Schleuning[2], Marin Rusu[2], Artem Musiienko[2], Szymon Zelewski[1], Akshay Rao[1] and Robert Hoye[3]; [1]University of Cambridge, United Kingdom; [2]Helmholtz-Zentrum Berlin, Germany; [3]University of Oxford, United Kingdom

Ternary chalcogenides are gaining increasing attention for photovoltaics, and we recently showed $NaBiS_2$ to have intriguing properties, including $>10^5$ cm^{-1} absorption coefficient at its pseudo-direct bandgap of 1.4 eV[1]. As a result, the spectroscopic-limited maximum efficiency (SLME) of this material can reach 26% with an absorber thickness of only 30 nm. This demonstration was made with nanocrystals (NCs) coordinated with long-chain organic ligands, which allowed us to probe the bulk properties, but severely limited intra-NC transport. Furthermore, we found that the inhomogeneous distribution of Na^+ and Bi^{3+} cations, which both occupy the same crystallographic lattice site, results in the formation of S *p* states within the bandgap of $NaBiS_2$ and facilitates the formation of small hole polarons that intrinsically limit the bulk mobility of this material.

In this work, we examined whether the intra-NC and inter-NC charge-carrier transport could be improved through ligand engineering. We showed through FTIR measurements that the long-chain organic ligands used during synthesis were completely substituted by short LiI, NaI, KI, or TMAI (tetramethylammonium iodide) ligands dissolved in methanol. $NaBiS_2$ NC films treated by these iodides all showed surface photovoltage (SPV) under illumination, with enhanced sum mobility from OPTP (optical-pump terahertz probe) and TRMC (time-resolved microwave conductivity) measurements. Together, these measurements suggest an enhancement in intra-NC mobility following ligand exchange. However, OPTP measurements showed that the enhanced mobility in iodide-treated films still decayed by ~80% within 1 ps, suggesting that carrier localisation cannot be suppressed through ligand exchange treatment. Nevertheless, from TRMC measurements, we noticed that the residual mobility after localisation was higher than the non-treated samples, meaning that more carriers could be extracted. Solar cells based on these iodide-treated $NaBiS_2$ NC films have reached external quantum efficiencies exceeding 50%, but their power conversion efficiencies were still below 1%. We showed that, apart from the low photocurrents limited by carrier localisation, ion migration is another hidden limitation for $NaBiS_2$ devices. We finish with a discussion of possible routes forward to overcome these limiting factors.

1. Huang, Y. T. *et al.* Strong absorption and ultrafast localisation in $NaBiS_2$ nanocrystals with slow charge-carrier recombination. *Nat. Commun.* **13**, (2022).

11:15 AM EN02.06.05

Phosphorus-Rich Phosphides: A New Frontier for Thin-Film Photovoltaics Andrea Crovetto[1,2,3], Thomas Unold[3] and Andriy Zakutayev[2]; [1]Technical University of Denmark, Denmark; [2]National Renewable Energy Laboratory, Gabon; [3]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany

Certain phosphorus-containing III-V semiconductors (GaP, InP and related alloys) are among the best-performing PV absorbers. Yet, there is hardly any other phosphide material that has received extensive attention for applications in PV or optoelectronics in general. Exciting progress has been reported within the family of Zn-based phosphide compounds (Zn_3P_2, $ZnGeP_2$, $ZnSnP_2$ etc.), but high PV efficiencies are yet to be demonstrated.

In this contribution, I will discuss a radically different class of semiconductors that is quite unique to phosphides. They can be referred to as “P-rich phosphides”. In stark contrast to almost any other compound semiconductor previously investigated for PV applications, P-rich phosphides contain bonds between nonmetallic atoms (in their specific case, phosphorus-phosphorus bonds).

Due to their distinct bonding mechanisms, phosphorus-rich phosphides give us an opportunity to find new materials design routes for high-efficiency PV, potentially overcoming some of the design limitations of “standard” semiconductor featuring only metal-nonmetal bonds.
I will present the first successful thin-film synthesis [1] of any polycrystalline P-rich phosphide. The synthesized material is CuP_2, which is a 1.5 eV band gap semiconductor with strong optical absorption and native p-type doping in an attractive range for thin-film heterojunction solar cells.

Finally, I will highlight a recent computational screening study [2], in which five P-rich phosphides were identified as highly promising materials for PV. These new materials are still awaiting thin-film synthesis.

[1] Crovetto et al. Crystallize It before It Diffuses: Kinetic Stabilization of Thin-Film Phosphorus-Rich Semiconductor CuP_2. *J. Am. Chem. Soc.* **2022**, *144*, 13334–13343.
[2] Kangsabanik et al. Indirect Band Gap Semiconductors for Thin-Film Photovoltaics: High-Throughput Calculation of Phonon-Assisted Absorption. *J. Am. Chem. Soc.* **2022**. Available online. https://doi.org/10.1021/jacs.2c07567.

11:30 AM *EN02.06.06

Emerging Chalcogenide for Thin Films Photovoltaics Lydia H. Wong; Nanyang Technological University, Singapore

In this talk, I will present a brief review of emerging binary (i.e.Sb_2S_3, $Sb_2(S,Se)_3$ etc), ternary (i.e $CuSbS_2$, $AgBiS_2$, etc), and quaternary ($Cu_2ZnSn(S,Se)_4$ and its emerging derivatives) chalcogenides, focusing especially on the comparative analysis of their optoelectronic performance metrics, electronic band structure, and point defect characteristics with established CdTe and CIGS thin film PV [1]. We found that the performance of these emerging materials are limited by Voc deficit which arises from non-radiative recombination. The defects in emerging chalcogenide are generally attributed to the anisotropy in binary and ternary compounds or due to the structural complexity of quaternary compounds. Here, I will also share our strategy to facilitate directional growth of the higher mobility [hk1] planes of $Sb_2(S,Se)_3$ resulting in power conversion efficiency of > 9% [2]. I will also show the effect of Zn substitution in CXTS (where X is Mn,Mg,Sr,Ba,Ni,Co,Fe) on the structural, optoelectronic and photovoltaic properties [3]. We found that cation substitute must have d-orbitals to replace Zn and form a stable quaternary compound. The most promising Zn substitute is Cd as it passivates the Sn deep defects and resulted in an efficiency of ~8% for Cu_2CdSnS_4 device [4].

[1] S. Hadke, L.H. Wong* et al, Chemical Reviews, 2021, https://doi.org/10.1021/acs.chemrev.1c00301
[2] X. Jin, L. H. Wong* et al, Advanced Material, 2021, 33, 2002887.
[3] S. Lie, L.H Wong* et al, J. Mater. Chem. A, 2022,10, 9137-9149
[4] S.Hadke, L.H. Wong* et al, Advanced Energy Materials, 2019, 9 (45), 1902509.

SESSION EN02.07: CdTe II
Session Chairs: Colin Wolden and Heayoung Yoon
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2002

1:30 PM *EN02.07.01
CdTe Photovoltaics: Successes and Challenges James Sites; Colorado State University, United States

CdTe has fundamental advantages for photovoltaics that include its near-optimal band gap for the solar spectrum and the ability to keep its defect level small in thin-film applications. At the same time panels with CdTe as an absorber can be manufactured on a large scale at low cost and demonstrated long-term stability. These advantages have translated into major commercial success in the U.S. and to some extent in China as well. Recent areas of progress have been the effective use of a CdSeTe alloy layer, enhancement of the transparent front contact, higher voltage with an organic PTAA rear layer, high luminescence efficiency of the cell structure, development of semi-transparent panels, and progress towards bifacial performance. However, several significant challenges remain, and the combination of these is limiting the voltage of the cells. Most fundamental is the large valence-band energy of CdTe, which makes it difficult to contact the typical p-type material. In addition, doping to a desired hole concentration while maintaining the low defect level has been difficult, and the passivation of interfaces and grain boundaries in a completed cell has been only partially successful. Each of these issues has been showing improvement, but the overall challenge is to find the right combination of materials and processes that can be collectively optimized. Since this challenge may be too large for an individual laboratory, researchers at several locations have formed a consortium to combine facilities and experience to jointly increase the overall progress of the CdTe technology.

2:00 PM *EN02.07.03
Control of Doping for Efficient CdTe-Based Thin-Film Solar Cells Yanfa Yan; University of Toledo, United States

Cadmium telluride (CdTe) photovoltaic is the most cost-competitive thin-film photovoltaic technology due to its low manufacturing cost and high module efficiency. In the past decade, the power conversion efficiency (PCE) has been significantly improved. For most efficient CdTe solar cells and modules, doping with Cu or a group-V elements such as As is essential. Introducing the appropriate amount of dopants at the appropriate location is critical for achieving high PCEs. In this talk, we will discuss the situation of Cu and group-V doping via an ex-situ process, i.e., diffusion of dopants into $CdCl_2$-treated CdTe thin films. For Cu doping, we fabricated CdTe thin film solar cells using a metallic Cu source and ionic Cu sources (solution processed CuCl and $CuCl_2$). We found that the ionic Cu precursors offer much better control of Cu diffusion than the metallic Cu precursor. Therefore, we also used group V high ionic materials (i.e., group V chlorides, VCl_3 such as PCl_3, $AsCl_3$, $SbCl_3$, and $BiCl_3$) as dopant precursors in a solution method for ex-situ group V doping of CdTe films. Our ex-situ group V doped CdTe solar cells achieved V_{OC}s as high as that of Cu doped CdTe solar cells. We found that a low dopant density increases the carrier lifetime, while excessive dopants reduces the carrier lifetime. A higher dopant density near the back interface is beneficial for maximizing the fill factor of CdTe solar cells. For thinner CdTe absorbers, it is necessary to tune the doping process to optimize the cell performance.

2:30 PM EN02.07.04
Controlling Device Instabilities with i-ZnO Oxygen Content in Chalcogenide Solar Cells Alejandro Navarro[1], Alex Jimenez[2,1], Kunal Tiwari[2,1], Sergio Giraldo[1], Edgardo Saucedo Silva[1], Zacharie Jehl Li-Kao[1] and Marcel Placidi[1,2]; [1]Universitat Politècnica de Catalunya, Spain; [2]Institut de Recerca en Energia de Catalunya, Spain

Intrinsic zinc oxide (i-ZnO) is systematically used in combination with a buffer layer (generally cadmium sulfide) and a transparent conductive oxide (TCO) for the fabrication of the n-type side of thin film chalcogenide solar cells. However, despite this near ubiquitous empirical use, its role remains debatable. Moreover, a particularly intriguing factor regarding the performances is the role of oxygen content in the ZnO. Its concentration modifies mainly the oxide stoichiometry, conductivity and transparency. Oxygen is commonly used during the preparation of the transparent oxides, and allows improving the transmission to the detriment of the resistivity. While incorporating a little amount of oxygen during the TCO deposition is generally used for this reason , the role of oxygen in i-ZnO remains unclear but appears necessary to obtain a high resistivity layer, by preventing oxygen vacancies or zinc interstitials responsible of the n-type conductivity. Moreover, adding oxygen during the i-ZnO deposition could also affect the CdS buffer surface in a similar way as sputtered oxygenated CdS (CdS:O) commonly used in CdTe heterojunction solar cells, and could also reduce the film crystallinity, increase the optical bandgap, change the composition at the surface of the CdS and/or increase the defects density. As a result of these multiple interplays between oxygen content and film properties, the solar cells' performance are significantly impacted.
The work here presented brings insights on the role of the i-ZnO layer in the solar cell structure by investigating the effect of the oxygen incorporation during its preparation and its influence on the performance of the devices. By varying the oxygen ratio (from 0 to 15% of oxygen in the total gas mixture with Ar) during the i-ZnO deposition, several batches of solar cells (using both CZTS and CIGS absorbers) were prepared and characterized. Limited differences were observed in their optoelectronic properties, with all the oxygen ratios leading to comparable values under illumination. However, a clear difference was observed in the dark behaviour before illumination, with devices with high oxygen content requiring longer light soaking times to reduce instabilities. To highlight this instability, a series of J-V measurements in (1) dark, (2) red light, (3) white light and (4) again dark conditions was

performed in CZTSe devices. These measurements were made after keeping the samples in dark for several days to avoid any possible effects from light-sensitive defects states. A first J-V measurement in dark (dark1) was recorded followed by a red illuminated J-V curve (using a 550 nm long pass filter with a 1 sun 1.5 AM spectrum white light), then a 1 sun 1.5 AM illuminated curve and finally another dark J-V curve (dark2). All the measurements are shown in the figure 1, and put in evidence a charging mechanism with white light illumination, that is required to stabilize the devices. It will be shown during the presentation that this relates to ionized acceptor defects at both the CdS and CdS/i-ZnO interfaces, which are neutralized when photogenerated holes are created with UV absorbed photons. The potential role of oxygen vacancies in this behaviour will be discussed. These results demonstrate the importance of controlling the defects density at interfaces to reduce device instabilities. More interestingly, this photo-induced mechanism, which shows reversibility after dark discharging, could be further exploited into specific light-based memory devices, which will be the developed in another presentation of MRS Spring 2023.

2:45 PM BREAK

SESSION EN02.08: Kesterite I
Session Chairs: Eric Colegrove and Maarja Grossberg-Kuusk
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2002

3:30 PM *EN02.08.01
Fabrication of Characterization of PERC-Like CdTe Solar Cells Heayoung Yoon; University of Utah, United States

Remarkable progress has been achieved in CdTe photovoltaics (PVs) to improve cell performance while reducing manufacturing costs. At the best efficiency of 22 %, researchers have demonstrated the short-circuit current (J_{sc}) and fill factor (FF) close to the limit of their maximum values via band-gap engineering and front-contact optimization. Considerable efforts have been devoted to increasing the carrier lifetime and the doping density ($N_A > 10^{16}$ cm^{-3}) to improve the open-circuit voltage (V_{oc}) of CdTe-based solar cells. Recent studies suggested that the Voc improvement in polycrystalline CdTe PVs requires well-passivated back contact. One possible strategy is to engineer the band-gap offset (e.g., CdMgTe; $\triangle E_{CB} \approx 0.2$ eV) to reflect minority carrier electrons, thereby decreasing surface recombination. Another approach is to utilize a stable Al_2O_3 layer as an electron reflector; experimental works confirmed the improved performance with a conformal Al_2O_3 layer. In this configuration, the precise control of Al_2O_3 ($\approx$ 1 nm) over the entire CdTe layer is essential because the J_{sc} greatly depends on the tunneling current. While promising, both CdMgTe and fully covered Al_2O_3 passivation on CdTe introduce unfavorable valence band offset that blocks the hole transport.

Here, we describe the design and fabrication of PERC-like (passivated emitter and rear contact) CdTe solar cells. Conventional lithography and wet-etching processes were used to pattern variable hole arrays on 20 nm-thick Al_2O_3 coated $CdSe_{(1-x)}Te_x$ (CST) solar cells. The CST absorber materials were doped with traditional copper elements or group-V dopants (e.g., P, As, Sb; GrV). We performed quantitative and qualitative PV analysis for a series of Cu-doped and GrV doped PERC devices. In contrast to the similar behaviors of J_{sc} and FF, we show a significant difference in the V_{oc} behaviors for Cu-doped and GrV-doped CdTe PERC solar cells. The V_{oc} of GrV-doped CdTe PERC remains constant, whereas the V_{oc} of the Cu-doped PERC shows a radical decrease with an increase in the exposed CdTe area. The defect chemistry of GrV-doped CdTe can be significantly different from that of traditional Cu-doped CdTe absorber materials. We will discuss the possible mechanisms responsible for these Voc changes of the CdTe PERC devices.

4:00 PM *EN02.08.02
Zinc Phosphide: a Promising Material for the Next Generation of Solar Cell Absorbers Mirjana Dimitrievska[1,2] and Anna Fontcuberta i Morral[2]; [1]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [2]École Polytechnique Fédérale de Lausanne, Switzerland

The path towards the next generation of inexpensive and high efficiency solar cells is based on the utilization of earth-abundant, environmentally-friendly, and chemically stable materials. One promising candidate is zinc-phosphide (Zn_3P_2), with a direct bandgap of 1.5 eV, high absorption coefficient ($> 10^5$ cm^{-1}), and excellent air stability. This work will present an overview of recent key findings related to the engineering of Zn_3P_2 absorbers for incorporation into high-efficiency solar cell devices.

First part of the talk will focus on three different approaches for synthesizing high crystal quality Zn_3P_2 thin films. These will include monocrystalline layer growth using molecular beam epitaxy [1], selective area epitaxy [2] and Van der Waals epitaxial growth on graphene substrates [3].

The second part of the talk will showcase the tunability of zinc-phosphide functional properties achieved by variation in the compositional stoichiometry [4,5]. In this case, we will show how electron and X-ray diffraction and Raman spectroscopy, along with density functional theory calculations, point to the favorable creation of P interstitial defects over Zn vacancies in P-rich and Zn-poor compositional regions. Photoluminescence and absorption measurements show that these defects create additional energy levels at about 180 meV above the valence band. Furthermore, they lead to the narrowing of the bandgap, due to the creation of band tails in the region of around 10–20 meV above the valence and below the conduction band. These results are also corroborated with the transport measurements on Zn_3P_2 devices.

Finally, we will discuss the device architecture for a polycrystalline Zn3P2 thin film solar cell on an InP substrate with a 4.4 % conversion efficiency. We will show the dominant recombination mechanisms in the device using different techniques and identify the key factors that limit the device efficiency. Additionally, we will provide a perspective on the next-generation Zn_3P_2-based solar cells.

[1] M. Zamani et al. J. Phys. Energy 3 034011 (2021)
[2] S. Escobar Steinvall et al., Nanoscale Adv., 3, 326-332 (2021)
[3] R. Paul et al., Cryst. Growth Des., 20, 6, 3816–3825 (2020)
[4] E. Z. Stutz et al. Faraday Discuss., 239, 202-218 (2022)
[5] M. Dimitrievska et al. Adv. Funct. Mater. 31, 2105426 (2021)

4:30 PM EN02.08.03
Crystallographic Structure and Point Defects vs. Efficiency and Stability in $Cu_2ZnSn(S,Se)_4$ Monograin Solar Cells (S/(S+Se)=0.8) Galina Gurieva[1], Kaia Ernits[2], Nikita Siminel[3], Alicia Manjon Sanz[4], Denis Sheptyakov[5], Maxim Avdeev[6], Melanie Kirkham[4], Dieter Meissner[2,7] and Susan Schorr[1,8]; [1]Helmholtz-Zentrum Berlin, Germany; [2]crystalsol OÜ, Estonia; [3]Institute of Applied Physics, Academy of Sciences of Moldova, Moldova (the Republic

of); [4]Neutron Scattering Division, Oak Ridge National Laboratory, United States; [5]Paul Scherrer Institute, Switzerland; [6]Australia's Nuclear Science and Technology Organisation, Australia; [7]Tallinn University of Technology, Estonia; [8]Freie Universität Berlin, Institute of Geological Sciences, Germany

In recent years quaternary chalcogenides have gained a lot of attention, especially the kesterite-type semiconductor compounds $Cu_2ZnSn(S,Se)_4$ (CZTSSe) which consist mostly of earth abundant and non-toxic elements. These compounds are a promising low-cost alternative absorber material for thin film solar cells due to their suitable criteria for photovoltaic applications: *p*-type semiconductor behavior, direct band-gap between 1.0-1.5 eV and absorption coefficient>10^4 cm^{-1}[1]. The record conversion efficiency of 13.5% reported for a CZTSSe based thin film solar cell was reached when the polycrystalline absorber layer exhibits an off-stoichiometric composition [2]. Deviations from stoichiometry cause intrinsic point defects (vacancies, anti-sites, interstitials), which determine the electronic properties of the semiconductor significantly [3]. It is agreed in literature that large band tailing observed in Cu-based kesterite-type semiconductors causes voltage losses limiting the efficiency of kesterite-based devices. The Cu/Zn disorder (Cu_{Zn} and Zn_{Cu} anti-sites in Cu-Zn planes at z=¼ and ¾), which is always present in these compounds [4,5], is discussed as a possible reason for band tailing. Conventional structural characterization is done with X-ray diffraction, but in the case of isoelectronic cations, like Cu^+ and Zn^{2+}, they are difficult to distinguish. Nevertheless, the neutron scattering lengths of Cu and Zn are different; by neutron diffraction we can distinguish between Cu^+ and Zn^{2+} site occupation in the crystal structure [4,5]. Kesterite-type based thin film solar cell technologies are mainly based on polycrystalline absorber layers, which makes it quite hard to correlate the crystallographic structure (determined via neutron diffraction) to the photovoltaic performance of these materials. A promising low-cost alternative technology uses CZTSSe monograins (single crystals of 50-100 µm size) which are fixed in a polymer matrix to form a flexible solar cell [6].

An in-depth analysis of neutron diffraction data provides information on the cation distribution in the crystal structure allowing the determination of the type and concentration of intrinsic point defects including a distinction between Cu and Zn [5]. On the other hand, neutron diffraction requires large sample volumes, thus kesterite monograins offer the unique possibility to correlate structural disorder in kesterite-type absorbers with device performance parameters.

We will present a detailed structural investigation of CZTSSe monograins with S/(S+Se)=0.8 based on neutron powder diffraction experiments, examining the influence of small changes in the chemical composition on the Cu/Zn disorder. We will show a correlation between all of the obtained knowledge on the chemical composition, the presence and types of secondary phases, the Cu/Zn disorder, the intrinsic point defects, the optical bandgap obtained from diffuse reflectance with the stability and efficiency of the respective devices. We will compare the “optimal” composition area of monograins with S/(S+Se)=0.8 to previously studied S/(S+Se)=0.6.

This work has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no.952982. A portion of this research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the ORNL. The authors gratefully acknowledge the PSI and the SINQ for providing us beamtime at the HRPT diffractometer and Australia's Nuclear Science and Technology Organisation (ANSTO) for providing us beamtime at the ECHIDNA diffractometer.

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4:45 PM EN02.08.04

Opto-Electrical Characterization of Back Bandgap-Graded $Cu_2Zn(Sn_{1-x},Ge_x)Se_4$ Kesterite Thin-Film Solar Cells Romain Scaffidi[1,2,3], Guy Brammertz[3,1], Jessica de Wild[3,1], Denis Flandre[2] and Bart Vermang[3,1]; [1]Hasselt University, Belgium; [2]UCLouvain, Belgium; [3]imec, Belgium

CZTSSe kesterite materials constitute a promising candidate for thin-film photovoltaics, based on abundant and non-toxic elements. Despite their high absorption coefficient and tunable bandgap for either single or tandem junctions, they suffer from significant V_{oc} losses impeding their efficiency to level with competing technologies such as CIGS, CdTe and Perovskites. Two main culprits for this large V_{oc} deficit are electrostatic fluctuations and high density of bulk defects, highly dependent on the absorber composition typically considered as ideal within well-established Cu-poor and Zn-rich ranges. An increasingly popular solution to tackle these two loss mechanisms and boost V_{oc} is the alloying of Ge to substitute Sn, leading here to $Cu_2Zn(Sn_{1-x},Ge_x)Se_4$ (CZTGSe) compounds, the bandgap of which is tunable through conduction band level following the x=Ge/Ge+Sn ratio. This work focuses precisely on the opto-electrical characterization of Sn-Ge bandgap-graded CZTGSe solar cells at both the absorber and complete device levels.

A sequential process is implemented and optimized, involving first the physical evaporation of a CZTG metallic precursor stack, then pre-annealed in N_2 and finally selenized. We obtain CZTGSe absorbers with low surface roughness and acceptable grain size within a Cu-poor and Zn-rich composition range. They exhibit an average x ratio around 45%, with a clear Sn-Ge segregation appearing naturally during the annealing step that leads to x=70% at the back surface and x=20% at the front surface. This corresponds to a back bandgap gradient which should simultaneously improve carrier collection and limit interface recombination, similarly to state-of-the-art CIGS. Yet, the low carrier lifetime is likely limited by poor top surface quality with observed surface defects and ZnSe secondary phases.

Advanced electrical characterization is performed on complete CZTGSe solar cell samples to gauge the impact of this Sn-Ge back bandgap grading approach and detect potential loss mechanisms. An efficiency of 7.2% is attained, along with values of 484 mV, 34.5 mA/cm^2 and 43.3 % for V_{oc}, J_{sc} and FF, respectively. Even though the performance is lower than record kesterite devices, the J_{sc} value is close to the Shockley-Queisser (SQ) limit for a confirmed minimum bandgap of 1.18eV, probably due to the largely enhanced carrier collection by our back bandgap gradient design. However, our devices are affected by important V_{oc} and FF deficits, i.e. about 50% of their SQ limits, for which the analysis of dark and light IV curves suggest are mainly the consequence of high-density deep defects as well as dominant electrical parasitics. This is investigated more deeply via temperature-dependent admittance spectroscopy, enabling the identification of a relatively deep defect level at the CZTGSe/CdS interface with activation energy of 260 meV and capture cross section of the order of 10^{-16} cm^{-2}. Minority carrier recombination via this defect state is likely the explanation for the poor V_{oc} and FF values observed. SCAPS-1D simulations are well in agreement with these experimental findings and allow to highlight this interface loss mechanism as the main limiting factor in our samples.

Eventually, Ge inclusion into kesterites effectively permits bandgap gradient to boost carrier collection and approach SQ limits in terms of J_{sc}. However, our study reveals that performance is still largely restrained by V_{oc} and FF losses at the CZTGSe/CdS interface which should be here the first area of improvement. This is preliminarily attempted via front surface sulfurization, but further investigations are required whether it concerns the Sn-Ge bandgap gradient design or the top interface quality using chemical treatments or alternative buffer materials.

This work has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement 952982 (CUSTOM-ART project).

SESSION EN02.09: CIGS
Session Chairs: Eric Colegrove and Jessica de Wild
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2002

8:15 AM EN02.09.01
A Tale of Two Siblings, i.e., Silicon and CIGS Solar Cells, and Their Rear Surface Passivation Gizem Birant[1,2,3], Jessica de Wild[4,2,3] and Bart Vermang[2,3,4]; [1]Fonds Wetenschappelijk Onderzoek – Vlaanderen (FWO), Belgium; [2]Hasselt University, Belgium; [3]EnergyVille, Belgium; [4]imec, Belgium

Since the origin of thin-film (TF) solar cells, there has been an ongoing comparison between silicon (Si) and TF solar cells. It is a fact that there is much to compare. However, we believe that the vast history of Si solar cells taught us a lot and will continue to teach, as it is currently the most efficient sibling of photovoltaic (PV) technologies. The passivation (P) concept came into play for silicon solar cells around the 1980s, and then *really* slowly, the P concept, i.e., PESC, PERC, PERL, became the standard production design for Si PV and boosted the efficiency from ~16% to 25% [1]. These remarkable achievements, of course, took the attention of the younger sibling, TF PV technology. In 2013, Vermang et al. integrated the rear surface passivation concept into CIGS solar cells and improved the solar cell performance compared to the unpassivated ones [2]. This advancement led many researchers to look further into the passivation integration to the CIGS solar cells, including me. Here, we will present the industrially viable approaches to applying a rear surface passivation layer in ultrathin-film CIGS solar cells. As a passivation layer, first, we tried aluminum oxide (AlO_x) since it has been proven to be an excellent passivation layer for Si and CIGS solar cells. One challenge, though, is that this layer blocks the current; hence there should be contact openings in the passivation layer to allow current flow to the back contact or the applied layer must be thin enough to allow tunneling. To create the openings in the passivation layer, we simply added alkali halide salt, which is proven to be beneficial for CIGS solar cells [3], via spin-coating before CIGS growth [4]. During the deposition, depending on the type of salt, we achieved nano to micron-sized openings in the dielectric layers up to 30nm thick [5]. The succession of the AlO_x passivation layer leads us to investigate another potential dielectric layer candidate, the hafnium oxide (HfO_x). As a result, with the same simple contacting approach, the solar cells' efficiency is considerably enhanced [6]. The fact that via spin-coating, randomly distributed openings have been created in the passivation layer; we investigated whether it is an ideal way to apply the salt solution or not. For this, we benefitted from hyperspectral imaging and checked the homogeneity of the process and its effect on the solar cell performance [7]. Despite the addition of various passivation techniques, the efficiency of the CIGS solar cells is still not in line with the sector leader, Si solar cells. However, it took ~20 years for Si technology to accept the passivation concept's success and integrate it into the production process; as a younger sibling, we still have close to 15 years to learn, improve and adapt the passivation approach for CIGS solar cells. Furthermore, Si solar cells require a lot of energy during their production phase due to the wafer production process. Hence, its carbon footprint, i.e., CO_2 production, is remarkably high. The TF PV technologies, e.g., CIGS, perovskite or organic, on the other hand, do not require high deposition temperature, i.e., they have a rather low carbon footprint. Considering that we need to reduce our carbon footprint for a sustainable future, we believe that TF technology has a brighter future than other siblings.

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8:30 AM EN02.09.02
Influence of Alkali Doping on the Grain Boundaries in CIGS Studied by Electrical and Capacitive Methods Aniela Czudek[1], Aleksander Urbaniak[1], Alexander Eslam[2], Roland Wuerz[2] and Malgorzata Igalson[1]; [1]Warsaw University of Technology, Poland; [2]Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Germany

Although the impact of alkali doping on the properties of CIGS solar cells has been a subject of ongoing debate for many years now, most research still focuses simply on the comparison between alkali-rich and alkali-free devices, without looking into the impact of the different alkali concentrations. We are convinced that in order to better understand the pathways of change and the specific factors impacting it, one has to study them over a broad range of different samples with controlled properties.

In this work, we present a systematic study of CIGS solar cells and corresponding thin films doped with a controlled concentration of sodium and potassium spanning three orders of magnitude. In case of thin films conductivity measurements were made, and on solar cells Deep Level Capacitance Profiling (DLCP) was used to estimate the doping level. Characterization of both cells and thin films together allows for further insight into the specific pathways of alkali impact – i.e. through distinguishing between the effects taking place on the interface and in the absorber – be it in its bulk or at the grain boundaries. Moreover, as the alkalis are known to segregate primarily on grain boundaries, a series of samples prepared with different evaporation methods, resulting in different grain sizes, were studied. Among all of these sample series, the dependence of conductivity, barrier height and free hole concentration on the alkali concentration (Na or K) follow a similar trendline, suggesting a common cause. One of effects that could lead to such result is the alkali-induced passivation of defects at the grain boundaries. As such, the values of energy barriers from conductivity measurements and the hole concentrations obtained from DLCP were then confronted with the results of 1D SCAPS simulations. The influence of donor defects at the grain boundaries on the barrier height and the average concentration of holes were studied. The simulation results were consistent not only qualitatively but also with good quantitative accuracy with the conductivity barrier heights and the free hole concentration values measured by DLCP.

All of those results point to the beneficial alkali effect being primarily linked to the passivation of donor defects and subsequent reduction of the energy barriers at the grain boundaries.

8:45 AM EN02.09.03
Development of Wide-Bandgap $Cu(In,Ga)Se_2$ Solar Cells by In-Line Co-Evaporation Wolfram Witte, Rico Gutzler, Wolfram Hempel, Stefan Paetel and Dimitrios Hariskos; ZSW, Germany

Chalcopyrite-type thin-film solar cells with bandgap energy (E_g) above 1.5 eV are ideal candidates for application as stable inorganic top cells in tandem devices. In recent years, the power conversion efficiency (PCE) could be increased for sulfide-based $Cu(In,Ga)S_2$ to 16.0% [1] and for pure $CuGaSe_2$ to 11.9% [2]. The implementation of a state-of-the-art post-deposition treatment (PDT) with heavy alkali elements like Rb or Cs resulted in an increased open-circuit voltage (V_{OC}) on wide-bandgap $Cu(In,Ga)Se_2$ (CIGS) with Ga/(Ga+In) (GGI) ratios above 0.7 [3]. Furthermore, the addition of Ag to wide-bandgap CIGS was demonstrated as a measure to reach higher V_{OC} values [4]. All these results were achieved with laboratory deposition coaters in a static mode. However, from an industrial point of view a fast and scalable in-line deposition process would be preferable for the growth of the wide-bandgap CIGS absorber by co-evaporation.

In this study, we present our results for wide-bandgap selenide-based CIGS solar cells deposited with an industrially relevant 30 × 30 cm^2 multi-stage co-evaporation system. So far, best cells with $E_g > 1.5$ eV achieved efficiencies up to 6% without RbF-PDT. After implementation of an in-line RbF-PDT the typical boost in V_{OC} and power conversion efficiency (PCE) could be obtained and best cells resulted in PCEs above 9%.

The solar cell performance strongly depends on the substrate temperature during CIGS growth and the choice of subsequent buffer and high-resistive layers. By exchanging the standard CdS/i-ZnO buffer layers with CBD-Zn(O,S)/(Zn,Mg)O, which is a good option for CIGS [5] and $Cu(In,Ga)(S,Se)_2$ [6] with E_g in the range of 1.0 – 1.2 eV, the V_{OC} gap between CdS- and Zn(O,S)-buffered wide-bandgap solar cells increased even further. Nevertheless, (Zn,Mg)O is a good partner for CdS and with this buffer combination we achieved a high V_{OC} of 899 mV for a CIGS cell with $E_g = 1.54$ eV (GGI = 0.83), resulting in an open-circuit voltage deficit (ΔV_{OC}) of 640 mV.

Moreover, we observe a gain in PCE as a result of slight Ag addition with low Ag/(Ag+Cu) ratios < 0.1 for CIGS absorbers with GGI > 0.6. Ag was incorporated by an additional evaporation source and these wide-bandgap $(Ag,Cu)(In,Ga)Se_2$ (ACIGS) solar cells exhibit increased FF values compared to the Ag-free CIGS reference samples. This observation was also made for our ACIGS cells compared to CIGS with standard GGI = 0.3, i.e. higher FF for Ag-containing samples. For high GGI values above 0.8, the Ag incorporation shifted E_g to lower values which resulted in an increased short-circuit current density and finally in an increased PCE which was accompanied by a slight increase in FF. We observe an increasing Na content in the bulk of the absorber with increasing AAC at GGI = 0.8, possibly due to altered absorber growth during deposition when more Ag is provided. Our best fully in-line prepared cell with a wide-bandgap ACIGS ($E_g \approx 1.5$ eV) achieved a PCE of 11.4% (without ARC). The corresponding V_{OC} and ΔV_{OC} values were 829 mV and 680 mV, respectively.

A minor reduction of E_g of about 0.2 eV to 1.34 eV (corresponding to GGI = 0.61), i.e. near the 2nd theoretical PCE maximum, resulted in a Ag-free CIGS cell with 18.2% PCE (with ARC) and a good V_{OC} of 856 mV with ΔV_{OC} = 480 mV.

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9:00 AM EN02.09.04

Chemical and Electronic Structure of $(Ag,Cu)(In,Ga)(S,Se)_2$ Absorbers with Varying Ag/(Ag+Cu) Ratios and Their Interfaces with the Molybdenum Back Contact in Thin-Film Solar Cells

Dirk Hauschild[1,1,2], Luisa Both[1,1], Ralph Steininger[1], Elizaveta Pyatenko[1], Mary Blankenship[2], Wolfram Witte[3], Rico Gutzler[3], Dimitrios Hariskos[3], Michael Powalla[3], Clemens Heske[1,1,2] and Lothar Weinhardt[1,1,2]; [1]Karlsruhe Institute of Technology (KIT), Germany; [2]University of Nevada, Las Vegas (UNLV), United States; [3]Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Germany

The introduction of alkali post-deposition treatments (PDTs) for $Cu(In,Ga)Se_2$ (CIGSe)-based thin-film solar cells has paved the way for efficiencies above 23 % on a laboratory scale.[1] For the next big step in solar-cell performance, new approaches need to be pursued. In recent studies, the incorporation of silver in CIGSe, i.e., forming $(Ag,Cu)(In,Ga)Se_2$ (ACIGSe), has been identified as a promising route.[2] The addition of Ag increases the absorber band gap, which could increase the open circuit Voltage (V_{OC}).[3] However, the impact of Ag on the chemical and electronic structure of the absorber surface, in particular with a PDT, is not yet understood.

In this contribution, we investigate in-line deposited and industrially relevant RbF-PDT ACIGSe absorbers and their interfaces with the molybdenum back contact as a function of the Ag/(Ag+Cu) (AAC)-ratio. For this purpose, the deeply-buried ACIGSe/Mo interface was accessed using sample cleaving and studied by synchrotron-based soft *and* hard x-ray photoelectron spectroscopy (PES and HAXPES, respectively), as well as laboratory-based x-ray and UV PES (XPS and UPS, respectively) and inverse photoemission (IPES). A detailed picture of the chemical and electronic structure of the ACIGSe surface and the ACIGSe/Mo interface as a function of the AAC-ratio is painted and will be discussed in view of the device performance.

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9:15 AM EN02.09.05

Peculiar Bond Length Dependence and its Impact on the Band Gap Bowing in $(Ag,Cu)(In,Ga)Se_2$ Thin Film Alloys

Hans H. Falk[1], Stefanie Eckner[1], Konrad Ritter[1], Sergiu Levcenco[1], Timo Pfeiffelmann[1], Edmund Welter[2], Jes K. Larsen[3], William N. Shafarman[4] and Claudia S. Schnohr[1]; [1]Leipzig University, Germany; [2]Deutsches Elektronen-Synchrotron DESY, Germany; [3]Uppsala University, Sweden; [4]University of Delaware, United States

The incorporation of Ag into $Cu(In,Ga)Se_2$ absorbers enables a reduced deposition temperature, which benefits the growth of thin film solar cells. Furthermore, Ag alloying leads to a wider optical band gap and improves the open-circuit voltage and thus the photovoltaic conversion efficiency. Contrary to other semiconductor alloys, however, the band gap increase occurs even though the crystal lattice expands with increasing Ag content. Moreover, the Ga-Se bond length of $(Ag,Cu)GaSe_2$ is predicted by theoretical calculations to decrease with increasing Ag content [1]. This prediction is counterintuitive, since in other chalcopyrite alloys, for example $Cu(In,Ga)Se_2$, all bond lengths increase as the lattice expands [2]. To unravel this mystery, we studied the atomic-scale structure, especially the element-specific bond lengths, of $(Ag,Cu)GaSe_2$, $(Ag,Cu)InSe_2$ and $Ag(In,Ga)Se_2$ alloys using extended X-ray absorption fine structure spectroscopy (EXAFS). The thin films were grown on Mo-coated soda lime glass by a single stage co-evaporation process [3]. The average Ag-Se and Cu-Se bond lengths determined by EXAFS clearly increase with increasing Ag content in both $(Ag,Cu)GaSe_2$ and $(Ag,Cu)InSe_2$, whereas the Ga-Se and In-Se bond length decreases despite the expansion of the chalcopyrite lattice. Thus, $(Ag,Cu)GaSe_2$ thin film alloys indeed exhibit the counterintuitive bond length dependence predicted by theoretical calculations and $(Ag,Cu)InSe_2$ shows the same behavior. In contrast, $Ag(In,Ga)Se_2$ exhibits a bond length dependence similar to that previously observed for $Cu(In,Ga)Se_2$. This clearly demonstrates that the peculiar behavior of a decreasing bond length with increasing crystal lattice is related to the mixing of the group-I lattice site, independent of the nature of the group-III atom. Furthermore, the element-specific bond lengths determined by EXAFS enable us to model the anion positions of the different local motifs present in the alloys and to estimate their contribution to the band gap bowing. Our study thus provides unique and systematic insight into the local structure of the $(Ag,Cu)(In,Ga)Se_2$ alloy system, including its impact on a key material property.

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9:30 AM *EN02.09.06
Developments in CIGS Energy Conversion Devices—From Solar Cells to Hydrogen Evolution Shogo Ishizuka; AIST, Japan

$Cu(In,Ga)Se_2$ (CIGS) and its derivative materials are versatile, as well as resource and cost-efficient and thus, attractive for photovoltaic energy conversion device applications. To date, we have developed lightweight and flexible $Cu(In,Ga)Se_2$ (CIGS) minimodules using a monolithically interconnected structure with independently certified photovoltaic efficiency values greater than 18% (number of cells: 17, designated area: 68 cm^2, without Ag or S alloying). This accomplishment was the culmination of techniques for controlling alkali-metal doping, the activation of metastable acceptors, and a minimodule fabrication process developed on flexible substrates. Modification of surface and interface, and bulk crystal quality by alloying with Ag or S, or other elements is expected to be a promising approach for further enhancements of the photovoltaic efficiency value. In addition, it has been suggested that mechanically scribed cell edges (equivalent to the side wall of P3 in the module fabrication process) can be an important factor in the degradation of device performance; therefore, there is room for improvement with proper passivation/termination treatments in the cell separation process. In fact, significant increases in the shunt resistance, fill factor (FF), and thus, photovoltaic efficiency values, and suppression of photovoltaic performance deterioration under low irradiance conditions were observed for CIGS solar cells fabricated using a photolithography-based cell separation process in lieu of a conventional mechanical scribing process.
Wide-bandgap CIGS-based photoabsorber materials are promising candidates for photocathode applications for the splitting of water into hydrogen as well as top-cell applications in tandem solar cells. We have demonstrated an over 8% half-cell solar-to-hydrogen (HC-STH) efficiency using ternary $CuGaSe_2$ (CGS)-based thin-films. This HC-STH value was demonstrated for a photocathode that underwent surface modification of CGS layer with RbF (q.e. not a postdeposition treatment). It has also been suggested that such surface modification of CGS thin-films with a Cu-deficient phase layer (CDL) may be effective in enhancing both the HC-STH and the open circuit voltage (V_{OC}) values of corresponding CGS solar cell devices. A CGS/CdS solar cell fabricated with a CDL demonstrated an independently certified photovoltaic efficiency value of 11.05% with a V_{OC} of 0.960 V, a short circuit current density of 15.9 mA/cm^2, and a FF of 72.4% (designated area: 0.497 cm^2, without RbF). These results suggest that improving wide-bandgap CIGS-based device performance requires different approaches from those used for conventional narrow-bandgap CIGS devices.

10:00 AM BREAK

SESSION EN02.10: Kersterite II
Session Chairs: Jessica de Wild and Mirjana Dimitrievska
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2002

10:30 AM *EN02.10.01
A Comparative Study of the Influence of Ag Alloying on the Performance of CZTSSe and CZTS Monograin Layer Solar Cells Maarja Grossberg-Kuusk, Idil Mengü, Jüri Krustok, Mati Danilson, Maris Pilvet, Kristi Timmo, Katri Muska, Valdek Mikli, Reelika Kaupmees and Marit Kauk-Kuusik; Tallinn University of Technology, Estonia

With the aim to reduce recombination losses in the kesterite based solar cells, the Ag alloying was performed on $Cu_2ZnSn(S,Se)_4$ monograins, leading to the formation of $(Ag_{1-x}Cu_x)_2ZnSn(S,Se)_4$ (ACZTSSe) solid solution. Ag is known to partially replace Cu in ACZTSSe, reducing the influence of Cu-Zn disordering and improving the open circuit voltage (V_{OC}) of the solar cells. Controversial results on the influence of the substitution of Cu by Ag in kesterite thin films have been reported in the literature. However, Ag alloyed kesterite thin film solar cells have been shown to have improved performance due to the reduced defect concentrations compared to the pure $Cu_2ZnSnSe_4$ and Cu_2ZnSnS_4 absorbers. Recently, Yuancai Gong et al. reported 13 % efficient thin film solar cells based on Ag alloyed kesterite CZTSSe[1].
We have previously studied the influence of Ag alloying on the properties of $Cu_2(Zn,Cd)SnS_4$ monograin powders and on the performance of the corresponding monograin layer solar cells[2]. The incorporation of Ag into the $Cu_{1.85}(Zn_{0.8}Cd_{0.2})_{1.1}SnS_4$ monograin absorber material improved the efficiency of monograin layer solar cells from 6.62% (x = 0) to 8.73% (x = 0.01) resulting from the changes in the defect structure, which led to reduced non-radiative recombination losses in the absorber.
Here, we report the influence of Ag incorporation into the $Cu_2ZnSn(S,Se)_4$ monograins on the structural, optical and electrical properties of the absorber material as well as on the performance of the monograin layer solar cells. Various ratios of [Ag]/ ([Cu] + [Ag]) were used in the synthesis process and losses of outcome Ag concentrations in the resulting material compared to the input were observed. The formation of ACZTSSe solid solutions is determined by X-ray diffraction as well as Raman spectroscopy. Changes in the defect structure and related radiative recombination mechanisms were studied by temperature dependent photoluminescence spectroscopy and correlated to the defects detected by admittance spectroscopy of the corresponding solar cells. Reduced recombination of photoexcited charge carriers as well as improved device performance of the ACZTSSe compared to the CZTSSe monograin layer solar cell devices is reported.

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11:00 AM EN02.10.02
Controlled Li Alloying of CZTSSe Absorbers by Electrochemical Treatment Simon Moser, Abdessalem Aribia, Ayodhya N. Tiwari and Romain Carron; Empa, Switzerland

$Cu_2ZnSn(S, Se)_4$ compounds, widely known as CZTSSe or kesterte referring to their crystal structure, are a promising material for thin film solar cells due to their composition out of non-toxic and earth-abundant elements and suitable optical and electronic properties . Yet, the performance of these solar cells is limited by defect-driven recombination, with the highest-ever reported power conversion efficiency being 13.6% so far. The properties and suitability for

PV application of thin-film kesterite absorbers are improved upon alloying with light alkali elements such as Li and Na, owing to defect passivation and increased carrier concentration. Moreover, Li alloying can be used to tune the absorber bandgap. However, the presence of light alkali elements, either added intentionally or diffused from the substrate, interacts with kesterite phase synthesis during annealing at high temperatures. As a consequence, Li-alloying in $(Li, Cu)_2ZnSn(S, Se)_4$ kesterite absorbers is limited to only a few percent of Li/(Li+Cu), before degraded morphology deteriorates the solar cell performances.

In this work we present an alternative strategy to incorporate controlled amounts of Li into crystallized kesterite absorbers, bypassing the alkali concentration limitations related to absorber synthesis. The Mo back contact of the spin coated and annealed CZTSSe absorbers is electrically connected to metallic Li and both are placed in a liquid electrolyte yielding a so-called half-cell configuration. Implementing this battery-inspired approach, we demonstrate the electrochemical treatment of CZTSSe and the successful transfer of Li into the absorber layer. We show that the treatment results in the incorporation of Li into the kesterite crystal grains, yielding alloyed $Li_xCu_{2-x}ZnSn(S,Se)_4$ absorbers with modified chemical composition. Using liquid electrolyte allows us to disassemble the half-cell after the treatment and deposit subsequent layers on top of the absorber to fabricate a working solar cell device with decent performance.

We present the benefits and limitations of our novel electrochemical Li alloying strategy based on morphological, structural, electrical, and optical characterization of treated absorbers layers and devices. We further discuss how this innovative approach could be combined with conventional alkali doping and alloying strategies in order to circumvent deteriorated solar cell performances related to the absorber synthesis in presence of high Li concentrations. Furthermore, the presented electrochemical approach opens new research directions, such as the investigation of ion migration in CZTSSe absorbers.

11:15 AM EN02.10.03

Identification and Performance Impact of Small Process Fluctuations in the Upsizing of Thin Film CZTSe/CdS Photovoltaic Technology Pedro Vidal-Fuentes[1], Fabien Atlan[1], Jacob Andrade-Arvizu[1], David Payno[1], Enric Grau-Luque[1], Alejandro Perez-Rodriguez[1,2] and Victor Izquierdo-Roca[1]; [1]IREC, Spain; [2]Universitat de Barcelona, Spain

Renewable energy production comes hand-to-hand with the development of suitable and future photovoltaic technologies, where large scale production depends on new concept thin film materials and device architectures, based on low cost processes and critical raw materials free, where $Cu_2ZnSnSe_4$ presents as a good candidate. In this context, it is a necessity to jump from small-scale laboratory sized cells to wider adaptable sizes, to achieve a plethora of different end applications, not only extensive (solar farms) but also for delocalized production (IoT, ViPV…), where the technological flexibility of the thin film technologies for the development of cells and modules with customized design is strongly relevant. The problems and difficulties of upscaling to a larger surface reveal themselves in an increased lateral inhomogeneity due to the increased ratio of area to cover vs thickness of the layers. The devices herein explored are based on a thin film structure, for the samples to perform properly, the layers need to present high quality and maintain their properties laterally, which is indeed a challenge, especially if the production cost has to be kept low. This challenge comes as a binary problem: the understanding of the specific physical or chemical phenomena, and the measurement of the effects of these variations in the final output of the PV devices. Usually, subtle variations, like thickness oscillations or compositional shifts, are unobserved at a small scale, because the process fluctuations can happen in areas larger than the measured cell, and finally define or limit the output of a device.

In this research a set of 3 samples (5x5 cm^2) are studied as the initial step for large-scale production of $Cu_2ZnSnSe_4$ devices. Each sample is isolated in 3x3 mm^2 individual cells, which permits to achieve a complete data library that aids to obtain a considerable amount of cell by cell information to implement statistical analysis. In those devices (3x3 mm^2), several characterization techniques are employed comprising: Raman spectroscopy (RS) with λ_{ex} = 442 and 532 nm; photoluminescence (PL) with λ_{ex} = 325, 442 and 532 nm, temperature dependent PL (PL-T) with λ_{ex} = 442 nm; current voltage characteristics (J-V); and image analysis. With the combination of those techniques, we can extract how the physicochemical properties of the front interface layers CZTSe/CdS/ZnO/ITO in the device architecture affect the final output of the device or influence each other. The data library is then composed of 3 x 196 cells that are analyzed as one complete dataset, where statistical correlations and small variations arise between the cells with some insightful results. Fluctuations are found in the CdS buffer layer as small thickness variations, bandgap changes and non-uniform defect energies. These variations of the CdS layer turn out to be strongly correlated to the final efficiency of the individual cells and define the observed patterns in optoelectronic performance along the surface of the 5x5 cm^2 samples, which also reflects in the visual appearance of the sample. These small changes, intrinsic to the processes, otherwise unseen in a discrete set of small samples or a set with strong variations in one of the fabrication steps (i.e. different samples with different absorber synthesis temperatures), imply strong modifications in the final efficiency of the individual devices, which are usually not perceived due to the low statistical significance of the data sets, this could potentially shadow or misguide the results of experiments and thus hamper progress in the development of these complex structures. In addition, the correlations found can be used as a quality control parameter in the fabrication of CZTSe modules, with simple approaches like visual inspection, applied in-line in the process.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 952982 (Custom-Art)

11:30 AM EN02.10.04

Enhanced Carrier Collection in Cd/In-Based Dual Buffers in Kesterite Thin Film Solar Cells from Nanoparticle Inks Stephen Campbell[1], Guillaume Zoppi[1], Leon Bowen[2], Matthew Naylor[1] and Yongtao Qu[1]; [1]Northumbria University, United Kingdom; [2]Durham University, United Kingdom

Increasing the power conversion efficiency (PCE) of kesterite $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cells has remained challenging over the last decade, in part due to V_{oc}-limiting defect states at the absorber/buffer interface. Previously, we found that substituting the conventional CdS buffer layer with In_2S_3 in CZTSSe devices fabricated from nanoparticle inks produced an increase in the apparent doping density of the CZTSSe film and a higher built-in voltage arising from a more favourable energy band alignment at the absorber/buffer interface. However, any associated gain in V_{oc} was negated by the introduction of photo-active defects at the interface (Campbell *et al.*, J. Appl. Phys 127, 205305, 2020). This present study incorporates a hybrid Cd/In dual buffer in CZTSSe devices which demonstrate an average relative increase of 11.5% in PCE compared to CZTSSe devices with standard CdS buffer, with the best performing dual buffer device ($CZTSSe/CdS/In_2S_3$) achieving 7.8% PCE (compared to 5.9% PCE in the $CZTSSe/In_2S_3/CdS$ hybrid buffer device). Spectral response measurements of hybrid buffer devices confirmed the presence of photo-active interface defects when the In_2S_3 buffer is adjacent to the CZTSSe absorber. Current density-voltage analysis using a double diode model revealed the presence of i) a large recombination current in the quasi-neutral region (QNR) of the CZTSSe absorber in the standard CdS-based device, ii) a large recombination current in the space charge region (SCR) of the hybrid buffer $CZTSSe/In_2S_3/CdS$ device and iii) reduced recombination currents in both the QNR and SCR of the $CZTSSe/CdS/In_2S_3$ device. This accounts for the notable 9.0% average increase in J_{sc} observed in the $CZTSSe/CdS/In_2S_3$ in comparison to the CdS-only CZTSSe solar cells.

Energy dispersive X-ray (EDX), secondary ion mass spectroscopy (SIMS) and grazing incidence X-ray diffraction (GIXRD) compositional analysis of the CZTSSe layer in the three types of kesterite solar cells suggests there is diffusion of elemental In into the absorbers with a hybrid buffer. In incorporation into the CZTSSe absorber increases the doping density of the SCR in the absorber. In diffusion arises from the post-deposition heat treatment (PDHT) of the hybrid buffer layers following their successive chemical bath depositions. When the In_2S_3 buffer is adjacent to the absorber of the hybrid buffer devices it is subjected to a double PDHT which greatly increases In incorporation into the absorber. As a result, the doping density in this absorber reaches 10^{17} cm^{-3} which negatively affects device performance. However, in the $CZTSSe/CdS/In_2S_3$ device, the single PDHT of the In_2S_3 layer is sufficient to increase the doping density of the SCR region of the CZTSSe without adversely affecting overall device performance.

It is expected that optimisation of the thickness of the hybrid buffer layers will lead to further improvements in device performance. These hybrid In_2S_3/CdS buffers provide a promising way to boost the efficiency of kesterite CZTSSe solar cells.

SESSION EN02.11: Tandem II
Session Chairs: Jessica de Wild and Johan Lauwaert
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2002

1:30 PM *EN02.11.01
Design and Optimization of Perovskite / CIGS Tandem Solar Cells Philip Schulz; Centre National de la Recherche Scientifique, France

Tandem photovoltaic devices based on CIGS and perovskite solar cell (PSC) sub-cells offer the implementation of all-thin-film tandems with all the advantages of thin-film technology, together with the possibility to achieve high efficiencies above the thermodynamic limit of single-junction solar cells. More precisely, the CIGS/perovskite tandem solar cell technology allows for low cost, light-weight, large area roll-to-roll fabrication and lower integration and installation costs, finally promising lower energy costs compared to current technologies. To this date, record power conversion efficiencies of over 24% and 27% have been achieved for monolithic two-terminal (2T) and stacked four-terminal (4T) tandems, respectively.
The crucial step for coupling CIGS and PSC devices in one tandem cell lies in the optimization of the layer stack with respect to light management and current collection, which include the growth of the transparent electrode layers. These requirements become even more stringent in monolithic 2T tandems, where cell performance requires current matching between top and bottom cells. This means that in particular for the CIGS cell we need to tailor the photoactive band gap to make optimum use of the partial illumination in the spectral region above ~750 nm wavelength, which is transmitted through the perovskite cell stack. One means to realize a beneficial trade-off between gains in the open circuit voltage and losses due to reduced photoabsorption is by the design of band gap grading, i.e. Ga in-depth distribution in the CIGS absorber film.
Hence, our approach to achieve high performance monolithic interconnected perovskite/CIGS 2T tandem solar cells rests on four major building blocks. (i) The adaptation of the CI(G)S bottom cell including control over the surface roughness, (ii) growth and optimization of the PSC layer stack on top, notably with focus on the hole transport layer, (iii) the design of the tunneling/recombination junction connecting the two sub-cells, and (iv) the implementation of light management structures for improved current matching.
All these tasks involve a dedicated focus on the control and analysis of the interfaces in each sub-cell and between the two cells, which will be the focus on my talk. I will lay out our methodology to assess the interface chemistry and the effect on its optoelectronic properties and functionality in the device. This point is particularly relevant for the optimized PSC and significantly affects the overall device performance and stability.

2:00 PM EN02.11.02
Perovskite/CIGS Tandem Solar Cell with an Efficiency Over 25% via Optimization of CIGS Bandgap Grading Hojin Lee, Passarut Boonmongkolras, Jaehyuk Koh, Chaeyoun Kim and Byungha Shin; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

By stacking two or more solar cells in a tandem configuration, the solar cell can more efficiently utilize the solar spectrum, and power conversion efficiency (PCE) is much higher than the Shockley-Quessier limit of single junction solar cells can be obtained. Theoretical calculations on tandem solar cells have predicted an ideal combination of ~1.1 eV and ~1.7 eV as suitable bottom and top cells, respectively. Wide bandgap perovskite and Cu(In, Ga)Se_2 (CIGS) are ideal materials for tandem solar cells, which carried out the theoretical calculations assuming that both the efficiencies of top and bottom cells reach the Shockley-Quessier limit. However, in reality, deviation from the Shockley-Quessier limit is more significant for a wider bandgap perovskite. Therefore, we adopted perovskite with a narrower bandgap than the ideal value (~1.7 eV) for tandem solar cells with CIGS. As the bandgap of perovskite was reduced, a CIGS bottom cell's bandgap must also be reduced for better current matching. Ga content can lower the overall bandgap of CIGS by precise control during deposition. Typical high-performing CIGS includes the so-called double grading bandgap profiles in which the bandgap first reduces with the thickness and opens up towards the front interface with n-type CdS buffer layer; however, it has not been confirmed whether the double-grading, which was optimized for single-junction CIGS solar cells, is still the best option for tandem solar cells. In this study, we controlled the bandgap profile of CIGS and compared single- and double-grading configurations of CIGS with a similar overall bandgap for applications to tandem solar cells with perovskite. Our investigation on the CIGS bottom cell under red light-filtered (i.e., wavelength smaller than 825 nm) illumination to mimic actual conditions during the operation of perovskite/CIGS solar cells showed that single-graded CIGS have a higher fill factor value than the double-graded counterpart. With further optimization of the monolithic tandem devices, we achieved PCE of 25.1% using perovskite of 1.65 eV and CIGS of 1.04 eV. Our study highlights the importance of bandgap tuning perovskite/CIGS tandem solar cells.

2:15 PM EN02.11.03
Steric Engineering Enables Efficient and Photostable Wide-Bandgap Perovskites for All-Perovskite Tandem Solar Cells Jin Wen and Hairen Tan; Nanjing University, China

Metal-halide perovskites are of tremendous interests for both single-junction and multi-junction photovoltaic devices due to their easy bandgap tunability via composition engineering. Perovskites possess long carrier diffusion lengths and high defect tolerance, enabling low-cost and solution-processed solar cells. To date, the power conversion efficiency (PCE) of single-junction perovskite solar cells (PSCs) has reached a certified value of 25.7%, which approaches that of crystalline silicon solar cells.
Monolithic all-perovskite tandem solar cells have the promise to deliver higher PCEs than do single-junction PSCs while maintaining the benefits of low-cost solution processing. Wide-bandgap (WBG, ≈1.8 eV) perovskite is a crucial component to pair with narrow-bandgap perovskite in low-cost monolithic all-perovskite tandem solar cells. However, the stability and efficiency of WBG PSCs are constrained by the light-induced halide segregation and by the large photovoltage deficit.
In this presentation, I will discuss our recent progress on a steric engineering that obtains high-quality and photostable WBG perovskites (≈1.8 eV) suitable for all-perovskite tandems. By alloying dimethylammonium and chloride into the mixed-cation mixed-halide perovskites, wide bandgaps are obtained with much lower bromide contents while the lattice strain and trap densities are simultaneously minimized. The WBG PSCs, with a considerably improved PCE of 17.7% and an increased Voc of 1.26 V, exhibited superior operational stability and maintain 90% of their initial PCEs after 1000 h operation at the maximum power point (MPP). With the triple-cation/triple-halide WBG perovskites enabled by steric engineering, a stabilized power conversion efficiency of 26.0% in all-perovskite tandem solar cells is further obtained. The strategy provides an avenue to fabricate efficient and stable WBG subcells for multijunction photovoltaic devices.

2:30 PM BREAK

SESSION EN02.12: Novel and Emerging II
Session Chairs: Byungha Shin and Andriy Zakutayev
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2002

3:30 PM *EN02.12.01
Novel (Sb,Bi)(S,Se)(Br,I) van der Waals Chalco-Halide Thin Film Photovoltaics—Current Status and Future Perspectives Ivan Caño Prades, Alejandro Navarro, Edoardo Maggi, Maykel Jiménez Guerra, Cibrán López Álvarez, Sergio Giraldo, Marcel Placidi, Zacharie Jehl Li-Kao, Claudio Cazorla, Josep-Lluís Tamarit, Joaquim Puigdollers and Edgardo Saucedo Silva; Universitat Politècnica de Catalunya, Spain

Quasi one-dimensional (Q1-D) structures based on van der Waals materials such as $(Sb,Bi)_2(S,Se)_3$ have demonstrated impressive progresses over the past 5 years. These types of materials typically form nano/micro-ribbons with strong covalent bonding in one direction, and at the same time, weak van der Waals bonding in the others two. This fingerprint feature confers unusual optoelectronic properties to these materials when properly oriented, and has allowed fast progresses in terms of conversion efficiency of solar cell devices, with a current record exceeding 10%. Beyond Sb and Bi-chalcogenide compounds, there is a limited body of knowledge on other Q1-D systems such as mixed chalco-halide van der Waals compounds, that combine chalcogens (S,Se) with halogens (Br,I) in the same structure. In fact, recent theoretical studies suggests that mixed chalco-halides can simultaneously achieve the robustness and stability of chalcogenide materials, along with the excellent optical and electrical properties of halides, and in particular showing high defect tolerance similarly to halide-perovskites.

This presentation will introduce a novel family of materials based on mixed Sb and Bi chalco-halides [(Sb,Bi)(S,Se)(Br,I)]. The first part will be devoted to reviewing the most relevant results reported so far for the few examples available in the literature, that have reached encouraging conversion efficiencies around 5% within a very limited timeframe, with a meso-porous solar cell configuration. In addition, the fundamental properties of these compounds obtained by DFT modelling will be discussed. The calculation of the bandgaps, band structures, optical and transport properties will be presented, discussing the trends of these properties depending on the chalcogen or the halogen introduced into the structure. The results will show that all these compounds can be relevant for different thin film photovoltaic applications, with bandgaps ranging from 1.6 eV for SbSeBr up to 2.3 eV for BiSBr.

In the second part of the presentation, the complexity of the synthesis of mixed chalco-halides will be discussed, and a new methodology for their synthesis, developed by the authors of this work, and based on the combination of co-evaporation of chalcogenides and high-pressure reactive annealing under halogen atmosphere, will be presented. This methodology allowed for the first time the demonstration of working solar cells with absorbers produced by vapor deposition techniques with these compounds. The tunability of the Q1-D structures by changing the synthesis temperature and pressure will be demonstrated. It will be shown that the synthesis of bromine-based compounds requires higher temperatures and pressures than iodine ones, due to the thermodynamics associated with the incorporation of Br and I in the chalcogenide phase. A detailed analysis of the mechanisms behind the formation of the different compounds will be presented by implementing interrupted-synthesis processes, and supported by the combination of thermo-gravimetric analysis, differential scanning calorimetry, and advanced structural/compositional characterizations.

The last part of the presentation will be devoted to the challenges and possible technological solutions for the fabrication of planar-heterojunction solar cell devices with these innovative photovoltaic absorbers. The use of different electrons and holes transport layers will be discussed, demonstrating for the first-time conversion efficiencies with these architectures between 1-5% and with very encouraging Voc values above 600 mV in some cases. Finally, the perspective of these materials and the possible advantages with respect to current chalcogenide and halide technologies, will be presented and discussed.

4:00 PM EN02.12.02
Bismuth Oxyiodide as a Nontoxic, Air-Stable Perovskite-Inspired Material for Energy Harvesting and Solar Fuels Robert Hoye; University of Oxford, United Kingdom

Although halide perovskites have taken the photovoltaics field by storm, concerns over the toxic and easily accessible lead content have prompted a search for lead-free alternatives. Bismuth-based compounds have particularly gained attention, owing to their electronic similarities to lead, but advantages of being free from the same toxicity limitations [1]. This talk focuses on our recent work on one of these materials: BiOI.

BiOI is not a perovskite, but replicates important features of the electronic structure of lead-halide perovskites that are believed to be conducive to defect tolerance. We show through computations and experiment that BiOI indeed tolerates the dominant vacancy and anti-site defects. Whilst the bandgap of BiOI (1.9 eV) is too wide for single-junction photovoltaics, we show that it is optimal for indoor light harvesting for sustainably powering Internet of Things (IoT) devices [2], and also suitable for solar energy harvesting as a photocathode for water splitting [3]. In the latter work, we develop a device structure that improves the operational stability of BiOI photocathodes from minutes to months, and combine these devices with $BiVO_4$ photoanodes to realise the first demonstration of all-oxide-based bias-free syngas production [3]. We also show this device structure to be beneficial for other novel halide photocathodes, such as lead-halide perovskites [4]. We finish off with a discussion of the key factors limiting charge-carrier transport and Urbach energies in BiOI, and how these could be overcome by tuning the composition and structure of this material.

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4:15 PM EN02.12.03
Aerosol-Assisted Chemical Vapour Deposition of $BiVO_4$ Photoanodes for Light-Driven Water Splitting Thom Harris-Lee[1,2], Matthew Surman[3], Andrew L. Johnson[1] and Frank Marken[1]; [1]University of Bath, United Kingdom; [2]Monash University, Australia; [3]ASM International, Finland

Bismuth vanadate ($BiVO_4$) is an outstanding candidate for visible-light driven water splitting due to its low production cost, high stability, low toxicity, and reasonable band gap with well-placed conduction and valence band edges relative to both hydrogen and oxygen evolution potentials.[1] In this presentation, the development and application of new and novel precursor systems tailor-made for the dual-source aerosol-assisted chemical vapour deposition

(AACVD) of highly nanostructured, phase-pure monoclinic-scheelite BiVO$_4$ thin films is outlined. Having identified the 'best in show' precursors for AACVD application, the BiVO$_4$ thin film deposition conditions are optimised for the most suitable precursor ratios and deposition temperatures for high quality films, with variations in nanostructure as a function of deposition time also being investigated in parallel by scanning electron microscopy (SEM). Light-driven water splitting performance is then evaluated using standard techniques including UV/Vis spectroscopy, linear sweep voltammetry under simulated sunlight irradiation, incident photon-to-current efficiency (IPCE) measurements, chronoamperometry, and electrochemical impedance spectroscopy (EIS). Pristine BiVO$_4$ films yielded photocurrent densities of 1.23 mAcm^{-2} at 1.23 V vs RHE, the highest photocurrent density of any CVD-grown BiVO$_4$ film to date.

The potential of AACVD for semiconductor doping and hybridisation studies are discussed, most importantly the compatibility of new metal precursors with existing ones. This is exemplified by the facile deposition of W-doped BiVO$_4$ without adding complexity or steps to the process. This work provides a roadmap in which an effective 'toolbox' of cross-compatible metal precursors can be rapidly deployed with AACVD to fabricate a range of doped and/or mixed-metal materials with high photocatalytic performance.

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4:30 PM EN02.12.04

Cation Disorder in Emerging Ternary Chalcogenides Absorbers (I-III-S$_2$; NaBiS$_2$ & AgBiS$_2$) Seán R. Kavanagh[1,2], Yi-Teng Huang[3], Robert Hoye[2], David O. Scanlon[1] and Aron Walsh[2]; [1]University College London, United Kingdom; [2]Imperial College London, United Kingdom; [3]University of Cambridge, United Kingdom

I-V-VI$_2$ ternary chalcogenides have recently attracted growing attention as earth-abundant, nontoxic, and air-stable absorbers for photovoltaic applications.[1,2] In particular, our recent work on the NaBiS$_2$ & AgBiS$_2$ members of this family has revealed ultra-strong optical absorption for these compounds – *the highest of all current PV materials*.[3] A key benefit of such intense light absorption is that it allows for ultrathin (<100 nm) solar cell devices, dramatically reducing material consumption, weight and manufacturing demand, directly lowering the cost and facilitating applications in space for example, in addition to benefitting quantum efficiency and photovoltaic (PV) performance.

Our collaborative work on AgBiS$_2$[3] showed the crucial importance of controlling cation distribution and disorder in these materials, yielding record-breaking efficiencies >9% – the highest of any Bi-based solar absorber.[3] However, the impact of disorder on the charge-carrier properties in these materials is remains poorly understood. Herein, we investigate the key properties which dictate the relationship between disorder on the cation sublattice and carrier transport in these materials. We find the band-edge orbital character to be a crucial factor in the sensitivity of carrier localisation (and thus solar cell efficiency) to cation disorder, resulting in ultra-fast carrier trapping, despite slow carrier recombination, in NaBiS$_2$.[4] We extend this analysis by explicitly calculating the phononic properties of these compounds, alongside Inelastic Neutron Scattering (INS) measurements, to probe the carrier de-population process in these compounds.

This work reveals the critical role of cation disorder in the photovoltaic performance of these disordered inorganic PV compounds, alongside key considerations for future research in this area.

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4:45 PM EN02.12.05

Innovative Low Dimensional SbSeI Micro-Scale Devices for Photovoltaics Ivan Caño Prades[1,2], Alejandro Navarro[1,2], Edoardo Maggi[1,2], Simon A. Svatek[3,4], José Ignacio Delgado Castaño[3], Carlos Bueno Blanco[3,4], Elisa Antolín Fernández[3,4], Shunya Yan[5], Esther Barrena[5], Joaquim Puigdollers[1], Marcel Placidi[1] and Edgardo Saucedo Silva[1,2]; [1]Universitat Politècnica de Catalunya, Spain; [2]Barcelona Research Center in Multiscale Science and Engineering, Spain; [3]Universidad Politécnica de Madrid, Spain; [4]Instituto de energía solar, Spain; [5]Institut de Ciència de Materials de Barcelona, Spain

The recent success of the van der Waals Sb$_2$(S,Se)$_3$ system has put low dimensional semiconductors in the spotlight to develop high efficiency photovoltaics (PV). Indeed, their performance has increased consistently, triplicating in less than a decade, and they also possess many benefits compared to other PV thin film systems, including earth-abundancy, low toxicity, thermal stability, and anisotropic crystal structure – resulting in unique electrical properties when the material is correctly oriented. However, van der Waals semiconductors beyond Sb$_2$(S,Se)$_3$ have been scarcely investigated, constituting an open field for research. Amongst this family of largely overlooked materials, antimony chalcohalides (*Sb[S,Se]X, X = Br, I*) are highly attractive due to their wide bandgaps in the 1.6-2.0 eV range (ideal for tandem and semi-transparent applications), customizable optical properties by using different halides or chalcogenides while retaining their quasi-1D structure, defect-tolerance, and ferroelectric properties, which might offer new opportunities (an alternative to perovskites) to improve electron-hole separation and achieve high photovoltages.

The first attempts to synthesize these materials for PV implementation have been essentially focused on low temperature (< 300^{o}C) and atmospheric pressure solution-based chemical routes, although PV performance of the resulting devices has been overall low. Aiming towards a more controlled, reproducible and versatile system, in this work, SbSeI has been synthesized by a novel procedure based on the selective iodination of co-evaporated Sb$_2$Se$_3$ films at pressures above 1 atm, developing an extremely uniform morphology consisting in single-crystal micro-columnar structures, which can reach lengths up to tens of microns, and which height and density can be finely tuned by adjusting the annealing temperature and pressure. Structure and crystalline quality have been characterized by advanced microscopy imaging techniques, Raman spectroscopy and X-ray diffraction. Also, Kelvin probe microscopy has been used to determine the local work function of these micro-columnar structures, revealing a work function variation among the exposed crystalline facets.

In addition to the excellent crystalline quality and low dimensional structure, SbSeI crystals show an overwhelmingly high photoluminescence (PL) signal, significantly larger than that of Sb_2Se_3 thin films, suggesting that they might have the capability of developing a remarkable PV effect. Indeed, electrical and optoelectronic measurements have been performed on micro-scale devices by transferring micro-columnar crystals to a SiO_2/Si wafer, and connecting them to Pt and Au contacts, yielding a clear diode response with the Au-Au and Au-Pt electrodes, which is greatly enhanced under illumination. Memory effect, capacitance-voltage and ferroelectric measurements have also been performed. Finally, solar cell prototypes have been prepared using a substrate configuration, resulting in high open-circuit voltages around to 600 mV.

Overall, this work presents a general study of synthesis and characterization of novel chalcohalide-based micro-scale solar cells, showing their compatibility with scalable physical vapor deposition techniques. We report the formation of highly crystalline SbSeI micro-columnar structures, showing excellent PL response, bandgap of 1.7 eV, and diode performance of micro-scale devices. These results demonstrate the potential of low dimensional chalcohalides to be implemented into innovative architectures and advanced functionalities (such as for enhanced carrier collection and light trapping), pointing the way to develop defect-tolerant and ferroelectric absorbers with anisotropic electrical properties for the next-gen PV, photo-electrocatalysis, piezo- and thermo-electric applications.

SESSION EN02.13: Poster Session II

Session Chairs: Byungha Shin, Colin Wolden and Yanfa Yan
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN02.13.02

Anatase Thin Film Growth—Optimizing Grains and Facets for Photoelectrochemical Applications Faven Berhane and Andrew Ichimura; San Francisco State University, United States

Reducing our dependence on fossil fuels for energy is important to eliminate greenhouse gas emissions. First-generation solar cell production is not sustainable, as manufacturing crystalline silicon is resource intensive. Anatase TiO_2 is a wide band-gap semiconductor oxide that has applications in third-generation solar cells and photoelectrocatalysis for water splitting and may become part of the portfolio of materials for clean energy production. One approach to improve devices based on TiO_2 thin films is to use crystallographic anisotropy to induce space-charge separation of photogenerated charge carriers. Exploiting the space-charge anisotropy intrinsic to the crystallographic directions and facets of anatase may improve both the reactivity and charge transport for photocatalytic and charge transport applications. It has been found that the (001) and (101) anatase facets are preferentially oxidizing and reducing, respectively. In addition, charge transport has lower resistance along the [001] direction. Therefore, anatase thin films for PEC should be designed with the c-axis normal to the conducting substrate and (001) facets at the surface to improve both charge transport and reactivity, respectively. Previously, we reported a synthesis for anatase thin films with [001] texture (Ichimura 2012). In this study, we examine thin film growth systematically to determine the conditions that maximize the [001] orientation and (001) facet expression of anatase thin films.

This work aims to optimize a one-pot hydrothermal synthesis of anatase TiO_2 thin films as a function of reagent concentration, pH, and temperature for photoelectrochemical applications. In this research, TiF_4 is the titanium source and HF is a structure-directing agent used to promote (001) facet growth. The TiO_2 thin films are synthesized in batches to reliably control concentration and pH. Preliminary syntheses have revealed that pH is an important factor to control grain size while temperature has a large effect on the growth of the (001) facets. The thin films are characterized by field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and grazing incidence X-ray diffraction (GIXRD). The TiO_2 film parameters (grain size and statistics, film thickness, and extent of orientation) will be correlated with reagent concentration, pH, and temperature. Preliminary PEC measurements that employ a Ni(II) based catalyst for the oxygen evolution reaction will also be reported. Additionally, ^{19}F NMR will be used to correlate film structure and solution composition.

5:00 PM EN02.13.04

Importance of Titanium Dioxide (TiO_2) Phase Control for Application as a Partner Layer in Antimony Selenide (Sb_2Se_3) Solar Cells Christopher Don and Jon Major; University of Liverpool, United Kingdom

Despite the successful history of CdS/Sb_2Se_3 heterojunction devices, cadmium toxicity, parasitic absorption from the relatively narrow CdS band gap (2.4 eV) and multiple reports of inter-diffusion at the interface forming Cd(S,Se) and $Sb_2(S,Se)_3$ phases present significant limitations to this device architecture. Among the options for alternative partner layers, the wide band gap (3.0-3.2 eV), non-toxic titanium dioxide (TiO_2) has demonstrated the most promise. FTO/TiO_2/Sb_2Se_3/P3HT/Au devices have achieved 7.3% PCE, compared with 10.6% for an FTO/CdS/Sb_2Se_3/spiro-OMeTAD/Au device structure. TiO_2/Sb_2Se_3 device structures deliver competitive J_{sc} and V_{oc} with these record PCE devices, however the devices are severely hindered by comparatively low FF (~52% and ~%68 respectively).

It's typically assumed that the meta-stable anatase phase of the polymorphic TiO_2 is attained for processing temperatures <500°C, since the anatase-rutile phase transition is commonly reported to be >600°C, however there is generally a lack of rigorous analysis of how the phase of TiO_2 may influence the device performance. In this study we correlate TiO_2 phase differences attained via low-temperature processed (500°C) RF magnetron sputtered and solution spin-cast TiO_2 window layers with 'S-Shape' 'kinks' in current-voltage measurements of TiO_2/Sb_2Se_3 solar cell device structures, which act to severely reduce FF in these devices. The S-Shape current-voltage curve under illumination is attributed to an interfacial charge barrier, highlighted by calculated J_{sc} discrepancy between JV and EQE measurement.

This work reports approaches to distinguish between TiO_2 polymorphic phases using both surface and bulk characterisation methods. We also demonstrate the impact that phase changes may have on both the front contact/TCO and antimony chalcogenide band alignment. A device fabricated with a rutile-TiO_2 window layer (FTO/r-TiO_2/Sb_2Se_3/P3HT/Au) achieved a PCE of 6.88% and near-record 32.44 mA cm^{-2} J_{sc}, which is comparable to established solution based TiO_2 fabrication methods which produced a highly anatase partner layer with 6.91% PCE. S-shape current-voltage curves are attributed to multi-phase TiO_2 films with a pure rutile surface and anatase bulk which generates a valley in conduction band minima alignment and drastically impedes electron extraction.

This result has implications for groups attempting to transition either from CdS partner layers to TiO_2, or even for transition from one TiO_2 deposition method to another. The work presented here shows that TiO_2 phase control is reliant on more factors than simply sintering temperature, which is significant considering TiO_2 phase is not always confirmed in Sb_2Se_3 device literature, especially in the context of our result which indicates TiO_2 phase differences alone can reduce PCE from ~7% to ~2% as a result of severe fill-factor losses in the face of this interfacial charge barrier. This is perhaps one of the reasons comparatively few groups are reporting high efficiency TiO_2/Sb_2Se_3 heterojunction devices, despite the clear limitations of CdS/Sb_2Se_3 structures.

5:00 PM EN02.13.05

Synthesis of Ag_3SX (X = Br, I) Chalcohalide Anti-Perovskites Thin Films Ivan Caño Prades[1,2], Jonathan Turnley[3], Marcel Placidi[1], Rakesh Agrawal[3] and Edgardo Saucedo Silva[1,2]; [1]Universitat Politècnica de Catalunya, Spain; [2]Barcelona Research Center in Multiscale Science and Engineering, Spain; [3]Purdue University, United States

Metal chalcohalides constitute an extended family of semiconductor materials encompassing different compositions, structural and optoelectronic properties. Indeed, since the 1960s, several chalcohalide materials have been reported to possess photoconductive, electro-optical and ferroelectric effects, and their wide variety of compositions and structures could lead to a broad bandgap range, potentially suitable for photovoltaics (PV). However, these semiconductors have been largely overlooked among the PV field, likely shadowed by the prevalence of Si in the solar cell market, and the success of other thin film technologies such as $Cu(In,Ga)Se_2$ and halide perovskites. Nevertheless, recent studies have reported excellent performance of several chalcohalide materials such as SbSI and SbSeI, reaching efficiencies up to 5% in a very short period of time, benefited by their quasi-1D structure, which favors a high mobility and excellent transport properties. But the chalcohalide family includes other members which have properties suitable for PV, as well as being constituted by low-toxicity and earth-abundant elements.

Among these, silver chalcohalides stand out for their crystalline structure analogous to the successful perovskite, suggesting that they could possess great tolerance to defects. Indeed, their structure corresponds to that of a perovskite, switching cation sites by anions, and anion sites by cations; hence denominated an anti-perovskite. Also, theoretical calculations have reported that silver chalcohalides have bandgaps in the 0.9-2.0 eV range, making them ideal for single-junction or tandem PV devices. Despite these promising properties, there is no published information on their implementation in solar cells, and so far, they have only been synthesized by solid-state reactions (powder) and laser ablation at high temperatures (ultra-thin films).

In this work, we present a procedure to prepare Ag_3SBr and Ag_3SI by low-temperature solution-based methodologies, using the amine-thiol solvent to dissolve Ag_2S and AgX (Br,I) precursors, followed by solution deposition by blade or spin-coating to obtain polycrystalline thin films on Mo and Al_2O_3-coated glass substrates. The structural properties of these films have been characterized by X-ray diffraction, confirming the formation of the anti-perovskite phase. Also, a series of samples have been subjected to different annealing treatments to determine the optimal synthesis conditions, whereby it has been observed that the anti-perovskite phase starts to form at 200ºC coexisting with Ag_2S (which decreases upon increasing temperature). Likewise, formation of AgBr has been detected at temperatures above 250ºC, bounding the range of optimum growth. Ag_3SBr and Ag_3SI films have also been characterized by scanning electron microscope imaging, Raman and transmission spectroscopies measurements.

Thus, this work demonstrates for the first time the viability of solution-processing methods to prepare Ag chalcohalide anti-perovskite thin films, using the amine-thiol ("alkahest") solvent. Importantly, this methodology has reduced the synthesis temperature to 200ºC, opening the door to its implementation with different substrates and the manufacture of solar cells. In addition, this versatile chemical system tolerates different cation and anion substitutions, offering a viable approach for bandgap tuning. Strategies to incorporate Cu_2S to the precursor solutions to prepare $(Cu,Ag)_3SX$ films and replace S by Se will also be presented and discussed.

5:00 PM EN02.13.07

Synthesis of Calcohalides by Sequential Co-Evaporation and High-Pressure Annealing Process for Photovoltaic Applications Alejandro Navarro[1], Ivan Caño Prades[1], Edoardo Maggi[1], Xavier Alcobé[2], Joaquim Puigdollers[1] and Edgardo Saucedo Silva[1]; [1]Polytechnic University of Catalunya, Spain; [2]Centres Científics i Tecnològics de la Universitat de Barcelona, Spain

The interest in low-dimensional materials has been regained due to the re-discovery of the high potential of these materials as absorbers for high-efficiency photovoltaic conversion. In particular, recent progresses in research on the quasi-1D material $Sb_2(S,Se)_3$, whose efficiency has been steadily increasing over the last decade, has attracted the interest of the scientific community to this class of materials. Among other interesting properties, these materials have the advantage of being constituted by abundant elements of low or no toxicity. Theoretical modelling has shown the very interesting properties of a new class of semiconductors based on semi-metal chalcohalides ([Bi,Sb][S,Se]X, with X = Br, I). Among them, they present unique electrical properties due to their anisotropic crystalline structure, potential defect tolerance and ferroelectricity similarly to the perovskite family. The potential applications of these materials range their implementation in tandem, semitransparent PV technologies and photocatalysis due to their bandgaps ranging from 1.6 to 2.3 eV.

In this work the properties of SbSeBr synthesized by co-evaporation of Sb_2Se_3, followed by a reactive annealing under halide atmosphere at different pressures above 1 atm that allows a better control on the incorporation of the halogen element into the crystal structure. A wide range of synthesis conditions are explored by modifying the reactive annealing pressure, temperature and duration. The first findings reveal that both the pressure and the temperature have a great effect on the size of the small irregular grains. Compared to analogous material such as SbSeI, this material requires relatively long process times to achieve a complete transformation of Sb_2Se_3 to SbSeBr. It is interesting to note that, so far, no reports on the synthesis of this particular material by means of the versatile, effective and easily scalable chemical routes are published.

The composition and crystal structure are characterized by combining X-Ray Fluoresence, X-Ray diffraction, Raman spectroscopy, and Energy-dispersive X-ray spectroscopy. The first results show that by the method developed in our lab it is possible to obtain a single-phase material with a very high degree of both purity and crystallinity. An identification of the main Raman modes will also be presented.

The absorber layers have been used to fabricate solar cells, reporting the first working devices for this material with efficiencies above 0.5% and with a very encouraging Voc (>600 mV). The main current limiting factor for the efficiency of the devices is the complex morphology of the SbSeBr layers, suggesting that a proper optimization of the novel synthesis process and an appropriate choice of Hole Transport Layer and Electron Transport Layer can boost the efficiency of these promising materials.

Finally, once the processing conditions are fully optimized, solar cell devices will be completed in both substrate and superstrate configurations, opening promising pathways for the development of highly efficient solar cells based on quasi-1D materials by a proper selection of device configuration, transport layers and material synthesis conditions.

5:00 PM EN02.13.08

Fine-Tuning Energy Levels and Molecular Packing of Asymmetric End Group Non-Fullerene Acceptor for Efficient and Stable Organic Solar Cells Huijeong Choi[1], Peddaboodi Gopikrishna[1], Do Hui Kim[2], Shinuk Cho[2] and BongSoo Kim[1]; [1]Ulsan National Institute of Science and Technology (UNIST), Korea (the Republic of); [2]University of Ulsan, Korea (the Republic of)

Organic solar cells (OSCs) have emerged as promising photovoltaic technology because of low-cost, lightweight, flexibility, and transparency. Recently, the power conversion efficiencies (PCEs) of OSCs have exceeded 18% with the development of non-fullerene acceptors (NFAs). Reported Y6 which has an A-DA’D-A structure, various Y-series derivatives have been designed. However, a trade-off between an open-circuit voltage (V_{OC}) and a short-circuit current density (J_{SC}) remains a problem even though the PCEs of OSCs based on the Y-series derivatives have increased rapidly. Hence, it is crucial to finely tune the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of photoactive materials for balance between V_{OC} and J_{SC}. In this work, we report efficient and stable OSCs based on a new asymmetric NFA, IPC-BEH-IC2F. This asymmetric NFA is comprised of a weak electron-donating core dithienothiophen[3,2-*b*]-pyrrolobenzothiadiazole (BEH) and two kinds of end groups having strong electron-accepting ability 9*H*-indeno[1,2-*b*]pyrazine-2,3-dicarbonitrile (IPC) with tricyclic fused ring and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (IC2F) which used as an end group in Y6. The IC2F-BEH-IC2F (or Y6) and IPC-BEH-IPC having symmetric structures were also characterized to compare with asymmetric IPC-BEH-IC2F. The IPC moiety significantly affects the optical properties and electronic structures of the NFAs. The asymmetric IPC-BEH-IC2F shows the highest extinction coefficient among the three NFAs due to its strong dipole moment and highly crystalline feature. Its HOMO and LUMO energy levels are successfully tuned between those of the IC2F-BEH-IC2F and IPC-BEH-IPC through the asymmetric structure. Besides, the IPC moiety promotes strong intermolecular π-π stacking due to their tricyclic fused system, which is beneficial for charge transport. Inverted type OSCs based on polymer:NFA blends were fabricated. Among all these polymer:NFA based OSCs, the asymmetric IPC-BEH-IC2F based OSC blended with PBDB-T showed a balance between V_{OC} and J_{SC}, leading to the highest PCE of 12.70% with a high V_{OC} of 0.85 V and a J_{SC} of 22.29 mA cm^{-2}. In addition, the PBDB-T:IPC-BEH-IC2F based OSC also exhibited the best long-term stability under ambient conditions due to the strongly interacting IPC moiety, which forms the densely packed morphology and prevents penetration of Ag atom into the photoactive layer. These results demonstrate that using asymmetric NFAs can be useful for improving the photovoltaic performance and stability of OSCs.

5:00 PM EN02.13.09
High Crystalline Regioregular Polymer by Thermal Treatment for Thickness-Insensitive Organic Photovoltaics Jiwoo Yeop[1], Kwang Hun Park[2], Bogyu Lim[2] and Jin Young Kim[1]; [1]Ulsan National Institute of Science and Technology, Korea (the Republic of); [2]Korea Research Institute of Chemical Technology, Korea (the Republic of)

To successfully develop a regioregular polymer, poly[4,8-bis(5-(2-hexyldecyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*’]dithiophene][5,5’-bis(7-(4-(2-butyloctyl)thiophen-2-yl)-6-fluorobenzo[*c*][1,2,5]thiadiazol-4-yl)-2,2’-bithiophene] (PDBD-FBT), symmetric monomer synthesized in high yield by tin homo-coupling reactions. PDBD-FBT is suitable as donor material in organic photovoltaics (OPVs) because it shows high crystallinity and strong face-on packing properties. These properties were amplified by thermal annealing (TA). It causes power conversion efficiency (PCE) enhancement in PDBD-FBT-based OPVs. Using PDBD-FBT as polymer donor and 2,2'-((2*Z*,2'*Z*)-((12,13-bis(2-heptylundecyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-*e*]thieno[2",3’':4’,5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile as electron acceptor, PCE of 7.91% was achieved without any additive and TA treatment at optimized film thickness approximately 100nm. After TA treatment, PCE of 12.53% was achieved with 58% increase compared with the reference devices. Owing to the strong crystallinities, trap-assisted recombination occurs by excessively formed grain boundaries; however, enhanced exciton dissociation probability covers these drawbacks. Even thick film condition approximately 340nm, this tendency is more pronounced (73% of PCE enhancement by TA treatment is observed). Although thick film’s OPVs are difficult to achieve high efficiency, it shows similar efficiency as the device with optimized film thickness. Our study demonstrates that it is possible to manufacture thickness-insensitive OPVs based on regioregular polymers with strong crystallinity and face-on characteristics, thereby providing a solution to the thickness variation of large-area organic solar cell modules.

5:00 PM EN02.13.10
Molecular Structure-Property Relation, Molecular Dynamics Simulation, and Charge Dynamics in Nonfullerene-based Organic Solar Cells Min Hun Jee[1], Dohun Yuk[2], Chang Woo Koh[1], Sungnam Park[1], Jin Young Kim[2] and Han Young Woo[1]; [1]Korea University, Korea (the Republic of); [2]Ulsan National Institute of Science and Technology, Korea (the Republic of)

In Organic solar cells, Y6 derivatives have a good candidate due to dominant face-on orientation, high electron mobility, and low energy loss with high electroluminescent quantum efficiency. However, Y6 derivatives have a long and complicated synthetic procedure to synthesize dithieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-e:2′,3′-g] [2,1,3]benzothiadiazole (BTP) core. So, we designed two new Y6 derivatives (YBO-2O/-FO) with a simplified synthetic procedure by moving solubilizing alkyl substituents on the BTP to the terminal (3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (INCN) groups. We investigated the intermolecular packing characteristics when the bulky alkyl side chain on the core of Y6 is removed through molecular dynamics (MD) simulation. YBO-2O/-FO are more formed in the core-core and terminal-terminal (CC-TT) with tighter packing structure than Y6 which coincides with GIWAXS (tighter packing than Y6) and SCLC (faster electron mobility than Y6). The HOMO and LUMO energy level was upshifted by the electron-donating terminal group (INCNO2). YBO-FO has an adequate HOMO energy level with that of the polymer donor PM6 which is a good hole transfer rate at the interface between donor and acceptor. In blend films, the hole transfer from YBO-2O/-FO to PM6 is investigated by transient absorption spectroscopy (TAS), demonstrating efficient hole transfer from YBO-FO to PM6. Despite the simplified synthesis, YBO-FO shows a power conversion efficiency of 15.01% similar to Y6.

5:00 PM EN02.13.12
Dimerized Small-Molecule Acceptors Afford High-Performance and Stable Organic Solar Cells with High Open-Circuit Voltage and Long Life-Time Jinwoo Lee[1], Cheng Sun[2], Soon-Ki Kwon[2], Yun-Hi Kim[2] and Bumjoon Kim[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Gyeongsang National University, Korea (the Republic of)

The power conversion efficiencies (PCEs) of small molecule acceptors (SMAs)-based organic solar cells (OSCs) have remarkably increased in recent years, but their thermal and long-term stabilities should be significantly enhanced for the commercialization. In addition, relatively lower open-circuit voltages (V_{oc}) of OSCs compared to other types of solar cells (*e.g.*, perovskite solar cells) should be addressed to further improve their PCEs. Here, we demonstrate that dimerizing a SMA with a properly-designed conjugated linker resolves the critical issues associated with the stability and V_{oc} of OSCs. The dimerized SMA (DYBO) connected by a benzodithiophene (BDT) conjugated linker affords OSCs with excellent PCEs (> 18%), which outperform those of the reference OSCs (PCE = ~17%) based on a monomer-type SMA (MYBO) with the identical SMA building block. The incorporation of the electron-donating BDT linker in DYBO effectively upshifts the lowest unoccupied molecular orbital energy level and reduces the voltage loss, synergistically increasing the V_{oc} of the devices. Importantly, the DYBO-based OSCs have excellent thermal and photo stabilities. For example, the DYBO-based OSCs retain more than 80% of the initial PCE even after 6000 hr of thermal exposure at 100 °C, whereas the MYBO-based OSCs sharply degrade their PCE to ~80% of the initial value after only 36 hr exposure. The main origins of the improved stabilities in the DYBO-based OSCs are (1) the significantly increased glass transition temperature (T_g) from 80 to 179 °C by the dimerization, which stabilizes the blend morphology during thermal stresses; (2) the improved miscibility of DYBO with a BDT-based polymer donor. Thus, we highlight the importance of the molecular design of dimerized SMAs for achieving OSCs with excellent PCEs and stabilities.

5:00 PM EN02.13.13
Perovskite Microcells Fabricated Using Swelling-Induced Crack Propagation for Semi-Transparent and Colored Solar Windows Jinhong Park and Dae-Hyeong Kim; Seoul National University, Korea (the Republic of)

Perovskite microcells have a great potential to be applied to diverse types of optoelectronic devices including light-emitting diodes, photodetectors, and solar cells. Although several perovskite fabrication methods have been researched, perovskite microcells without a significant efficiency drop during the patterning and fabrication process could not be developed yet. We herein report the fabrication of high-efficiency perovskite microcells using swelling-induced crack propagation and the application of the microcells to colored solar windows. The key procedure is a swelling-induced lift-off process that leads to patterned perovskite films with high-quality interfaces. Thus, a power conversion efficiency (PCE) of 20.1 % could be achieved with the perovskite microcell, which is nearly same as the PCE of our unpatterned perovskite photovoltaic device (PV). The semi-transparent PV based on microcells exhibited a light utilization efficiency of 4.67 and a color rendering index of 97.5 %. The metal–insulator–metal structure deposited on the semi-transparent PV enabled to fabricate solar windows with vivid colors and high color purity.

5:00 PM EN02.13.14
Modifying Additive Engineering with 2D-MXene in Perovskite Layer for Highly Efficient Inverted Perovskite Solar Cells Exceeding 23% Efficiency Hye Seung Kim, Ju-Hyoung Han, Soon-Yong Kwon and Myoung Hoon Song; Ulsan National Institute of Science and Technology, Korea (the Republic of)

On account of the excellent photovoltaic properties (e.g. tunable bandgap, long carrier diffusion length, and high absorption coefficient) and solution processability of the perovskite, a number of studies have been conducted on the perovskite as a next-generation solar cell. The rapid increase of the power conversion efficiency (PCE) of the perovskite solar cells (PSCs) has been achieved in the last decade, however, it has been implemented only in the conventional (n-i-p) structure of the PSCs. The inverted (p-i-n) structure, which has low-temperature processability, negligible hysteresis effects, and better device stability than n-i-p structure, is in the spotlight. Furthermore, p-i-n structure is suitable for fabricating tandem solar cells that can overcome the Shockley-Queisser limit (S-Q limit) of single junction solar cell.
In order to catch up with the efficiency of the n-i-p structure, numerous efforts have been made in the p-i-n structure. Due to the ionic nature of perovskite, which generates defect states, a typical method is to use an additive to passivate the defects in the perovskite layer. The perovskite crystal can be passivated during crystal growth process with incorporated additive, or prevent halide ion migration which leads to decrease efficiency of solar cells and device stability with placing additive material between perovskite and electron transporting layer (ETL).
A new family of 2D materials, called MXene, has emerged as a great candidate for additives in PSCs replacing other materials due to its outstanding electrical conductivity, tunable optical properties, and robust physical, chemical properties. Since MXene's surface has negatively charged groups (e.g. -OH, -O, -F, and -Cl), it is reasonable to expect that interaction of MXene with Pb^{2+} ion in perovskite not only passivates the defect sites of the perovskite but also affects to the crystal growth of perovskite. Moreover, MXene would decrease the charge transfer resistance in PSCs by its high electrical conductivity, increase the thermal stability by its good thermal conductivity. Lastly, incorporation of MXene in the perovskite cause the change of work function of perovskite to improve the device performances.
Herein, we demonstrate the affect of MXene as an additive in the p-i-n PSCs by engineering two different incorporating methods. We compared the difference in the mechanism of each crystal growth when MXene is added by two different methods, following compare the differences in morphology of perovskite and device performance according to each method. Consequently, the short-circuit current density (Jsc) and open-circuit voltage (Voc) are greatly improved, so that obtain over 23% of PCE.

5:00 PM EN02.13.15
Self-Encapsulated Semitransparent Perovskite Solar Cells for Long-term Stability via Thermocompression Bonding Process Heeyun Jeong and Taeyoul Yang; Chungnam National University, Korea (the Republic of)

Organic-inorganic hybrid perovskite solar cells (OIHPs) have attracted the PV community due to low cost and high power conversion efficiency, but still have suffered from poor stability. In order to shield perovskite solar cells (PSCs) from extrinsic degradation factors such as oxygen and moisture and assure long-term stability, effective encapsulation technology is indispensable. Here we designed a facile process to build glass-glass encapsulated semitransparent PSCs by laminating two half cells where a perovskite layer is formed on a hole transport layer (HTL, p-type) and an electron transport layer (ETL, n-type), respectively, with a transparent conducting oxide (TCO) glass substrate. By laminating the half cells through a thermocompression bonding process, the device is self-encapsulated during manufacturing. Soft mechanical characteristics and atomic migration nature of the perovskites enable the lamination between the perovskite layers with minimizing voids and good adhesion properties. During the lamination process, surface of the perovskite transformed into bulk with enlarged grains, and the interfaces has much smoother and denser morphology. Through surface iodine extraction experiments and TRPL analysis, it was confirmed that defects and trap density decreased in the laminated perovskite. The thermcompression increases hydrophobicity on interfaces of the perovskite. Therefore, the laminated perovskite has higher stability against moisture. The self-encapsulated semitransparent PSCs with a wide bandgap perovskite (E_g ~ 1.67eV) is performed with the PCE of 17.24 %, and thermal stability at 85 °C is secured for over 3,000 hours.

5:00 PM EN02.13.16
Vapor-Transport-Deposited SnSe for Thin-Film Solar Cells Pravin S. Pawar, Raju Nandi, KrishnaRao E. Neerugatti, Jae Yu Cho and Jaeyeong Heo; Chonnam National University, Korea (the Republic of)

The binary chalcogenide-based thin-film solar cells (TFSCs) have attracted great attention due to their low-cost and nontoxic constituents, simple structure, and ability to exhibit high power-conversion efficiency (PCE). The orthorhombic tin selenide (a-SnSe), a binary chalcogenide, is a potential candidate for the low-cost TFSCs due to its appropriate optical bandgap, high optical absorption coefficient (α〉 10^5 cm^{-1}) in the visible region, intrinsic p-type conductivity, and high hole mobility (200 cm^{2}V^{-1}s^{-1}). However, the reported PCE for SnSe TFSCs is significantly low (less than 1%) in most cases due to poor crystallinity, small grains, and a large number of defects. Herein, we report the highest cell efficiency of 2.51% and a high short-circuit current density of 28.07 mA cm^{-2} for a-SnSe TFSCs grown via vapor-transport-deposition (VTD). The effect of evaporation temperature and duration was studied on the performance of SnSe TFSCs. The grain size and surface roughness of the SnSe thin films were mainly affected by the evaporation temperature and duration and were found to be the main parameters to influence the shunt properties of the device. Significantly large shunt losses are detected in the case of both small and extremely large grains. The shunt losses for SnSe thin film with small grains are associated with high grain-boundary scattering. The presence of extremely large grains results in increased surface roughness of the SnSe thin film, which causes nonuniform deposition of the CdS buffer layer and, consequently, higher shunt losses. The SnSe thin film with moderate-sized grains and inferior surface roughness exhibits improved shunt properties owing to uniform deposition of the CdS buffer layer and subsequent layers and significantly improved the device performance. Detailed studies on the morphological and structural properties of the orthorhombic VTD-SnSe thin films and their impact on the photovoltaic device performance will be discussed.

5:00 PM EN02.13.17
PbS Quantum Dot Solar Cell with Reduced Hysteresis by Controlling Interface and Thickness of Hole Transport Layer Using Transfer Printing Hyungcheoul Shim[1,2], Areum Kim[1] and Seungmin Hyun[1,2]; [1]Korea Institute of Machinery and Materials (KIMM), Korea (the Republic of); [2]University of

Science and Technology (UST), Korea (the Republic of)

We fabricated a hole transport layer (HTL) using transfer printing to fabricate high efficiency PbS quantum dot solar cell with minimized hysteresis. We applied PbS-EDT(1,2-ethanedithiol) as an HTL and controlled the adhesive properties between the donor substrate and the HTL through the UVO process in order to effectively transfer the HTL to the PbS layer, which enabled multilayer transfer printing as a result.
During the transfer printing process, a densly packed gradient solid-solution layer without pinholes was created at the interface with the existing PbS layer to reduce the hysteresis phenomenon, and to improve the power conversion efficiency to about 10% according to the HTL thickness optimization.
In addition, the use of the EDT solvent can be remarkably reduced by using the transfer printing when forming the PbS-EDT layer. This can reduce the amount of organic solvent consumed in the process and improve the potential of environmentally friendly processes.

5:00 PM EN02.13.18
Hybrid Pulsed Laser Deposition Growth of Chalcogenide Semiconductors Mythili Surendran, Shantanu Singh, Huandong Chen, Boyang Zhao and Jayakanth Ravichandran; University of Southern California, United States

Chalcogenide semiconductors, especially 2D transition metal dichalcogenides, are extensively studied owing to their intriguing physical properties for electronic and photonic applications. However, in the past few years, ternary chalcogenide semiconductors such as chalcogenides perovskites have gained substantial interest as a new class of semiconductors due to their tunable chemistry, structure, and opto-electronic properties. For instance, $BaZrS_3$ (BZS) (band gap = 1.9 eV), a prototypical chalcogenide perovskite, is promising as an ultra-thin absorber in tandem solar cells[1-3], whereas $BaTiS_3$ (BTS) (band gap = 0.27 eV) exhibits a giant birefringence and large optical anisotropy in the infrared region[4]. Growth of thin-film chalcogenide perovskites is a critical step to enable investigations into their fundamental properties and also device applications. But the thin-film growth of chalcogenide perovskites is challenging due to a large mismatch in the vapor pressure of the cations and chalcogens, corrosive and reactive nature of most chalcogen precursors, the propensity to oxidize easily in the presence of oxygen at high temperatures and the lack of suitable non-reactive substrate surfaces for epitaxial growth.

Recently, we have demonstrated direct, single-step, epitaxial growth of BZS[1] and BTS[5] thin films on oxide substrates by pulsed laser deposition (PLD) using Argon-H_2S background gas. H_2S is a toxic, hazardous, and flammable gas and reacts with many materials, and the ionized Argon and/or H_2S lead to significant degradation of the crystallinity of both the surface and film at the high growth temperatures. Here, we report an alternative hybrid PLD approach using organo-sulfur precursors as sulfurizing agents to grow chalcogenide semiconductors. To demonstrate the efficacy of this approach, we have demonstrated epitaxial growth of 3D binary chalcogenides such as BaS and SrS (wide band gap) and 2D binary chalcogenides such as TiS_2 (metallic) and ZrS_2 (semiconducting). The potential of these binary sulfides as suitable candidates for transparent and conducting layers in chalcogenide-based photovoltaic devices will be discussed. We have also realized epitaxial BZS and BTS films using hybrid PLD and a comparison of this approach to PLD using Ar-H_2S will be provided. Further, we will also discuss our future growth efforts and the applications of this novel growth method.

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SESSION EN02.14: Novel and Emerging III
Session Chairs: Jon Major and Byungha Shin
Friday Morning, April 14, 2023
Moscone West, Level 2, Room 2002

8:30 AM EN02.14.01
Highly Transparent ITO/Ag/ITO Sandwich Structure with an Ultra-Thin Silver Layer for Solar and Display Applications Thanh P. Tran[1], Maheshwar Shrestha[2] and Qi Hua Fan[1,1]; [1]Michigan State University, United States; [2]Scion Plasma LLC, United States

A highly and evenly transparent conductive electrode is fabricated on glass substrate thanks to the ability to produce stable continuous ultra-thin silver films, the computational global search of optical properties on ITO/Ag/ITO (IAI) sandwich structures using the transfer matrix method (TMM), and annealing process in the air at high temperature. First, ion beam treatment and aluminum cap layer enable the depositing of stable ultra-thin silver films at 6 and 7 nm. Particularly, ion beam treatment helps to prepare a surface with better wettability toward silver, and the aluminum cap layer help to protect silver film by impeding the movement of silver surface atoms. Secondly, the film thicknesses are then used as the inputs for the simulation of the ITO/Ag/ITO sandwich structure and we found the optimum design of ITO (45 nm)/ Ag (6-7 nm)/ITO (50 nm)/ Glass. Finally, the stable silver film allows further processing of annealing at high temperatures (200C) in the vacuum and in the air, which is not possible for a stand-alone silver film. The resulting 7 nm film on glass substrate has a sheet resistance of 10 Ohm/ sq. an average transmittance in the range of 400-800 nm of 89%. This process can be implemented in other substrates as well as other transparent conductive oxides such as SnO_2, AZO, TTO, and TiO_2. Therefore, a couple of TCOs were taken into consideration for a similar sandwich structure to compare the optical performance showing potential replacements for ITO in optoelectronic applications in the circumstance that indium is getting costly.

8:45 AM EN02.14.02
The Renaissance of Selenium Thin-Film Solar Cells – The Elemental High Bandgap Photoabsorber Rasmus Nielsen, Tobias Hemmingsen, Andrea Crovetto, Ole Hansen, Ib Chorkendorff and Peter C. Vesborg; Technical University of Denmark, Denmark

In the pursuit of lowering the cost and increasing the penetration of solar energy technologies, a family of inorganic thin-film photovoltaic materials is

emerging. The oldest member of this family, selenium, is experiencing renewed interest due to its high bandgap of 1.95 eV in its trigonal phase, as well as its irresistible monoatomic simplicity. The high bandgap makes selenium a potential partner in tandem photovoltaic devices featuring e.g., silicon as the lower bandgap photoabsorber, but high-efficiency selenium thin-film solar cells have yet to be realized.
We present selenium thin-film solar cells with power conversion efficiencies exceeding 5% and following a novel optimization of the carrier-selective contacts, we demonstrate a record open-circuit voltage of 0.99V and highly encouraging fill-factors beyond 60%. These state-of-the-art devices are investigated in a combined experimental and first-principles study to reveal the origin of the still-significant photovoltaic losses [1]. In view of these results, we set forth strategies for continued improvements to the photovoltaic performance by means of non-equilibrium growth and defect engineering.

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9:00 AM EN02.14.03
Challenges and Prospects Towards Developing Emerging Antimony and Bismuth-Based Chalcogenide for Next Generation, Earth Abundant Photovoltaics Nicolae Spalatu, Sajeesh Vadakkedath Gopi, Mykhailo Koltsov, Robert Krautmann, Malle Krunks and Ilona Oja Acik; Tallinn University of Technology, Estonia

The emergence of new PV applications in the society requires the design of materials and devices with a different set of properties. At this scale, for a new photovoltaic (PV) technology is not sufficient to be only competitive with the Si and CdTe technologies in efficiency and reliability but one should also rely on green, environmentally friendly, and earth-abundant materials. An emerging class of highly promising PV materials currently under widespread investigation in the PV community are the inorganic antimony-and bismuth-based chalcogenide compounds. The excellent intrinsic material properties of these compounds allowed to rapidly approach 8-10% conversion efficiency, opening a new chapter in PV research, full of new possibilities but also scientific challenges. This talk will discuss the latest achievements in bismuth- and antimony-based thin film solar cell technology with the main emphasis on Sb_2Se_3 and Bi_2S_3 compounds. I will summarize the knowns and unknowns of their defect chemistry, including highlights of unique optoelectronic characteristics that are not yet fully explained. The discussion will highlight the progress achieved in our group, toward growth of high-quality Sb_2Se_3 and Bi_2S_3 absorber films and solar cells by rapid, high-volume, and in-line close-spaced sublimation and vapor transport deposition techniques. Special emphasis will be put on the key processing strategies to optimize absorber material properties (doping and alloying), understanding of buried interfaces and push the boundaries of understanding and performance. A thorough look at the formation chemistry and shed light on some of the synthesis and doping challenges, potential doping elements, the impact this has on carrier density and the impact on solar cell performance.

9:15 AM EN02.14.04
Experimental and Computational Studies of Solution Processed $CuSbSe_2$ for Photovoltaic Applications Yuchen Fu[1], Hugh Lohan[1], Yi-Teng Huang[2], Marcello Righetto[1], Szymon Zelewski[2,3], Chang-woo Cho[4], Young Won Woo[5], Harry Demetriou[6], Martyn A. McLachlan[6,6], Sandrine Heutz[6,6,6], Benjamin Piot[4], Akshay Rao[2], Laura Herz[1,7], Aron Walsh[6] and Robert Hoye[1]; [1]University of Oxford, United Kingdom; [2]University of Cambridge, United Kingdom; [3]Wroclaw University of Science and Technology, Poland; [4]Université Grenoble Alpes, France; [5]Yonsei University, Korea (the Republic of); [6]Imperial College London, United Kingdom; [7]Technical University of Munich, Germany

The exploration of novel absorber materials composed by earth-abundant and low-toxicity elements is important for thin-film solar cells. Among these materials, $CuSbSe_2$ is promising because of its suitable optical and electrical properties such as ≈ 1.1 eV bandgap and high absorption coefficient. However, the practical application of the reported hydrazine solution process is limited by the hazardous nature of hydrazine, and more detailed investigations into charge-carrier transport properties of $CuSbSe_2$ is needed. In this study, a novel thiol-amine solution processing route is used to fabricate $CuSbSe_2$ thin films. The fundamental properties of $CuSbSe_2$ thin films are investigated, including phase purity, absorption coefficient and bandgap, to demonstrate the feasibility of the thiol-amine route. Next, the charge-carrier kinetics are studied by transient absorption (TA) and optical-pump terahertz-probe (OPTP) spectroscopy, which reveal that, in contrast to other heavy pnictogen-chalcogenide compounds studied recently [1], $CuSbSe_2$ avoids carrier localisation. To further study the carrier-phonon coupling and carrier transport properties, the temperature-dependence of the mobility is determined through Hall-effect measurements, and compared with DFT calculations to show that Fröhlich coupling dominates in $CuSbSe_2$. The coupling to acoustic phonons is weak, owing to low deformation potentials. The cause of the low deformation potential is studied by investigating how the lattice distorts along the dominant phonon modes. The combined experimental-computational studies shown in this work lead to new insights into how materials avoiding carrier localisation could be designed in the future.

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9:30 AM EN02.14.05
Antimony Trichalcogenide Materials for Short-Wavelength Infrared Photovoltaic (SWIR-PV) Devices Jitendra Kumar, Yaniv Dror, Anchal Vashishta and Eran Edri; Ben-Gurion University of the Negev, Israel

Coupling a short wavelength infrared (SWIR) PV device with a bandgap of 0.6-0.7 eV to tandem PV technologies can improve overall power conversion efficiency (PCE) by 5-11%. Alternatively, a SWIR device can be used in a thermophotovoltaic system and (ideally) furnish a PCE > 50%. However, there is a limited variety of low-cost light absorbers for the SWIR region. Antimony trichalcogenides, such as Sb_2Se_3, exhibit a large absorption coefficient (~10^5) and a long diffusion length (~1.7 µm). Made of earth-abundant materials and by rapid and low-cost deposition methods, Sb_2Se_3 solar cells with PCE > 10% were recently reported. Three other qualities make Antimony trichalcogenides promising SWIR-PV materials: i) Due to the unique quasi-one-dimensional crystal structure, certain grain boundaries in Sb_2Se_3 thin films are expected to be electronically benign. ii) due to the antibonding states at the top of the valence band, Sb_2Se_3 is expected to be (point) defect tolerant. iii) The bandgap of Sb_2Se_3 can be tuned to the SWIR region by alloying with Bi. Here we report a method for making thin films and solar cells of Bi-alloyed PV. By using closed space sublimation, we successfully incorporated Bi in Sb_2Se_3 up to 40%At. without forming secondary phases. The absorption edge extended from 1050 to 1370 nm. Proof-of-concept solar cells will also be presented.

9:45 AM EN02.14.06
Beyond 6 % Efficient Ultrasonic Spray Deposited Sb_2S_3 Solar Cells from 100 nm Thick Pristine Absorbers for Semi-transparent Applications Sreekanth Mandati, Atanas Katerski, Jako S. Eensalu, Nicolae Spalatu, Malle Krunks and Ilona Oja Acik; Tallinn University of Technology, Estonia

Antimony sulphide (Sb_2S_3) is an emerging semiconductor material with excellent promise for future photovoltaic (PV) technologies owing to its superior optoelectronic properties coupled with earth-abundant and environmentally friendly elements. The relatively wide bandgap of Sb_2S_3 (1.7 eV) makes it wiser choice for application in semi-transparent PV and tandem solar cells. Although the material has potential even for single junction cells with a Shockley-Queisser efficiency limit of ≈ 28 % but the open circuit voltage deficiencies arising from defects and/or self-trapping of photogenerated carriers by lattice deformation limit the maximum efficiency to ≈ 16 %. Therefore, despite numerous attempts and various device architectures, the efficiency of

Sb_2S_3 solar cells is still considerably low with an achieved maximum of 8 %, even for an absorber thickness ranging from 200 nm to over 2 µm. And, most of the high efficiency devices (7-8 %), which utilize an absorber thickness of at least 200 nm, are fabricated by either spin coating, chemical bath deposition (CBD) or vacuum deposition techniques. While CBD has the promise for large area upscaling, its throughput is relatively low and requires longer deposition time (≈ 4 hours). In this context, the study herein demonstrates 6.2 % efficient Sb_2S_3 solar cells from an absorber thickness of ≈ 100 nm deposited using industrially benign and scalable ultrasonic spray pyrolysis (USP) with high throughput (deposition time ≈ 20 min). The solar cells are apt for semi-transparent applications with an average visible transmittance of 27 % (400-800 nm) for the device stack with P3HT as hole transport material without the back metal contact. To the best of authors' knowledge, the efficiency of 6.2 % is a reasonable record achieved for pristine 100 nm Sb_2S_3 absorbers devoid of any doping or post deposition treatment. The individual layers and solar cells are comprehensively characterized using advanced characterization techniques like photoelectron emission spectroscopy, photoluminescence, TRPL, and DLTS to understand the band energetics, device physics, defects and interfaces. The USP process parameters towards obtaining high quality absorbers leading to record efficiencies will be discussed in detail while emphasizing the role of defects on the performance of Sb_2S_3 solar cells. In addition, the roadmap towards complete semi-transparent Sb_2S_3 solar cells by replacing back metal contact, which is being pursued, will be presented.

10:00 AM BREAK

SESSION EN02.15: PSC, OPV and other PV
Session Chairs: Jessica de Wild and Colin Wolden
Friday Morning, April 14, 2023
Moscone West, Level 2, Room 2002

10:30 AM EN02.15.01
Spatio-Temporal Mapping Uncouples Exciton Diffusion from Singlet-Singlet Annihilation in the Electron Acceptor Y6 Giulia Lo Gerfo M.[1], Luca Bolzonello[1], Francisco Bernal-Texca[1], Jordi Martorell[1] and Niek F. van Hulst[2]; [1]ICFO - The Institute of Photonic Science, Spain; [2]ICREA -Institució Catalana de Recerca i Estudis Avançats, Spain

Understanding the spatial dynamics of nanoscale exciton energy transport beyond the temporal decay is at the core of photosynthesis and essential to provide a better framework for further improvements of nanostructured optoelectronic devices, such as solar cells. The diffusion coefficient (D) of photovoltaic films has so far only been determined indirectly, from transient singlet-singlet annihilation (SSA) experiments.
Here, we present the full picture of the exciton distribution dynamics, adding the spatial domain to the temporal one, by spatio-temporally resolved photo-luminescence microscopy. In this way, we directly track diffusion and we are able to decouple the real spatial broadening from its overestimation given by SSA. We measured the diffusion coefficient, $D = 0.017 \pm 0.002$ cm^2/s, of the non-fullerene electron acceptor Y6, which combined with an exciton lifetime of $\tau = 840$ ps, gives a Y6 film diffusion length of $L = (D\tau)^{1/2} \approx 35$ nm. Thus, we provide an essential tool that enables a direct and free-of-artifacts determination of diffusion coefficients, which we expect to be at the core of further methodical studies on exciton dynamics in energy materials.

10:45 AM EN02.15.04
Improvement of Stability of Perovskite Solar Cells with a PbS Buffer Layer Formed by Solution Process Sooah Kim and Taeyoul Yang; Chungnam National University, Korea (the Republic of)

Perovskite solar cells (PSCs) have not yet been commercialized due to their low stability against external factors such as light, moisture, and heat. The migration of iodide ions out of the perovskite is also one of the critical mechanisms of the poor stability of PSCs. In order to inhibit the degradation of PSCs due to external factors and ion migration, it is necessary to form an inorganic buffer layer by surface treatment on the surface of the perovskite. We introduced an inorganic PbS buffer layer by spin coating of Na_2S solution on surface of the perovskite. A PbS buffer layer prevent direct contact of moisture to perovskite and diffusion of the iodide ions. As a result, the PSCs with the PbS buffer layer maintained higher efficiency than those without PbS buffer layer under light and in the moist air and 85 °C heat test. In addition, PbS buffer layer improves charge transfer at the Perovskite/Spiro-OMeTAD interface, so increases power conversion efficiency of PSCs.

11:00 AM EN02.15.05
Halide Perovskite Improved Diffusion Length by AlON Passivation, as Measured by Steady-State Optoelectronic Measurements Anat Itzhak[1], David Keller[1], Tatyana Bendikov[2], Adi Kama[1], Oded Millo[3], Isaac Balberg[3] and David Cahen[1,2]; [1]Bar Ilan University, Israel; [2]Weizmann Institute of Science, Israel; [3]The Hebrew University of Jerusalem, Israel

Metal oxides (MO) are sturdy materials; therefore, MO selective contacts can substantially improve PSCs' stability. However, MO surfaces are reactive, and thus they tend to react at the interface with HaPs and harm both stability and reproducibility of HaP-based electronic devices. ZnO is an extreme case of a reactive MO due to its highly alkaline surface, which readily reacts with HaP. We used steady-state measurements to understand the passivation of ZnO-HaP interface by Aluminum oxynitride (AlON) sub 2 nm layer deposited by atomic layer deposition (ALD). The effect of AlON passivation on the diffusion length of HaP under steady-state conditions, mimic real-life operation conditions for most solar cells. Yet, steady-state measurements require as high as possible photoconductivity (σ_{ph}), which is typically restricted to the absorber. To enable a steady-state charge transport measurement, we used ALD to grow a conformal, ultra-thin (~4 nm) ZnO electron transport layer that is laterally insulating due to its thickness. The formation of ultra-thin continuous inorganic films enables steady-state measurements on stacks of layers. We show that the presence of the AlON layer prevents HaP degradation caused by the interaction with the ZnO layer, improves the HaP σ_{ph}, and doubles the HaP carrier diffusion lengths.

11:15 AM EN02.15.06
Study of Phase Formation of Oxide Derived Cu-Bi-S Compounds Daniely R. Santos[1,2], Lorenzo Milano[3,2], Bjorn Joos[1,2], Jan D'Haen[1], Hans-Gerd Boyen[1], Sudhanshu Shukla[2,1] and Bart Vermang[1,2]; [1]Hasselt University, Belgium; [2]imec, Belgium; [3]Politecnico di Milano, Italy

Copper-based oxides ($Cu_xBi_yO_z$) with a p-type character comprise wide band gap. However, these compounds suffer from the phenomenon of photocorrosion (leading to self-oxidation or self-reduction) and insufficient light absorption, which limits their usage and long-term durability for different applications. To address these limitation, copper-based chalcogenide has shown a prospective alternative. Copper-bismuth chalcogenides, Cu-Bi-S, have been explored as a promising material for solar energy conversion. Recently, devices based on wittichenite-type (Cu_3BiS_3) compound has spurred interest for photovoltaics and water splitting application[1,2], due to its favorable optoelectronic properties, such as p-type conductivity and direct band gap (Eg ≈ 1.10–1.86 eV) with high optical absorption coefficient (>10^5 cm) in the visible region[3]. The aforementioned properties imply that the $Cu_xBi_yS_z$ could be suitable for different applications, however, CBS is still largely unexplored as photo absorber in photovoltaic devices (maximum 1.281% PEC)[4] and as a semiconductor/photocatalyst. This is largely due to the lack of control over different Cu-Bi-S phases, such as Cu_3BiS_3 and $CuBi_3S_5$, for which the stability domains are quite narrow in the phase diagram[5]. In this work, we obtain CBS phases by sulfurization of $Cu_xBi_yO_z$ (CBO) precursor films, with varying Cu:Bi stoichiometry (1:3, 3:1) in the optimized temperature range (350-425°C). The films were characterized by SEM, RAMAN, XRD, optical absorption spectroscopy. XPS studies were performed in order to identify the stoichiometry and oxidation states of the 3:1 and 1:3 (Cu:Bi) precursor sulfurized at the best temperature condition. The results confirmed the total conversion of CBO to CBS. Although mixed phases were identified for both Cu:Bi ratio at different sulfurization temperature, 3:1 (Cu:Bi) precursor film sulfurized at 350°C yields Cu_3BiS_3 single phase, which is corroborated by Raman peaks at 279 and 470 cm^{-1} corresponding to Cu3BiS3 phase. Sulfurization of 1:3 (Cu:Bi) precursor film at 425°C leads to $CuBi_3S_5$ phase; while at 350°C both Cu_3BiS_3 and $CuBi_3S_5$ phases are observed, however, Cu_3BiS_3 is more evident, which is in agreement with Raman. Optical measurements showed that 1:3 and 3:1 (Cu:Bi) precursor sulfurized at 350°C presented similar Eg (1.61 and 1.54 eV, respectively); while 1:3 sulfurized at 425°C has low Eg (1.0 eV), indicating that the presence of $CuBi_3S_5$ phase decreases the band gap energy. Band-edges from XPS confirmed that CBS is promising for different applications.

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SESSION EN02.16: Novel and Emerging IV

Session Chairs: Eric Colegrove and Byungha Shin
Friday Afternoon, April 14, 2023
Moscone West, Level 2, Room 2002

2:00 PM EN02.16.01

2D and 3D Phases of Chalcogenide Perovskites Giulia Longo[1], Prakriti Kayastha[1], Lucy Whalley[1], Devendra Tiwari[1] and Ken Durose[2]; [1]Northumbria University, United Kingdom; [2]University of Liverpool, United Kingdom

Chalcogenide perovskites have been recently under the researchers' spotlight as novel absorber materials for photovoltaic applications. $BaZrS_3$, the most investigated compound of this family, shows high absorption coefficient, a bandgap of around 1.8 eV, and excellent environmental and thermal stability.[1-3] Despite the high temperature synthesis that has been traditionally employed to prepare this material, milder conditions have been successfully applied recently, opening the possibility for its deposition in thin film and device integration.[4] In addition to the 3D perovskite $BaZrS_3$ the Ba-Zr-S compositional space contains 2-D Ruddlesden-Popper phases $Ba_{x+1}Zr_xS_{3x+1}$ (with x= 1, 2, 3) which have recently been reported. [5, 6] It is important to note that, differently from hybrid lead halide perovskites in which RP phases are achieved through the addition of a bigger cation, these lower dimensional phases can be obtained only through stoichiometric variation of the 3D elements. Consequently, 3D-2D mixtures, with different optoelectronic properties compared to the pure phases, can be easily created, requiring a deep understanding and control of the mechanisms to avoid the formation of secondary phases.
In this paper we report solid state synthesis and characterization of Ba-Zr-S phases. In order to avoid the use of the easily oxidised metals the starting materials used were BaS and ZrS_2. We report the protocols for synthesis at 900°C in quartz capsules, changing the precursor ratio BaS: ZrS_2 and revealing the formation of a mixture of 3D and 2D chalcogenide perovskite phases. To carefully resolve the composition, we complemented the XRD, SEM and EDS characterization of the synthetic products with the analysis of the Raman-IR spectra. For this purpose, we calculated the phonon mode, deriving the Raman and IR spectra, for the 3D and 2D Ba-Zr-S chalcogenide perovskites and for the binary precursors. This thorough characterization will show how complex can be to distinguish between different phases in the Ba-Zr-S compositional space, stressing the importance of the use of multiple techniques to soundly resolve the composition of these materials.

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2:15 PM EN02.16.02

Liquid Flux Assisted Growth Mechanism for The Chalcogenide Perovskite – $BaZrS_3$ Kiruba Catherine Vincent, Shubhanshu Agarwal, Jonathan Turnley and Rakesh Agrawal; Purdue University, United States

Chalcogenide perovskites are emerging photovoltaic materials with attractive optoelectronic properties including a high absorption coefficient, tunable bandgap, and high dielectric constant. In contrast to their halide counterparts, these materials have been shown to be stable, and earth-abundant with nontoxic constituents. However, the current rudimentary synthesis techniques have limited the growth of these materials. Traditional solid-state and vacuum processing methods demand temperatures in excess of 800-1000 °C bringing up difficulties in identifying suitable substrates and subsequent device fabrication. Hence, gaining insights into the growth mechanism of these materials becomes integral for engineering robust fabrication methodologies.
To address this, we systematically studied the growth mechanism of the $BaZrS_3$ perovskite through our earlier reported hybrid precursor route utilizing barium thiolate and zirconium hydride precursors. Preliminary findings demonstrate that the high-temperature requirements are related to mass transfer

barriers between precursors rather than thermodynamic limitations. We also identified an accessible liquid phase capable of overcoming these diffusional barriers and driving the reaction towards lower temperatures as well as assisting in grain growth.
In conclusion, this work is focused on understanding the growth mechanism of the $BaZrS_3$ perovskite and identifying the potential liquid phase to drive low-temperature synthesis and support subsequent thin film fabrication.

2:30 PM EN02.16.03
Optoelectronic Characterization of Solution-Processed $BaZrS_3$, $BaHfS_3$, and Ruddlesden-Popper Phases Synthesized Using Dithiocarbamates and Dithiocarboxylates Apurva A. Pradhan, Madeleine Uible, Daniel C. Hayes, Shubhanshu Agarwal, Jonathan Turnley, Suzanne C. Bart and Rakesh Agrawal; Purdue University, United States

Chalcogenide perovskites have recently garnered great interest for photovoltaic applications due to their predicted and experimentally verified high stabilities compared with halide perovskites while retaining their excellent optoelectronic properties. One of the greatest challenges with using chalcogenide perovskites for applications in solar cells is that they have historically required high synthesis temperatures, making them incompatible with the glass substrates and the conductive rear-contact layers required to create a photovoltaic device.
Our group has recently published two routes of synthesizing $BaZrS_3$ and $BaHfS_3$ using solution-deposited routes utilizing inks with solid suspensions. However, both synthesis routes resulted in island growth of these materials. In this work, we explore methods to create continuous films of $BaZrS_3$ and $BaHfS_3$ using inks containing fully dissolved molecular precursors consisting of metal dithiocarbamates and metal dithiocarboxylates. By adjusting the barium to transition metal ratios in the inks, this solution processed synthesis route was also extended to the synthesis of Ba-Zr-S and Ba-Hf-S Ruddlesden-Popper phases, a class of materials that has not been extensively studied. Analytical characterization of the molecular precursors and optoelectronic characterization of the ternary phase materials were then carried out to determine their properties.

2:45 PM BREAK

SESSION EN02.17: Flexible and Bifacial
Session Chairs: Eric Colegrove and Colin Wolden
Friday Afternoon, April 14, 2023
Moscone West, Level 2, Room 2002

3:30 PM EN02.17.01
Radically Reimagining III-V Compound Semiconductor Photovoltaics: Epitaxy-Free Approach to Scalable Synthesis of Flexible Low-Cost Thin Film Solar Cells Phillip Jahelka, Andrew Nyholm, Sara Anjum, Michael Kelzenberg and Harry A. Atwater; California Institute of Technology, United States

For III-V compound semiconductor solar cells to achieve scalability for very large-scale photovoltaics, we need to radically reimagine how they are fabricated. We outline an approach for scalable synthesis of GaAs thin film solar cells that bypasses epitaxial growth and eliminates or minimizes vacuum processing. Starting with thin film absorbers that are formed by mechanical exfoliation from GaAs bulk ingots, we demonstrate that high efficiency cells are possible using methods adopted from silicon and perovskite thin film photovoltaics, such as use of diffused junctions formed at ambient pressures, and solution processing of ohmic contacts and passivation layers using earth-abundant materials. We demonstrate diffused junction GaAs solar cells with 1-Sun AM1.5G efficiencies as high as 23.5%.

Thin-film GaAs photovoltaic pn junction structures were synthesized from bulk GaAs crystals by diffusion doping and spalling to mechanically exfoliate 3-micron thick films of GaAs. The p/n junction is fabricated with a simple zinc-diffusion doping technique, which has yielded open circuit voltages > 960 mV. The films are spalled onto electroplated nickel stressor layers that also serve as the mechanical support for the film. Using 110 oriented GaAs crystals results in large-area mirror-smooth spalled films with 0.1 nm RMS roughness. Preliminary fabrication of thin film diodes yielded implied V_{oc} values over 830 mV, with ideality factor of two, and an absence of parasitic shunts. The diodes are supported on a Kapton tape, demonstrating their potential application for lightweight photovoltaic manufacturing and deployment. These diodes represent the first steps toward high-efficiency low-cost, epitaxy-free, III-V photovoltaics. Finally, we also performed a technoeconomic analysis indicating a scalable pathway for epitaxy/vacuum-free III-V photovoltaics to achieve LCOE parity with future silicon photovoltaics, with a capital cost of 8cent/Watt for module manufacturing.

3:45 PM *EN02.17.02
Bifacial CdTe Photovoltaics: Studies, Progress, and Next Steps Adam Phillips[1], Kamala Khanal Subedi[1], Dipendra Pokhrel[1], Aesha Patel[1], Manoj Jamarkattel[1], Abdul Quader[1], Prabodika N. Kaluarachchi[1], Jared Friedl[1], Tyler Brau[1], Dengbing Li[1], Jialiu Ma[2], James Becker[2], Chungho Lee[2], Gang Xiong[2], Bill Huber[2], Wyatt Metzger[2], Abasi Abudulimu[1], Zhaoning Song[1], Robert W. Collins[1], Nikolas Podraza[1], Yanfa Yan[1], Ebin Bastola[1], Michael J. Heben[1] and Randy Ellingson[1]; [1]University of Toledo, United States; [2]First Solar, United States

The increased energy yield of bifacial PV reduces $/kWh costs and accelerates solar PV adoption. Successful interface passivation at c-Si contacts has enabled excellent bifacial performance for that technology. In contrast, poor electronic and chemical passivation at the back contact of thin film solar cells have thus far prohibited commercially viable bifacial CIGS and CdTe PV technologies, which utilize a p-type polycrystalline absorber. In these devices, the product of electron density and interface recombination velocity yields high recombination current density at the back contact. We review recent progress towards improved experimental and computational understanding and control of the CdTe back contact properties using viable transparent interface materials. As just one example of many, we have studied $CdCl_2$-treated CdTe devices subjected to low-temperature annealing following deposition of copper and chromium nitrate solutions intended to form Cu_xCrO_y as a p-type buffer layer. The approach has demonstrated backside illuminated devices with high current density and high fill factor, with performance that persists even for thicker absorber layers, showing efficient charge collection even without a fully-depleted device. Our modeling efforts aim to delineate whether passivation consists of reduced downward band-bending (electronic passivation), reduced back-contact defect density (chemical passivation) and back surface recombination velocity (BSRV), or both types of passivation. Devices with 8% back-illuminated efficiency and >50% bifaciality have been demonstrated, but significant progress remains in order to demonstrate high-efficiency state-of-the-art devices with beneficial energy yield. Future bifacial performance gains rely on improved understanding and control of the back contact interface, remediating defects to reduce BSRV, and engineering band-bending which propels electrons away from the back contact region. We will also discuss the implications for bifacial CdTe devices of transitioning from Cu-doped to As-doped absorbers.

4:15 PM *EN02.17.03

High-efficiency Flexible Chalcogenide Photovoltaics and Their Tandem Cell Applications Donghyeop Shin[1], Awet Mana Amare[1], Inyoung Jeong[1], Inchan Hwang[1], Soomin Song[1], Young-Joo Eo[1], Ara Cho[1], Jun-Sik Cho[1], Joo Hyung Park[1], Seung Kyu Ahn[1], Jinsu Yoo[1], SeJin Ahn[1], Jihye Gwak[1], Hojin Lee[2], Byungha Shin[2], Jae Ho Yun[3] and Kihwan Kim[1]; [1]Korea Institute of Energy Research, Korea (the Republic of); [2]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [3]Korea Institute of Energy Tecnology, Korea (the Republic of)

<p>Cu-based chalcogenide thin films such as chalcopyrite, kesterite, and etc. have drawn significant attentions as a photovoltaic absorber since the Cu(In,Ga)Se_2 (CIGSe) record cell achieved the power conversion efficiency of 23.35% on a glass substrate. In recent years, there is high demand on lightweight and flexible photovoltaic devices to realize BIPV and VIPV applications. As a result, flexible solar cells have been studied using various flexible substrates such as stainless steel (STS), polyimide (PI), and etc. Furthermore, ultra-thin glass (UTG) is being considered as an emerging potential for flexible solar cells. Despite the successful achievement of high-efficiency flexible CIGSe solar cells (> more than 20%), each flexible material has advantages and disadvantages. The STS substrate contains detrimental Fe element that leads to formation of deep-level defects. Besides, they have a rough surface compared to flat glass substrate. On the other hand, the PI substrate is vulnerable to high-temperature processes so that it is hard to adopt commonly applied conditions (ex. high-temperature process of >550C) for glass substrate to produce high-quality CIGSe films. Presumably, the performance gap between rigid and flexible cells originates from limitations on the material properties and/or high-temperature process. In order to overcome these drawbacks, UTG is also attempted as a flexible substrate of CIGSe solar cells. In this work, we have developed compatible deposition process for high-efficiency CIGSe solar cells on various flexible substrates: STS and PI as well as UTG. Their efficiencies of PV devices on STS, PI, and UTG yielded more than ~19% which was higher than CIGSe solar cells on the rigid glass substrate (~17%). It means that UTG could be also suggested as a novel flexible substrate for CIGSe solar cells. In addition to flexible solar cells, the CIGSe PV devices can be used as a bottom cell in tandem configuration combined with a highly efficient perovskite-based top cell. To maximize use of the full spectrum of incident light, we fabricated monolithic perovskite/CIGSe tandem solar cells. The best tandem cells showed higher than 20%. Consequently, the obtained results indicate that chalcogenide solar cells still possess versatile potential to demonstrate flexible and tandem applications</p>

4:45 PM EN02.17.04
High Performance Bifacial Cu(In,Ga)Se_2 Thin Film Solar Cells and its Application in Tandem Devices with High Power Generation Density Shih-Chi Yang[1], Huagui Lai[1], Tzu-yin Lin[2], Mario Ochoa[3], Radha K. Kothandaraman[1], Ayodhya N. Tiwari[1], Fan Fu[1] and Romain Carron[1]; [1]EMPA, Switzerland; [2]National Tsing Hua University, Taiwan; [3]University of Cantabria, Spain

Thin film solar cells based on polycrystalline Cu(In,Ga)Se_2 (CIGS) have reached efficiencies of 23.35% on glass and 22.2% on flexible substrates to date. It becomes more and more appealing to develop advanced device architectures like bifacial or semi-transparent devices. However, transparent electrical back contacts (TBC) required in these applications typically suffer from unfavorable transport properties due to the formation of detrimental GaO_x at the CIGS/TBC interface after high temperature CIGS deposition process. The combination of short diffusion length of carriers and high rear interface recombination results in low performance under rear illumination. As a result, efficiencies of devices with TBC remain below that of Mo back contact counterparts, with the highest reported efficiency of 16.1%. The highest efficiency of bifacial devices measured under front and rear illuminations are 9.0% and 7.1%, respectively. Therefore, further development of TCO-based devices including bifacial, bifacial tandem, semi-transparent, and ultra-thin rear-back-contact (RBC) devices remained stagnant.

To overcome those challenges, we investigated prospects of reducing the absorber deposition temperature by adding a small amount of Ag (equivalent of few nanometers) in CIGS to get rid of the detrimental GaO_x interface layer while maintaining the high quality of the absorbers. In this work, absorbers were grown by co-evaporation method on Ag-coated ITO/glass substrates at nominal temperatures ranging from 300°C to 450°C. We identify an optimal process temperature of around 350°C, which gives rise to GaO_x-free interface, high absorber quality, high transmittance of ITO back contact and suitable GGI back gradings. A bifacial CIGS solar cell was obtained with efficiencies of 19.77% and 10.89% under front and rear 1-sun illumination, as independently certified by Fraunhofer ISE. To the best of our knowledge, both values are the highest efficiencies reported for a chalcopyrite-based TBC structure.

Finally, we demonstrate high performance 4-terminal bifacial perovskite/CIGS tandem solar cells. We achieved a power generation density of 28.0 mW/cm^2 $BiFi_{300}$ with a gain of 8.9 mW/cm^2 as compared to the performance of the stand-alone CIGS cell. Further improved performance will be presented. Another promising application is all-thin-film 2-terminal bifacial perovskite/CIGS tandem solar devices. Due to higher J_{SC} in the bottom cell resulting from the additional albedo light, the current matching condition allows perovskite top cell with a reduced bandgap, which generally has less stability issue from halide segregation. Therefore, anticipated high performance and improved stability of bifacial monolithic perovskite/CIGS tandem solar cells could feature a prominent place in future photovoltaics markets.

Our study provides insights into the key limiting factors for bifacial CIGS thin film solar cells. It paves the way for the development of not only TBC-based chalcopyrite solar cell architectures but also next generation of PV technologies toward high-energy yield.

SESSION EN02.18: Virtual Session I
Session Chairs: Eric Colegrove and Byungha Shin
Wednesday Morning, April 26, 2023
EN02-virtual

8:30 AM *EN02.18.01
Characterization and Modelling of Thin Dielectric Layers for Advanced PV Cells Denis Flandre; UCLouvain / ICTEAM / ELEN, Belgium

Thin dielectric layers are widely introduced as passivation, tunneling or carrier-transport layers in advanced photovoltaic (PV) cells, implemented in Si as well as more recently other thin-film semiconductor materials.

Specific characterization techniques and physical models need to be considered to identify and assess their electrical properties of importance for the performance of the PV cells.

The main concepts and their significance will be reviewed based on study cases incorporating different reference or innovative materials.

1) The electrical passivation performance (i.e. fixed oxide charges, interface traps and carrier lifetimes) of different Al_2O_3/SiO_2 thin dielectric stacks

realized on monocrystalline Si substrates have been extracted from ac measurements of capacitance (C) and conductance (G) over wide ranges of frequencies and temperatures, with an analytical model comprising a 6-element equivalent circuit [1, 2]. The dc leakage current (I) at low voltage was furthermore related to the trap-assisted tunneling. The effective carrier lifetimes were measured by the contactless photoconductance decay method [3]. Lifetimes of almost 1 ms were obtained at low excess carrier density for the dielectric stack featuring the lowest values of oxide charges, interface states and trap-assisted tunneling current. Bias temperature instability was lately investigated on MOS capacitors, before and after annealing, towards optimizing the process conditions for long-term reliability [4].

2) Such extensive electrical characterization methodology, supported by modelling via numerical simulations (SCAPS, Silvaco Atlas), has been extended to Al_2O_3, HfO_2 and SiO_x layers implemented as a rear passivation layer for ultra-thin (UT) CIGS PV cells [5-7]. Extraction of intrinsic cell parameters from the dark current and ac measurements can be correlated with the PV performance under light [8]. Subsequently, the measured parameters have been introduced in a 2D model of rear-passivated UT-CIGS cells in ATLAS. The model has been exploited to understand and optimize the trade-off between passivation quality and series resistance (related to the ratio of passivated area versus the sizes of the rear opening contacts) that impacts gains or losses of cell performances, confirming experimental trends [9].

3) A third category of materials include TiO_2 or SnO_2 metal oxides that we have studied as electron-transport layers on Si, CIGS or perovskite substrates [10-11]. For such doped oxides, the C-V characteristics often show large variations and unexpected behaviors. Based on simulations that fairly reproduce our main observations and provide new physical insight, the results have been related to full or partial depletion effects, depending on the oxide doping level and thickness.

References : [1] Yan Y. et al, *Microelectronic Engineering* (2022); [2] Yan Y. et al, *Solid-State Electronics* (2022); [3] Yan Y. et al, *Proc. of the IEEE Latin America Electron Devices Conference (LAEDC,* 2021); [4] Yan Y. et al, *submitted* (2022); [5] Kotipalli R. et al, *AIP Advances* (2015); [6] Cunha J. et al, *Solar RRL* (2021); [7] Scaffidi R. et al, *Physica Status Solidi A* (2021); [8] Lontchi J. et al, *E-MRS Spring Meeting Symp. A* (2020, canceled), replaced by *Virtual Chalcogenide PV Conference* 2020; [9] Lontchi J. et al, *IEEE Journal of Photovoltaics* (2020); [10] Lontchi J. et al, *Applied Physics Express* (2021); [11] Cunha J. et al, *Advanced Materials Interfaces* (2021)

9:00 AM EN02.18.02
Effects of Growth Conditions on Formation Behavior of the Recombination Center in $ZnSnP_2$ Bulk Crystals Isshin Sumiyoshi and Yoshitaro Nose; Kyoto University, Japan

Zinc tin diphosphide (ZTP) is an alternative material for commercialized thin-film photovoltaics due to of the non-toxic and earth-abundant constituent elements, the suitable bandgap, and the high absorption coefficient[1,2]. Our group has reported the ZTP bulk crystal-based solar cell with the record conversion efficiency of 3.87% which is still lower than the theoretical limit[3]. In particular, the short circuit current density of 12.1 mA cm^{-2} is lower compared with that of CIGS solar cells, which is probably due to the really short minority carrier lifetime of sub-nanosecond[4].
We prepared ZTP bulk crystals by solution growth method using Sn as flux. In our previous work, the starting composition was on the line of the Sn–ZnP_2 pseudo–binary system[5], while it is well known that the formation behavior of intrinsic defects which could be carrier traps depends on the chemical potentials of constituent elements. In this study, we thus attempted to enhance the minority carrier lifetime of ZTP crystals by the control of composition, namely chemical potentials in the system. We actually performed the crystal growth in the compositions with 1.3 and 4 mol% of Zn (Zn-rich and P-rich) in addition to the conventional composition, and the other conditions were the same in the previous report[5].
We characterized the ZTP crystal grown under the conventional condition by deep-level transient spectroscopy (DLTS) in which Schottky diodes with Ag (Schottky) /ZTP / Cu_3P / Cu (ohmic) were used. DLTS measurement showed that ZTP had two traps for electrons and five traps for holes within the bandgap. Particularly, the nearest electron trap level to conduction band minimum (CBM), E1, had extremely high capture cross section of ~10^{-11} cm^2 compared with other traps. Furthermore the time constant for electron capture from CBM to E1 was estimated to be ~10^{-4} ns, which was equivalent to the reported minority carrier lifetime[4], indicating that the trap E1 might be the recombination center of ZTP.
We also evaluated the influence of growth condition on the properties of recombination. The fluorescence lifetimes of minority carriers were characterized by time-resolved photoluminescence (TRPL) at the photon energy of 1.69 eV under room temperature. The net fluorescence lifetime of samples of Zn-rich, conventional, and P-rich conditions were estimated to be 0.39, 0.066, and 0.065 ns, respectively. The lifetime of Zn-rich sample is higher than others and the results in the literature[4]. Steady–state PL spectra were also measured at 77K and found to be contained several emissions with energy of around 1.28, 1.52, and 1.77 eV. The emission at 1.77 eV might come from Band-to-Band transition and its intensity in the sample of Zn-rich condition was higher than that of others. This indicates that the concentration of the active recombination center E1 is low in Zn-rich sample, which is consistent with the results of TRPL.
In spite of the change of defect properties by growth conditions, the compositions of all the obtained ZTP were stoichiometric. Therefore, it was implied that the compositional difference of a few mole could affect the formation of intrinsic defects, especially related to E1. We consider two contributions of this phenomena from the viewpoint of thermodynamics: entropy and enthalpy. Both of them depend on chemical potentials of constituent elements in the system during crystal growth, where ZTP and liquid are in thermodynamic equilibrium. Hence, we evaluated the chemical potential of elements in liquid phase using sub-regular solution model, and clarified the precipitation temperature is lower in Zn-rich condition. In the presentation, we will discuss more quantitatively the effects of the entropy and the enthalpy on the formation of defects in ZTP.
[1] S. Nakatsuka and Y. Nose, *JPCC* (2017). [2] T. Yokoyama et al., *APEX* (2013). [3] T. Kuwano et al., *SOLMAT* (2021). [4] S. Nakatsuka et al., *PSSa* (2017). [5] S. Nakatsuka et al., *PSSc* (2015).

9:05 AM EN02.18.03
Multiwavelength Excitation Raman Scattering Study of Sb_2S_3: Fundamental Vibrational Properties and Application in the Evaluation of Crystallographic Orientation Victoria Rotaru[1], Pedro Vidal-Fuentes[1], Alex J. Lopez-Garcia[1], Tariq Jawhari[2], Xavier Alcobé[2], Alejandro Perez-Rodriguez[1,3], Victor Izquierdo-Roca[1] and Maxim Guc[1]; [1]Catalonia Institute for Energy Research (IREC), Spain; [2]Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB), Spain; [3]Departament d'Enginyeria Electrònica i Biomèdica, Universitat de Barcelona, Spain

Sb_2S_3 has become popular in several research fields [1,2] and most prominently among the PV community, achieving efficiency values close to 8% in short time. One of the key aspects of this compound is its high structural anisotropy, where the atoms are bonded by covalent bonds along one crystallographic axis forming ribbons, which are attached together by van der Waals forces along the other two directions [3]. This translates into highly anisotropic properties that are, in fact, an important parameter to control when implementing Sb_2S_3 in optoelectronic devices, where, for example, increased mobility is achieved along the covalently bonded axis. Likewise, this anisotropy is expected to have a strong impact on the vibrational properties of Sb_2S_3.
Being a material that attracted significant interest in the last years, the vibrational properties of this anisotropic compound are still not properly understood in the literature. In order to establish a clearer understanding of the discrepancies between Raman spectra of Sb_2S_3 in existing articles, an investigation of the fundamental vibrational properties of the Sb_2S_3 compound by Multiwavelength Raman spectroscopy was performed. As a starting point, in order to fully identify the features present in the Raman spectra of Sb_2S_3, a single crystal grains powder sample was analyzed in order to minimize the possible influence of the crystallographic orientation, with a multiwavelength approach using eight excitation wavelengths in the range from 325 up to 1064 nm.

Resonance and pre-resonance effect yielded changes in the intensity of several Raman peaks, highlighting them in dependence on the excitation laser employed. Furthermore, low temperature (~20 K) measurements were also carried out with λ_{ex} = 632.8 nm excitation on the powder sample, reducing the thermal agitation of the material and reducing the width of the peaks, which allowed to better resolve the low intensity peaks. Finally, polarization dependent Raman scattering measurements have been also performed on a Sb_2S_3 single crystal mineral, which not only enrich the knowledge about the specific peaks, but also give rise to some changes in peak intensities in the different configurations. As a result, the deconvolution of the obtained Raman spectra for each wavelength, polarization and temperature was performed, thus enabling the generation of a complete fitting function using a combination of Lorentzian curves. This permitted us to establish the position of up to 19 Raman active optical modes from the 30 theoretically predicted, which serves as an important stepping stone for the correct interpretation of the experiments through all the research fields interested in the material.
The study is completed by a deeper analysis of the Sb_2S_3 single crystal mineral. X-ray diffraction analysis allowed to identify the specific crystallographic orientation of these facets, and Raman scattering measurements showed a clear difference in the spectra measured at different fundamental crystallographic planes. The found variations allow the implementation of Raman spectroscopy, a non-invasive technique with lateral micrometric precision, to be used as a quality control tool for the in-situ and in-sample crystallographic orientation assessment of Sb_2S_3 thin films that are proposed as emerging PV technologies with a relevant cost-efficient potential. Finally, application of Raman scattering in device grade layers and finished solar cells corroborates the potential of the technique for the identification of the potential presence of secondary phases and the crystalline assessment of the layers, which provides with a powerful non-destructive characterization tool for device optimization.

This work is part of the R+D+i MaterOne project Ref. PID 2020-116719RB-C42 funded by MCIN/AEI/10.13039/5011000110033.

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9:20 AM EN02.18.04

Engineering a Thin-Film Absorber of Silver Antimony Sulfur Selenide Solar Cells Sanghyun Lee[1] and Kent Price[2]; [1]University of Kentucky, United States; [2]Morehead State University, United States

Silver Antimony Sulfur Selenide, $AgSb(S_xSe_{1-x})_3$ thin-film solar cells have been emerging as third-generation photovoltaic devices with promising properties of the tunable bandgap (0.7 - 1.9 eV), good doping concentration (10^{16} cm^{-3}), high absorption coefficient (>10^4 cm^{-1}), and simplified processing conditions with high vapor pressure and low melting point (550 C). There have been several studies about $AgSb(S_xSe_{1-x})_3$ thin-film absorbers by depositing $Sb_2(S_xSe_{1-x})_3$, Ag, and Se thin-film precursors, followed by the heat treatment. With the favorable optical bandgap of $AgSb(S_xSe_{1-x})_3$ thin-films (x=0.53, 0.58, and 0.61), the efficiency has been improved with >2.77 %. In another approaches, $AgSbSe_3$ thin-film absorber devices demonstrate <0.1 %, whereas $AgSbS_3$ thin-films devices show approximately 0.27 %. Since Antimony Sulfur Selenide, $Sb(S_xSe_{1-x})_3$ thin-films have demonstrated good optical and electronic properties as an absorber layer, further optimization of thin-film absorber layers could be achieved by utilizing both $Sb(S_xSe_{1-x})_3$ and $AgSb(S_xSe_{1-x})_3$ thin-films. As we reported earlier, substituting Ag in $Sb(S_xSe_{1-x})_3$ thin-films tends to increase the bandgap of the absorber layer by lowering the valence band based on studies of other thin-film absorber layers such as Copper Indium Gallium Diselenide (CIGS) and Copper Zinc Tin Sulfur Selenide (CZTSSe) thin-films.

In this study, we have conducted a theoretical study on thin-film absorbers of $AgSb(S_xSe_{1-x})_3$, $Sb(S_xSe_{1-x})_3$, and the combination of $AgSb(S_xSe_{1-x})_3$ and $Sb(S_xSe_{1-x})_3$ thin-films from the electronic band structure perspective. To fully utilize the promising properties of both $Sb_2(S_xSe_{1-x})_3$ and $AgSb(S_xSe_{1-x})_3$ films, we investigated different compositions and concentrations of Sulfur and Selenium with proposed empirical equations for electron affinity and bandgap energy. Furthermore, we varied the doping of thin-film absorbers to search for the optimal conditions for the band alignment to Molybdenum metal back contact films. For our analytical simulation, we have used in-house MATLAB modeling suites that have been developed in our group.

Four different structures of thin-film absorbers have been modeled above Molybdenum metal thin-films. The workfunction of Molybdenum metal thin-films is 4.9 eV and an inevitable MoS_xSe_{1-x} interlayer was inserted during our simulation throughout this study. For both $AgSb(S_xSe_{1-x})_3$ and $Sb(S_xSe_{1-x})_3$ thin-films, the electron affinity and bandgap energy increase as Sulfur (x) composition increases. However, the increased bandgap is not directly translated into improved solar cells efficiency due to the alignment of thin-film electronic structures. For example, the best efficiency was achieved with 2 um $AgSb(S_{0.4}Se_{0.6})_3$ thin-film devices (18.4 %) at sulfur concentration, x = 0.4. However, once we combine two $AgSb(S_xSe_{1-x})_3$ and $Sb(S_xSe_{1-x})_3$ thin-films while keeping a total thickness, 2 um (1 um/1 um), an interface between $AgSb(S_{0.4}Se_{0.6})_3$/ $Sb_2(S_{0.4}Se_{0.6})_3$ and Molybdenum metal thin-films is preferably formed due to reduced effective Schottky hole barrier. If we assume the same amount of defect states at the interface, the improved effective Schottky hole barrier is 128 mV due to the favorable band alignment, which is approximate 4.3 times better than a $AgSb(S_{0.4}Se_{0.6})_3$ thin-film structure. With a bi-layer $AgSb(S_{0.4}Se_{0.6})_3/Sb_2(S_{0.4}Se_{0.6})_3$ thin-film absorber, we studied various doping concentrations impact on device efficiency based on the modified electronic band structure of each thin-film. The doping concentration of a $AgSb(S_{0.4}Se_{0.6})_3$ thin-film mainly increases the photogenerated current while a $Sb_2(S_{0.4}Se_{0.6})_3$ thin-film improves open circuit voltage.

9:35 AM EN02.18.05

Double In and Ga Donor Doping and Self-Compensating Process in ZnO Nanocrystal Films Tetyana v. Torchynska[1], Brahim el Filali[1], Georgiy Polupan[1] and Lyudmyla Shcherbyna[2]; [1]Instituto Politecnico Nacional, Mexico; [2]4V.Lashkaryov Institute of Semiconductor Physics at the NASU, Ukraine

Zinc oxide has attracted attention for decades due to its important optical, electrical, chemical and microstructural properties, interesting for optoelectronic applications in light emitting devices, transparent conduction oxide (TCO) in solar cells, gas sensors, flat screens and touch panel displays, in vacuum fluorescent displays, in photovoltaics or thermal mirrors. But the n-type conductivity of non-doped ZnO films is not high enough to be used in devices. Group–III atoms (Al, Ga, In) are very important donors for ZnO film–based technology. However, the free electron density in doped ZnO films was revealed to be limited to 10^{19} - 10^{21} cm$^{-3.}$ due to the self-compensating effect, related to generation of the acceptor-type defects to counteract of donor doping. The nature of these acceptor type defects and the factors that stimulate the self-compensating effect still remain to be investigated.
It was supposed that one reason for the self – compensating effect can be connected with a high level of elastic stresses in the doped ZnO films with high donor contents. In the present work, the variation of the optical, structural and electrical parameters of the ZnO nanocrystal (NC) films doped with Ga and In atoms has been investigated. ZnO films of 2 groups were grown by ultrasonic spray pyrolysis with the In contents 1.0 at% (1) or 2.0 at% (2) and the different concentrations of Ga from the range 0.5-3.0 at %. Using co-doping by Ga and In atoms with lower (Ga) and higher (In) ionic radii compared to the Zn ions, it is expected to lower the stresses in the films and gain insight into the factors favored to the self-compensating effect.
The ZnO films have been studied using scanning electron microscopy (SEM), energy dispersive X ray spectroscopy (EDS), X ray diffraction (XRD), photoluminescence (PL) and X-ray photo electronic spectroscopy (XPS). Non-monotonic changes in the morphology of films were revealed that correlates with non-monotonic changes of oxygen and indium contents in ZnO films with variation of Ga contents. Compressive stresses arising due to In doping prevent effective oxidation at the film crystallization. The Ga doping up to 1.5 at% allows to compensate the compressive stresses in the films that is favored to the effective ZnO oxidation and the dissolution of In ions in the thermal annealing. High donor doping was shown to be accompanied by the

appearance of a new near band edge (NBE) emission band, related to carrier recombination in the shallow donor-acceptor pairs (DAPs), which is a "fingerprint" of a beginning of the self-compensating process. Simultaneously, the effective charges of the Ga (In) ions decrease and the rate of electrical resistivity reduction slows down. The nature of shallow donors and acceptors in DAPs, as well as the impact of co-doping by Ga and In atoms on the self-compensating effect have been discussed.

9:40 AM EN02.13.01
Growth of $SrHfS_3$ and $SrZrS_3$ Thin Film by Magnetron Sputtering Haolei Hui[1], Zhonghai Yu[2], Chang Huai[1], Thomas Hahn[1], Sen Yang[2] and Hao Zeng[1]; [1]University at Buffalo, The State University of New York, United States; [2]Xi'an Jiao Tong University, China

Chalcogenide perovskite is an emerging class of semiconductor materials with potential applications in electronics and optoelectronics. $SrHfS_3$ in the distorted perovskite structure is shown to be a direct gap semiconductor with strong green photoluminescence. Together with its high stability defect tolerance, it many find applications such as LEDs. In this work we report the synthesis of $SrHfS_3$ and $SrZrS_3$ thin films by magnetron sputtering using metal targets, followed by CS_2 sulfurization. Salts was used improve the film crystallinity. Sample growth on conductive substrates was also attempted, with an eye for device fabrications. Our work demonstrates a new way of fabricating $SrHfS_3$ and $SrZrS_3$ thin films with controllable composition.

9:45 AM EN02.04.19
Surface Photovoltage Spectroscopy to Evaluate Rear Passivation Strategies in CdTe Photovoltaics Nathan D. Rock[1], Mike Scarpulla[1], Kristopher O. Davis[2] and Amit Munshi[3]; [1]University of Utah, United States; [2]University of Central Florida, United States; [3]Colorado State University, United States

We present developments in surface photovoltaic spectroscopy (SPS), aimed at characterizing passivation strategies for CdTe cell interfaces, particularly the rear contact. Effective rear contact passivation has been predicted to increase device efficiency by as much as 3.5% when coupled with a hole selective contact. We demonstrate how SPS is a critical tool in evaluating novel solutions to eliminate voltage loss at interfaces. We examine the effect of known wet etchant strategies on SPS signal, correlating and contrasting the information gained with that available via TRPL. We also explore passivating interface layers in CdTe and Si based devices. SPS signals are evaluated via SCAPS 1D modeling and analytical modeling and the effects of surface recombination velocity, band bending, and recombination in bulk and SCR are extracted.

SESSION EN02.19: Virtual Session II
Session Chairs: Jessica de Wild and Colin Wolden
Thursday Morning, April 27, 2023
EN02-virtual

8:30 AM *EN02.19.01
Silver-Alloying in Wide-Gap CIGS Absorbers—Challenges and Latest Advances Toward Application in a Tandem Device Jan Keller, Lars Stolt, Patrick Pearson, Kostiantyn Sopiha and Marika Edoff; Uppsala University, Sweden

This presentation summarizes our latest research on wide-gap, silver-alloyed $Cu(In,Ga)Se_2$ (CIGS) solar cells (i.e. forming ACIGS). The processed absorber layers had band gap values (E_G) in the range of 1.40 to 1.65 eV, making them attractive for application in top cells of tandem devices. To reach this high E_G level, the [Ga]/([Ga]+[In]) (GGI) ratio needs to be at least 0.65. For pure CIGS solar cells, such high Ga concentrations not only lead to a large deficit in open-circuit voltage (V_{OC}), but also to a distinct deficit in short-circuit current density (J_{SC}) and fill factor (FF). The main problem seems to be a deteriorating absorber quality with increasing GGI. However, since the application of alternative buffer layers can mitigate the V_{OC} loss, wide-gap CIGS devices with standard CdS buffers must be partly limited by interface recombination as well.

Alloying silver into wide-gap CIGS has been explored by several groups before [1-3]. Although the performance gap to low-E_G devices could not be closed completely, the results highlight the potential for solar cells with $E_G > 1.4$ eV.

In our recent works [4-8], we first focused on identifying the optimum compositional window for high-performance ACIGS solar cells, while keeping the GGI level above 0.65. Calculations based on density functional theory show that the conduction band shifts downwards with Ag addition. A beneficial positive conduction band offset with CdS is predicted for an [Ag]/([Ag]+[Cu]) (AAC) value of at least 0.3 (increasing with increasing GGI). Our experimental results, with highest efficiencies for AAC = 0.5 at a band gap of 1.45 eV (GGI = 0.72), confirmed this trend. The champion device with a (Zn,Sn)O buffer exhibited an efficiency of 15.1% without anti-reflection coating (ARC) [4]. However, for higher GGI and AAC values (i.e. $E_G > 1.5$ eV), the efficiency starts to decline significantly.

To investigate the limitations for ACIGS solar cells with higher E_G, the effect of the absorber stoichiometry was studied for a constant GGI = 0.85 and AAC = 0.8, yielding $E_G = 1.62$ eV (i.e. sweet-spot for tandem applications) [5]. It was found that already a minor group-I deficiency leads to a substantial formation of ordered vacancy compounds (OVCs). For too off-stoichiometric ACIGS, OVC patches form at the back interface, leading to a significant FF drop. The highest efficiency of 10.2% (no ARC) is reached for a reverse voltage sweep (hysteresis found).

Next, the AAC and GGI ratios were simultaneously reduced again to about 0.60 and 0.75, respectively. Although the OVC formation was mitigated, our analysis of a large sample set proved a clear stoichiometry effect on the solar cell characteristics [6]. It was revealed that near-stoichiometric absorbers approach full depletion, whereas off-stoichiometric materials have doping densities "common" for CIGS absorbers. Due to the generally low diffusion length, this results in a low carrier collection (but higher V_{OC}) for off-stoichiometric, and perfect carrier collection (but lower V_{OC}) for stoichiometric samples. Consequently, the highest V_{OC} of 916 mV was measured for an off-stoichiometric sample ($E_G = 1.46$ eV, CdS buffer). By applying an RbF post-deposition treatment, the V_{OC} could be further increased to 926 mV and an efficiency of 16.3% (no ARC) was achieved [7].

Finally, the Mo back contact was exchanged by an In_2O_3:H film, with almost complete near-infrared transparency [8]. After fine-tuning the sodium supply, an efficiency of 12% (no ARC) was reached, using a stoichiometric ACIGS absorber with $E_G = 1.44$ eV.

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[4] J. Keller et al., Prog. Photovoltaics Res. Appl. 2020, 28, 237.

[5] J. Keller et al., Sol. RRL 2020, 4, 2000508.
[6] J. Keller et al., Sol. RRL 2021, 5, 2100403.
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[8] J. Keller et al., Sol. RRL. 2022, 6, 2200401.

9:00 AM EN02.19.02
Characterisation of Electronic Defects on the Sub-Micron Scale of the Absorber-Buffer Interface between $Cu_2ZnSn(S,Se)_4$ and ZnSnO Alice Sheppard, Raphael E. Agbenyeke, Jude Laverock, Neil A. Fox and David J. Fermin; University of Bristol, United Kingdom

Transitioning into global carbon neutrality by 2050 is vital to ensure the health and future of Earth. The fabrication of a low-cost, high efficiency thin film photovoltaic (PV) material for building-integrated PV will help fulfil the need for renewable energy sources moving forward. $Cu_2ZnSn(S,Se)_4$ (CZTSSe) is an earth-abundant, non-toxic thin film solar absorber with a theoretical power conversion efficiency (PCE) of 20%, [1] and can help fulfil this PV requirement. Severe voltage deficits due to deep-level defects and interfacial recombination have plagued the performance of a CZTSSe/CdS device, where little is known about the surface electronic landscape of the key absorber-buffer interface. This study replaces the use of toxic CdS with ZnSnO (ZTO) as the buffer material, deposited using atomic layer deposition, due to ZTO having a larger, tuneable bandgap between 3.3 to 3.7 eV. The electronic structure of the CZTSSe/ZTO interface will be probed using energy-filtered photoemission electron microscopy (EF-PEEM) to identify possible harmful features hindering performance. Furthermore, band alignment studies, using ultraviolet photoelectron spectroscopy, will investigate the suitability of ZTO as a buffer layer.

[1]: S. Kim, J. A. Márquez, T. Unold and A. Walsh, Energy Environ. Sci., 2020, 13, 1481-1491

9:15 AM EN02.19.03
Mapping the Energetics of Bulk and Surface Defect States in Solution-Processed Cu_2ZnSnS_4 Thin-Film David J. Fermin[1], Devendra Tiwari[2], Alice Sheppard[1] and Raphael E. Agbenyeke[1]; [1]University of Bristol, United Kingdom; [2]Northumbria University, United Kingdom

Inorganic solar cells based on $Cu_2ZnSn(S_xSe_{1-x})_4$ thin-film absorbers have reached power conversion values of 11.5% [1] and 13.0 % [2] in the sulfide and sulfo-selenide forms, respectively. Although these performance levels are some of the most promising in In-free *substrate* device configuration, they remain far below their theoretical limit.[3] It is widely recognised that cell voltage is the key limiting factor in these devices, and a variety of strategies have been investigated including doping and alloying the absorber layer.[4-6]

The complexity in the composition of these compound semiconductors offers key advantages such as tuneable band energetics, but also brings about significant challenges in terms of secondary phases and point defects which can be detrimental to device performance.[7] For instance, voltage loss has been linked Cu/Zn antisites as well as Sn defect.[3,7,8] In this contribution, we investigate the position and distribution of defect states in the bulk and at the surface of Cu_2ZnSnS_4 (CZTS) thin films prepared by solution based methods, employing variable temperature photoluminescence (PL) spectroscopy and high-resolution energy-filtered photoemission of electron microscopy (EF-PEEM), a technique which can unravel valuable information on variations of the surface electronic properties of these complex materials.[9,10,11]

Variable temperature PL spectra are dominated by emission from quasi-donor acceptor pairs (QDAP) with activation energy values strongly affected by the introduction Sb and Na:Sb as dopants.[12] Indeed, we will show that incorporation of Sb in the range 0.05% wt leads to a clear transition from localized to non-localized QDAP emission. EF-PEEM also reveals significant changes in the surface electronic landscape upon doping, with mean local effective work function decreasing by more than 0.2 eV upon Sb doping. PL and EF-PEEM clearly show that Na can regulate Sb doping levels, keeping the same PL characteristics of CZTS without any added dopants but with a smoother surface electronic landscape as probed by EF-PEEM.[10,12] We will also correlate variable temperature PL of the thin-films with variable temperature admittance spectroscopy of full devices. This analysis allows linking spectroscopic signatures associated with Cu/Zn and Sn defect states with admittance responses of the device. We will show that dopants such as Na and Sb can affect not only carrier density, but also decrease the density of defects associated with elemental disorder in the film as well as the relative position of the band edges, which can have a profound defect in device performance.

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9. D. Tiwari et al. iScience 9 (2018) 36
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12. D. Tiwari et al. ACS Appl. Energy Mater. 5 (2022) 3933

9:30 AM EN02.19.04
Tails States, Voc Loss and Semiconductor Compensation Susanne Siebentritt and Omar Ramirez; Univ of Luxembourg, Luxembourg

It has been shown for many solar cell absorbers that Voc loss correlates with the Urbach energy, that describes the decay of tail states into the band gap. In chalcopyrites it was furthermore observed that heavy alkali postdeposition treatments reduce both: Urbach energy and Voc loss. This behaviour has been attributed to passivation of grain boundaries [1]. However, recently we have shown, that alkali treatment in single crystalline films without grain boundaries also leads to a reduction of Voc loss and Urbach energies [2]. This behaviour can be traced back to a reduced compensation by increasing the doping level [3]. It is to be expected that a similar mechanism plays a role in polycrystalline films.
Part of the dependence of the Voc loss on Urbach energy can be attributed to radiative and non-radiative recombination in and through tail states [4]. However, the dependence is stronger than would be expected from the increased recombination. We now understand that this is due to a simultaneity: increasing doping has a simultaneous effect, increasing Voc and decreasing tail states.
Thus, we propose, that one effect of heavy alkali treatment is due to the observed increase of Na doping inside the grains, because it increases the net-doping, reduces tail states and thereby reduces radiative and non-radiative recombination. All this increases Voc.

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9:45 AM EL15.06.04
UV and X-ray Stability of CsPbBr$_3$ Perovskite Nanocrystals Azmat Ali[1], Fredrik O. Johansson[1,2], Mariam Ahmad[3], Hervé Cruguel[1], Erika Giangrisostomi[4], Ruslan Ovsyannikov[4], Lenart Dudy[5], Mathieu G. Silly[5], Morten Madsen[3], Emmanuel L'Huillier[1] and Nadine Witkowski[1]; [1]Sorbonne Université, France; [2]KTH Royal Institute of Technology, Sweden; [3]University of Southern Denmark, Denmark; [4]Institute for Methods and Instrumentation in Synchrotron Radiation Research, Germany; [5]Synchrotron SOLEIL, France

Understanding of electronic band structure and charge carrier dynamics of halide perovskites and their interface is critical for the advancement of perovskite photovoltaics[1,2]. Inorganic Cesium lead bromide (CsPbBr$_3$) perovskite nanocrystals (NCs) with a bandgap of 2.3 eV are regarded as one of the potential candidates as an active layer in solar cells devices, thanks to significant progress made recently in terms of improving its intrinsic properties and stability under environmental conditions. However, stability under UV and X-ray exposure remains an open question[3-6]. The stability of spin-coated CsPbBr$_3$ NCs deposited on gold (Au) substrates is investigated here under the impact of the UV laser light and X-rays. Under the UV laser pulse, the NCs exhibit distinctly different behavior depending upon the energy of the laser pulse, its fluence and time NCs exposed to it. When the NCs are exposed to UV laser pulses with the photon energy of 3.6 eV (greater than the bandgap), the NCs are modified irreversibly. Both metallic lead and ionic lead with a new component of Pb4f are detected in the Pb4f core-level spectra. Similarly, when NCs exposed exclusively to X-ray with high flux, same components of Pb4f were found in Pb4f spectrum. The modification is more or less similar in either case; however, under UV laser exposure, a large chemical shift of 0.69 eV towards higher binding energy observed after the exposure, which is not the case with X-ray exposure alone. The chemical shift could be attributed to the accumulation of charge carriers at the interface under UV laser and getting trapped by the metallic lead (donor-type surface states) [6]. Therefore, depending on the type of radiation exposure either UV laser or X-rays, the CsPbBr$_3$ NCs show different behavior and thus the energy level alignments. We show that the chemical properties of NCs are sensitive to UV laser and X-rays irradiation, and investigation of these changes under the type of radiation exposure might help us understand the underlying phenomenon that governs these changes.

SYMPOSIUM

April 11 - April 27, 2023

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SESSION EN03.01: Magnetocaloric Materials and Devices I
Session Chairs: Franca Albertini and Xavier Moya
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2003

10:30 AM *EN03.01.01
Thermal Management in Caloric Devices Andrej Kitanovski, Katja Klinar, Katja Vozel and Nada Petelin; University of Ljubljana, Slovenia

Caloric energy conversion is an emerging field of cooling, heat-pumping and power-generation technologies. The potentially high energy efficiency and use of environmentally friendly and safe solid-state working substances has stimulated increased research activity in the past two decades. Most of today's caloric devices use so-called active regeneration, in which the working fluid oscillates through the matrix of the caloric material - the caloric regenerator. This is associated with irreversible viscous and heat-transfer losses and limits the operating frequency and related power density of the device.

Thermal Control Devices (TCDs) represent an alternative thermal management technique to active regeneration processes, which are widely used as a heat transfer principle in caloric technologies. TCDs allow non-linear, switchable and active control of the heat, similar to the control of electrical current by their electrical counterparts. Their integration in the form of thermal diodes, thermal switches, thermal regulators, and thermal conductors in caloric energy conversion system has the potential to significantly increase power density through rapid and oscillatory heat transfer from/to the caloric material and the heat sink/source while maintaining high energy efficiency, thus meeting the most important market condition and facilitating the commercialization of caloric technologies.
Despite some research activities on TCDs integrated in caloric technologies, research in this particular area is still at an early stage. There is a great lack of knowledge and experience regarding the operational performance of the different types of TCDs as well as their performance when integrated into caloric

devices. On the other hand, the scientific community dealing with materials should focus on various possible (new) materials or their composites, whose thermal properties correspond to the desired properties of thermal diodes, and approach them systematically with proper data collection on their thermal properties.

In this work, we provide a critical and an up-to-date review on the research activities and applications of TCDs in all types of caloric devices, as well as an overview of various mechanisms that have not yet been applied in calorics. Based on this, we provide guidelines and target characteristics for future research activities in the field of caloric technologies.

11:00 AM *EN03.01.02
Materials Design for Fe-Based Magnetic Refrigerants from the Perspective of Utilization for the AMR-Type Modules Asaya Fujita; AIST Chubu, Japan

Among various types of caloric phenomena, magnetocaloric effect is relatively easy to control in a non-contact external field, and therefore, external-field sources are installed by keeping thermal insulation from the heart of the thermal cycle. Meanwhile, attenuation of magnetic flux according to the Coulomb law leads to "gigantic" scales in both the size and cost of the magnetic field generators, such as the electromagnetic or permanent-magnet circuits. For the portability and cost-reduction of the magnetic heat-pump systems, a central issue imposed on materials is a compatibility between realization of highly sensitive magnetocaloric response against smaller magnetic fields, and superior workability for forming compact and efficient beds.
Our recent benchmark in an isothermal entropy change $\triangle S_M$ reaches about 20 J/kg K under 1 T for $(La,Pr)(Fe,Mn,Si)_{13}H$ compounds around 300 K. However, in the active magnetic regenerator (AMR)-type system, which is considered as a most viable technology, no isothermal process is incorporated but only iso-field and adiabatic temperature changes construct the heat cycle. Accordingly, the critical metrics are amount of latent heat η under (even) zero magnetic field and a span of adiabatic temperature change $\triangle T_{ad}$. In this work, we will introduce recent achievements in the materials design, in addition to the theoretical aspect, to improve and analyze η and $\triangle T_{ad}$. We also evaluate the durability of magnetocaloric performance against various fabrication techniques of the bed with integrated microchannel structures. In this regard, careful attention must be paid on the metallographic aspects such as the peritectic reaction in phase diagram, and affinity for (contaminating) light elements. We will discuss the advantages and disadvantages of each method for the bed fabrication.

11:30 AM *EN03.01.03
A Material Study on Magnetocaloric Liquefaction of Hydrogen Tino Gottschall, Eduard Bykov, Timo Niehoff, Marc Strassheim and Catalina Salazar-Mejia; Helmholtz-Zentrum Dresden-Rossendorf, Germany

Magnetic cooling is a refrigeration technique that is based on the so-called magnetocaloric effect, the change of temperature caused by a magnetic field [1]. It can be utilized to construct environmentally friendly cooling devices, air conditioners, and heat pumps [2]. Originally, magnetic cooling was used to achieve ultra-low temperatures by adiabatic demagnetization of magnetic salts. Recently, low temperatures have once again become the focus of attention as an area of application for magnetocaloric cooling namely for hydrogen liquefaction [3,4].

Hydrogen is light, energy dense and clean. If produced from sustainable resources, it represents the ultimate energy carrier for many of our needs. Liquid hydrogen has more than twice the energy density of the gas at 700 bars. What is more, it can be transported in conventional, unpressurised dewars. However, conventional liquefaction means we use 40 % of the energy content of the gas we are compressing, just to liquefy it! Magnetocaloric materials enable an alternative and more efficient approach. A large number of compounds are already known that show magnetocaloric effects in the desired temperature range and new candidates are constantly being added. In this work, we would like to discuss our current progress for the creation of a materials library for cryogenic applications. The basis for this is our characterization infrastructure for materials research at the Dresden High Magnetic Field Laboratory in static and pulsed fields. With this, we want to able to understand these materials in order to further optimize the magnetic-cooling performance near the boiling temperature of hydrogen.

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SESSION EN03.02: Elastocaloric Materials and Devices I
Session Chairs: Ichiro Takeuchi and Jaka Tusek
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2003

1:30 PM *EN03.02.01
Caloric Effects Owing to Elastic Coupling at Electronic Phase Transitions Peter Littlewood[1], Charles Liang[2] and Gian Guzman-Verri[3]; [1]U Chicago, United States; [2]University of Chicago, United States; [3]University of Costa Rica, Costa Rica

All electronically driven phase transitions are coupled to local ionic displacements, sometimes as their principal manifestation (e.g. charge density waves, ferroelectrics) and sometimes as a side effect (e.g. magnetism, metal to insulator transitions).
The coupling to the lattice induces elastic strain fields, which have intrinsic long-range interactions, which deform the metric of space and cannot be screened. When strain fields are produced as a secondary order parameter in phase transitions - as for example in ferroelectrics - this produces unexpected consequences for the dynamics of order parameter fluctuations.
I will discuss the consequences of electro-strictive coupling in Mott insulators such as the nickelates[1] and phase change materials such as GeTe[2], and flexoelectric coupling for the so-called quantum paraelectrics such as strontium titanate[3].

GG Guzmán-Verri, RT Brierley, PB Littlewood Nature 576 (7787), 429-432 (2019)
SAJ Kimber, *et al.,* arXiv preprint arXiv:2202.05565
GG Guzmán-Verri, CH Liang, PB Littlewood, arXiv preprint arXiv:2205.14171

2:00 PM *EN03.02.02

Elastocaloric Measurements of Quantum Materials—The Case of $TmVO_4$ and the Prospect of Cryogenic Elastocaloric Cooling Ian R. Fisher; Stanford University, United States

We have developed an AC method to probe the elastocaloric effect and have applied it to a variety of quantum materials. The technique can be used to study the entropy landscape associated with continuous phase transitions, but is especially useful for the study of materials for which strain couples to order parameter fluctuations in non-trivial ways. In particular, I will discuss the elastocaloric signature of nematic fluctuations, and the observation of a giant elastocaloric effect in $TmVO_4$, a material that provides a prototypical example of the cooperative Jahn-Teller effect at low temperature.

2:30 PM *EN03.02.03
The Origin of Functional Fatigue in Shape Memory Alloys Huseyin Sehitoglu and Ahmed Sameer Khan Mohammed; University of Illinois, United States

There are a large number of elasto-caloric shape memory alloys (SMAs) with considerable future potential. However, the functionality of SMAs degrades with cycling and this is common to all shape memory alloys with no exception. The degradation of functionality means that the transformation strains decrease and the transformation domains reduce with cycling. The degradation results in changes in hysteresis and transformation stress as well. If the loops shakedown to an elastic state in the limit, the forward and reverse transformation no longer occurs and elasto-caloric effect would disappear. The presentation will explain the underlying causes of the cyclic-induced degradation in shape memory alloys from theoretical considerations. In particular, we will focus on generation of dislocations from crystallographic misfit at interfaces using advanced theory, including first principle calculations, anisotropic elasticity, and theory of martensitic transformations. This understanding at the lattice level will allow refined phenomenological models to be developed that can be utilized in engineering applications.

3:00 PM BREAK

3:30 PM *EN03.02.04
Twist-Based Refrigeration, Actuation, and Mechanical Energy Harvesting Using Twisted, Coiled, and Plied Yarns Ray H. Baughman; The University of Texas at Dallas, United States

Higher efficiency, lower cost refrigeration is needed for both large- and small-scale cooling. We show that high cooling results from twist changes for twisted, coiled, or supercoiled fibers, including those of natural rubber, NiTi, and polyethylene fishing line. By using opposite chiralities for twist and coiling, supercoiled natural rubber fibers and coiled fishing line fibers result that cool when stretched. Similar mechanics involving twist transfer between yarn twist and coiling are here used to make compact, energy-efficient refrigerators, thermal and electrochemical artificial muscles, and twistron electrochemical mechanical energy harvesters. For harvesting between 2 and 120 Hz, our most recent twistron carbon nanotube harvesters have higher gravimetric peak power and average power than previously reported for any prior-art, material-based mechanical energy harvester.

4:00 PM EN03.02.05
Improving Efficiency of Elastocaloric Cycles by Applying Novel Thermodynamic Cycles and Proper Training Regime Parham Kabirifar[1], Ichiro Takeuchi[2] and Jaka Tusek[1]; [1]University of Ljubljana, Slovenia; [2]University of Maryland, United States

Vapor-compression technology emerged nearly a century ago by utilizing natural refrigerants, which had inherent problems, i.e., low efficiency, inflammability and toxicity. Consequently, stable and more efficient synthesized refrigerants such as chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs) were developed, nevertheless, CFCs depleted the ozone layer and HFCs had high global warming potential. Therefore, due to significant environmental impact, vapor-compression technology should soon revert to natural refrigerants. As a result, caloric cooling/heating technologies that use environmentally benign solid-state refrigerants have been considered as serious alternatives to vapor-compression technology, among which, elastocaloric technology, which is based on the latent heat of phase transformation of shape memory alloys (SMAs), has been nominated as the most promising one by the US Department of Energy and the EU Commission. Accordingly, elastocaloric effect of different SMAs has been investigated, and several elastocaloric devices using different geometries and thermodynamic cycles have been designed and tested with promising results. Developing durable elastocaloric devices that are more efficient than their vapor compression counterparts is still the main focus of the ongoing research. However, some of the basics of the elastocaloric cycle have been either overlooked or have not been investigated thoroughly. This study investigates the effects of training (stabilization of thermomechanical response) and the parameters of the elastocaloric cycle on the elastocaloric response of NiTi wires under tensile loading. Multiple training regimes with different stress amplitudes and strain rates have been applied to NiTi thin wires and the elastocaloric response of the samples has been evaluated subsequently. A typical elastocaloric cycle consists of an adiabatic loading and an adiabatic unloading segment each of which is followed by a holding period throughout which the heat can be transferred to/absorbed from the heat transfer medium or a contact heat sink/source. The parameters of the holding period have been systematically investigated by applying constant stress and constant strain throughout the holding period resulting in isostress and isostrain thermodynamic cycles respectively[1]. In addition to the applied training regime, the parameters of the holding period can significantly affect the generated elastocaloric effect and alter the nature of the applied thermodynamic cycle. While the typically applied isostrain cycle results in a Brayton thermodynamic cycle, applying the isostress cycle with partial phase transformation changes the thermodynamic cycle and shifts it toward the Carnot cycle, which has the maximum theoretical efficiency. In addition to the efficiency of the cycle, the isostress cycle generates larger adiabatic temperature changes under lower applied stress levels that can enhance the tensile fatigue life of the wires and reduce the size of the actuators that are needed in practical devices. In multielement configurations like elastocaloric regenerators[2], lower stress levels needed in isostress cycles allow for increasing the number of elastocaloric elements that improves the performance of the regenerator by increasing its heating/cooling power.

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[2] Z. Ahčin et. al, Joule 6, 2338 (2022).

Acknowledgments: J. Tušek and P. Kabirifar acknowledge support of European Research Council (ERC Starting Grant No. 803669).

4:15 PM EN03.02.06
Characterization of Natural Rubber Tubes for Elastocaloric Cooling Applications Giulia Lombardi[1], Gael Sebald[1,2], Gildas Coativy[2], Jacques Jay[2] and Atsuki Komiya[1]; [1]Tohoku University, Japan; [2]Institut National des Sciences Appliquées de Lyon, France

The elastocaloric effect of natural rubber (NR) was first studied at the beginning the 19th century, by John Gough in 1805, and James Joule in 1850, giving rise to what is today known as the Gough-Joule effect [1]. This describes the property of NR to give out heat when stretched and to contract when heated. Despite these findings now date back to more than 170 years ago, it was only recently that this elastomer gained interest among the scientific community for space cooling applications. Contrary to most caloric materials, NR is non-toxic, abundant and low-cost.
When stretched between elongation of 1 to an elongation to 6, it was proved experimentally an adiabatic temperature change up to 10~15 K with rather low

mechanical losses leading to a ratio between potential heat exchange and the mechanical work around 3~5 (also known as COP_{mat}) [2]. This attractive elastocaloric activity is however not applicable because of the excessive geometry change during operation. For example, the surface at an elongation of 1 might be too small for fast heat exchange compared to the fully elongated one (change of exchange area combined with the large increase of the thickness). Therefore, up to now, we can mention only two works that explored the development of elastocaloric cooling based on NR: the single-tube system developed by Sebald *et al.* in 2020 [3] and the membrane-inflation system developed by Greibich *et al.* in 2021 [4]. This is highly in contrast with the number of published works of caloric cooling systems based on other elastocaloric materials, the most used being NiTi-based shape-memory alloys (SMAs) mainly due to its high adiabatic temperature (between 15 K and 40 K). However, these materials require high values of applied tensile force (300 MPa or more), which are not ideal for system scale-up.
The objective of this work is devoted to the experimental evaluation of the elastocaloric activity of elastocaloric elastomers, that will be presented in detail. As a focus, we demonstrate that NR is indeed a good candidate for elastocaloric cooling applications, despite the limited adiabatic temperature exhibited by the material when subjected to cyclic elongations. Cyclic elastocaloric properties of NR tubes were studied by imposing trapezoidal cycles at 0.1 Hz under various elongations. The maximum temperature variations on the material were recorded for elongations between 400% and 600% of its initial length, giving a ΔT of 4 K. The main advantage of NR lies on the applied tensile stress, two orders of magnitude lower than that required by SMAs. We recorded, in fact, a maximum stress on the NR tubes of 2 MPa for cyclic elongations at 0.1 Hz between 350% and 550% of its initial length. The corresponding mechanical losses were found to be equal to 0.27 MJ m^{-3}. In order to estimate the material efficiency for elastocaloric cooling, we calculated the material coefficient of performance COP_{mat} , defined as the potential absorbed heat divided by the hysteresis loss. We found a COP_{mat} value of 22 when considering the first 50 cycles, which is one of the highest recorded values among elastocaloric materials. As the characterization proceeded until 10^4 cycles, the COP_{mat} reached 53, thanks to a drop of the mechanical losses of the material. These values, along with the low tensile force required, demonstrate the high elastocaloric potential of NR, a future key material to be used in cooling applications, given that further improvements both on the material and on the system side are achievable.

[1] G. A. Holzapfel and J. C. Simo, Comput. Methods Appl. Mech. Eng. 132, 17 (1996).
[2] Z. Xie, G. Sebald and D. Guyomar, Appl. Phys. Lett. 108, 041901 (2016).
[3] G. Sebald, A. Komiya, J. Jay, G. Coativy and L. Lebrun, Appl. Phys. 127, 094903 (2020).
[4] F. Greibich, R. Schwödiauer, G. Mao, D. Wirthl, M. Drack, R. Baumgartner, A. Kogler, J. Stadlbauer, S. Bauer, N. Arnold and M. Kaltenbrunner, Nature Energy, 6, pages260–267 (2021)

4:30 PM EN03.02.07
Elastocaloric Response of Isotropic Liquid Crystalline Elastomers Jeremy Herman and Timothy White; University of Colorado Boulder, United States

Liquid crystalline elastomers (LCE) are anisotropic, soft materials that align or reorient to deformation. The order of LCE has led to both theoretical and experimental consideration of their potential as elastocaloric materials. Elastocaloric responses in materials are typified by an association of deformation, change in entropy, and an associated temperature change. We have recently reported that mechanotropic phase changes (e.g., mechanically induced liquid crystalline phases) exhibit temperature changes of 2°C upon deformation (100% strain). Here, we examine the elastocaloric response of what we refer to as "isotropic" LCE (iso-LCE). Iso-LCE are materials that exhibit nematic to isotropic transition temperatures (T_{NI}) below room temperature. Accordingly, at room temperature, they are in the isotropic (paranematic) state. Enabled by the utilization of a two-step thiol-Michael/thiol-ene chemistry, we examine iso-LCE that exhibit enhanced elastic recovery to deformation while exhibiting low hysteresis. The deformation of these materials induces orientational order (entropy change) that result in elastocaloric temperature changes (> 3°C) in response to minimal stress (<< 1 MPa) and strain (< 200%). The responsivity of these materials exceeds natural rubber and shape memory alloys.

4:45 PM EN03.02.08
Large Negative Electrocaloric Effect in $BiFeO_3$-$BaTiO_3$ Solid Solution Ceramics Gangsan Kim, Yerok Choi, Jeong Seog Kim and Chae Il Cheon; Hoseo University, Korea (the Republic of)

The electrocaloric effect (ECE) has attracted considerable interest due to the possible application for new environmental-friendly solid-state cooling devices. The ECE is an adiabatic temperature change or isothermal entropy change induced by an external electric field in (anti)ferroelectric materials. A material with a high ECE in a broad temperature range near room temperature (RT) is favorable for efficient refrigeration. The cooling devices with EC materials have not been realized for many decades due to small ECEs in most ferroelectric materials. In recent years, very large adiabatic temperature changes over 10 ^oC have been reported in several (anti)ferroelectric and relaxor thin films such as $Pb(Zr,Ti)O_3$, $(Pb,La)(Zr,Ti)O_3$, and $(Bi,Na)TiO_3$-$BaTiO_3$. Most ferroelectric materials show positive ECE that the heat is released and absorbed by applying and removing electric field alternately. The performance of an ECE-based cooling device has been reported to be improved by adopting a positive and a negative EC material together. However, the negative ECE has been reported only in a few EC materials. Giant negative ECE over wide temperature range has been observed in a few antiferroelectric and relaxor ferroelectric thin films recently. In most reports, the giant positive and/or negative ECEs have been observed in thin film EC materials by applying much larger electric fields than those for saturated polarizations. The practical application of a thin film EC material for cooling devices is, however, restricted due to its small thermal mass. Lately, very large negative ECE with an adiabatic temperature change of 11.5 ^oC has been reported in $(Pb,La)(Zr,Sn,Ti)O_3$ antiferroelectric bulk ceramics. And the negative ECE with an adiabatic temperature change of 2 ^oC was reported in eco-friendly lead-free $0.68BiFeO_3$-$0.32BaTiO_3$ ceramics with coexisting ferroelectric rhombohedral and non-polar cubic phases. Several interpretations for the negative ECE in (anti)ferroelectrics and relaxor ferroelectrics have been suggested: non-collinearity between electric dipoles and an applied electric field, electric field-induced phase transition to a high entropy phase and so on., but the origin is still controversial.
In this work, ECE were investigated in lead-free $(1\text{-}x)BiFeO_3$-$xBaTiO_3$ (BF-xBT) (x = 0.1-0.5) solid solution ceramics. The samples were fabricated by a conventional ceramic process. The crystal structure changed from a ferroelectric rhombohedral (R3c) to relaxor-like pseudo-cubic as the BT content increased. Two phases were coexisted in samples with the composition range of x = 0.25 to 0.4. Polarization-electric field (P-E) hysteresis curves were measured at temperatures from RT to 150 ^oC. The temperature changes due to ECE were calculated indirectly with the Maxwell relation, using the temperature dependence of polarization. Polarization increase with increasing temperature and very large negative ECE with an adiabatic temperature change over 10 ^oC were observed in the sample with a rhombohedral ferroelectric phase. The origin for polarization change and the large ECE will be discussed.

SESSION EN03.03: Poster Session
Session Chairs: Sakyo Hirose, Xavier Moya, Julie Slaughter and Jaka Tusek
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN03.03.01
Comparison of the Antiferromagnetic and Magnetocaloric Properties of Rare-Earth Chromites Jianhang Shi[1,1], Mohindar S. Seehra[2], Gayanath Fernando[1], Jacob Pfund[1] and Menka Jain[1,1]; [1]University of Connecticut, United States; [2]West Virginia University, United States

The magnetocaloric effect (MCE) is a thermodynamic phenomenon being exploited for the next generation of highly efficient refrigeration technologies. MCE is an intrinsic property of the magnetic materials where the temperature change and the magnetic entropy change are caused by the application or removal of magnetic field under adiabatic and isothermal conditions, respectively. High magnetic moment values associated with the rare-earth ions in rare-earth chromites, $RCrO_3$ (R= Gd, Tb, Dy, Ho, Er, and Tm), lead to the large changes in isothermal magnetic entropy near their magnetic transition temperatures and hence large MCE. In this work, we present magnetic properties of $RCrO_3$ in a temperature range of 4 – 300 K and present the effect of ionic radii on the ordering temperatures, symmetric exchange constant, spin canting angle, and MCE. Bulk powder samples of $RCrO_3$ are synthesized using a citrate gel combustion technique. First-principles calculations based on density-functional theory within the generalized gradient approximation (GGA) of Perdew- Burke- Ernzerhof and strongly constrained-and-appropriately normed (SCAN) meta-GGA are also employed to calculate the structural and electronic properties of $RCrO_3$. The ground-state energy, lattice constants, electronic structure, and density of states (DOS) of $RCrO_3$ are also calculated. The experimental dc magnetization data are fitted with modified Curie-Weiss law including the Dzyaloshinsky-Moriya antisymmetric exchange interaction, and the symmetric exchange constant and spin canting angle are obtained. Magnetic entropy change ($-\Delta S$) for a given change in magnetic field (ΔH) and the corresponding adiabatic temperature change (ΔT_{ad}) are calculated. Among $RCrO_3$, $GdCrO_3$ shows the largest value of ($-\Delta S/\Delta H$), and its magnitudes of ($\Delta T_{ad}/\Delta H$) and ($-\Delta S/\Delta H$) compare well the reported values for the perovskites $GdFeO_3$ and $GdCoO_3$. These comparisons presented here provide useful information on the potential use of these materials in magneto-refrigeration technology.

5:00 PM EN03.03.02
Tailoring Pyroelectricity in Internally Biased Thin Film $BaTiO_3$ via Polarization Reversal Joshua W. Adkins[1,2,3], Ignasi Fina[4], Florencio Sanchez[4], Saidur R. Bakaul[2] and Jeremiah Abiade[1,1,3]; [1]University of Illinois Chicago, United States; [2]Argonne National Laboratory, United States; [3]Laboratory for Oxide Research and Education, United States; [4]Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Spain

The ability to simultaneously take advantage of controllable polarization reversal and built-in electric fields offers an interesting opportunity to tailor pyroelectric effects in ferroelectric nanomaterials. To explore this opportunity, we examined the sensitivity of the magnitude of a $BaTiO_3$ thin film's pyroelectricity to the film's extent of polarization reversal. Using a modified indirect method that utilizes variable write-read pulses to control polarization reversal, we found that the pyroelectric response of the sample is less than -3×10^{-5} C/m^2 K at low fractions of switched polarization and grows monotonically to greater than -2×10^{-4} C/m^2 K as larger fractions of polarization are reversed. This apparently 'tailorable' pyroelectric behavior is the result of a persistent internal built-in field induced by asymmetric Pt/LSMO electrodes, which destabilizes low fractions of switched polarization and produces a diminished pyroelectric effect after calculations. Greater fractions of switched polarization are more stable against backswitching and permit a larger pyroelectric response. Our findings provide insight into indirect examinations of pyroelectric behavior in relatively simple ferroelectric materials and highlight the ability to utilize an otherwise unfavorable device characteristic to tailor pyroelectric/electrocaloric behavior in a device via purely electric means.

SESSION EN03.04: Electrocaloric Materials and Devices I
Session Chairs: Brahim Dkhil and Sakyo Hirose
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2003

8:30 AM *EN03.04.01
Electrocaloric Effects in Epitaxial Films of $SrTiO_3$ Neil D. Mathur; University of Cambridge, United Kingdom

I will describe electrocaloric effects near the 243 K ferroelectric phase transition in epitaxial films of $SrTiO_3$ on $DyScO_3$ substrates. Results will be compared with (1) bulk $SrTiO_3$ and (2) the canonical Landau description of this system.

9:00 AM *EN03.04.02
Electrocaloric Properties of Defect-Engineered $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ Ceramics Upon Neutron and Gamma Radiation Barbara Malic[1,2], Ankita Sarkar[1], Anze Jazbec[1], Matej Šadl[1,2], Hana Uršič Nemevšek[1,2] and Luka Snoj[1,3]; [1]Jozef Stefan Institute, Slovenia; [2]Jozef Stefan International Postgraduate School, Slovenia; [3]University of Ljubljana, Slovenia

The heating of electronic components has been identified as a severe deficiency in consumer electronics, and even more in professional electronics, where harsh conditions, such as radiation or elevated temperature, add additional requirements to the stability of operation. Application areas include medical diagnostics and therapy, such as proton therapy, space technologies, particle colliders, or nuclear fusion and fission reactors. Electrocaloric (EC) cooling – technology based on the EC effect, i.e., temperature change triggered by the change in applied voltage, could be used to cool electronic components. Relaxor ferroelectrics, exemplified by $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ (PMN–10PT), represent a material system that exhibits high enough EC temperature changes of a few K in a broad enough temperature interval of a few 10 K. However, the peak EC values not only increase until we reach the breakdown field but also shift towards higher temperatures as we increase the field amplitude. By introducing defects into the perovskite lattice via aliovalent doping, the temperature range of the peak EC response may be shifted and/or broadened, as shown in the case of Mn-doped PMN-10PT [1]. When considering using EC-based cooling in harsh conditions, the radiation hardness of the EC material is one of the criteria that need to be fulfilled. Neutron and gamma radiation are expected to affect the functional properties of the irradiated materials and, thus, the performance of the entire component or device. We show that PMN-10PT ceramics exhibit similar dielectric, ferroelectric and EC properties after exposure to doses up to 10^{17} neutrons / cm^2 as the pristine samples [2]. But what about PMN-10PT ceramics in which defects are introduced by donor or acceptor doping and contribute to changes in the dielectric, and ferroelectric properties? How do such materials respond to neutron and gamma radiation?
We prepared undoped, acceptor (Mn) and donor (La) doped PMN-10PT ceramics and irradiated them in the TRIGA Mark II research reactor [3]. The ceramics were exposed to 1 MeV equivalent neutron fluence for silicon of 10^{16} cm^{-2} and 10^{17} cm^{-2} of and gamma ray dose of 145 kGy and 1200 kGy. In the lecture, we discuss the influence of neutron and gamma radiation on crystal structure, microstructure, dielectric, ferroelectric and EC properties of defect-engineered PMN-10PT ceramics and compare them with those of undoped material used as reference.

[1] A. Bradeško, M. Vrabelj, L. Fulanović, Š. Svirskas, M. Ivanov, R. Katiliute, D Jablonskas, M. Šimenas, G. Usevičius, B. Malič, J. Banys, T. Rojac, Implications of acceptor doping in the polarization and the electrocaloric response of $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ relaxor ferroelectric ceramics, *J. Mater. Chem. C*, 9, 2021, 3204-3214.
[2] H. Uršič Nemevšek, U. Prah, T. Rojac, A. Jazbec, L. Snoj, S. Drnovšek, A. Bradeško, A. Mirjanić, M. Vrabelj, B Malič, High radiation tolerance of electrocaloric $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$, *J. Europ. Ceram. Soc.*, 42, (13), 2022, 5575-5583.
[3] L. Snoj, G. Zerovnik, A. Trkov, Computational analysis of irradiation facilities at the JSI TRIGA reactor, *Appl. Radiat. Isot.*, 70(3), 2012, 483-488.

9:30 AM DISCUSSION TIME

9:45 AM EN03.04.04
Towards Spatially Resolved Mapping of the Electrocaloric Effect with Nanoscale Resolution using Scanning Thermal Microscopy Olivia Baxter, Amit Kumar, Marty Gregg and Ray McQuaid; Queen's University Belfast, United Kingdom

The electrocaloric effect is a well-known phenomenon where adiabatic application of an external electric field to a material results in a reversible temperature change. Interest in using these materials for environmentally friendly solid-state refrigeration applications has been rejuvenated by the discovery of this effect in commercially available multilayer ceramic capacitors and of giant electrocaloric effects in thin films. While the electrocaloric effect can be well described macroscopically through a thermodynamic approach and is understood to arise from changes in dipolar configurational entropy, the effect at the microscopic scale is not as well characterised. To date, infrared cameras represent the best spatial resolution available for in-situ imaging of temperature fields associated with electrocaloric effects, but features are limited in detail to the level of a few microns.
In this work, we build on previous Scanning Thermal Microscopy studies of electrocaloric materials and demonstrate how this imaging mode can be adapted to measure local electrocaloric response with sub-micron resolution, here demonstrated in a multilayer ceramic capacitor. At a given point on the surface, the tip monitors the temperature while an electric field applied via the capacitor electrodes is cycled on and off. Once the measurement is complete, the tip moves to a neighbouring location and the field cycling and temperature recording process is repeated. Iterating this process across the surface allows for an MxN grid of temperature versus time plots to be created. From this data, the electrocaloric heating and cooling can be extracted to create 2D maps of the electrocaloric response, here demonstrated using a multilayer ceramic capacitor. We intend to use this technique to elucidate the behaviour of other electrocaloric materials and to examine the influence of microstructural inhomogeneity on electrocaloric response.

10:00 AM BREAK

10:30 AM *EN03.04.05
Solid-State Compact Cooling Devices Based on Electrocaloric Polymers Qibing Pei; University of California, Los Angeles, United States

Electrocaloric cooling may offer important advantages over traditional cooling in compactness, flexibility, COP, and voidance of greenhouse gases. Major technical challenges remain to realize these potentials. We have examined the solution processing and thermal annealing to fabricate poly(vinylidene fluoride-trifluoroethylene-chlororfluoroethylene) terpolymer thin films for high electrocaloric temperature change. Introducing an electrostatic actuation mechanism allows compact, solid-state cooling device designs with high COP and cooling power. The technical approach, results, remaining challenges, and opportunities will be presented.

11:00 AM *EN03.04.06
Electrocaloric Effect in Substrate-Supported and Freestanding Relaxor Ferroelectric Thin Films Jiyeob Kim, Djamila Lou, Abel Fernandez and Lane Martin; University of California, Berkeley, United States

There is a new demand for the next generation cooling system with the limited use of fluorinated gases that are widely used as coolants in the conventional cooling system that contributes to global warming. There is a growing interest in caloric studies based on solid-state phase transitions that can meet the new demand for cooling in compact spaces such as integrated circuits and batteries. Electrocaloric materials are considered relatively easy to drive with an electric field. They are often studied in thin-film form to achieve a large breakdown field. Thin films have a small thermal mass that limits from direct measurement and many studies use indirect method to report electrocaloric effects. However, this could lead to erroneous values due to substrate clamping and heat dissipation to the substrate.

In this work, we explore indirect and direct methods to study the electrocaloric effect in relaxor ferroelectric $0.68PbMg_{1/3}Nb_{2/3}O_3$-$0.32PbTiO_3$ (PMN-32PT) thin films. PMN-32PT is known to have an extremely high electromechanical coupling, especially with compositions near morphotropic phase boundary (MPB). $Ba_{0.5}Sr_{0.5}RuO_3$ (30 nm) ‖ PMN-32PT (150 nm) ‖ $Ba_{0.5}Sr_{0.5}RuO_3$ (30 nm) heterostructures were grown on $NdScO_3$ (110) substrates via pulsed-laser deposition providing -0.5% strain on PMN-32PT. Subsequently, a 6-terminal electrothermal testing platform, adapted from a 3-omega device configuration, was fabricated via photolithography. This device allows us to apply an electric field to PMN-32PT and measure polarization and temperature change to study electrocaloric effect using both indirect and direct methods, respectively. Furthermore, we have successfully prepared freestanding versions of these same heterostructure and fabricated them into the testing platform to explore how the removal of the substrate constraints (clamping) impacts the evolution of these properties. This study should clarify the elements that contribute to discrepancies in indirect and direct electrocaloric studies in thin films and provide a guide for indirect studies for accurate calculations.

11:30 AM EN03.04.07
From Electrocaloric Cooling to Pyroenergy Harvesting using Lead Scandium Tantalate Multilayer Capacitors Pierre Lheritier[1], Alvar Torelló[1,2], Tomoyasu Usui[3], Youri Nouchokgwe[1,2], Ashwath Aravindhan[1,2], Junning Li[1], Uros Prah[1], Veronika Kovacova[1], Olivier Bouton[1], Sakyo Hirose[3] and Emmanuel Defay[1]; [1]Luxembourg Institute of Science and Technology, Luxembourg; [2]University of Luxembourg, Luxembourg; [3]Murata Manufacturing Co., Ltd., Japan

Electrocaloric (EC) materials display a reversible change in temperature with a varying electric field, which could be utilized for solid-state cooling. To enhance the performance of electrocaloric coolers, it is crucial to improve the intrinsic EC effect of the material and develop appropriate heat management strategies. Torelló et al. [1] developed a fluid-based active EC regenerator based on lead scandium tantalate (PST) multilayer capacitors (MLCs). In addition to the sharp first-order transition of PST, they also took advantage of the multilayer structure to increase the active volume of the material to obtain a temperature span of 13 K. Due to their strong electrothermal coupling, PST MLCs can also be used to convert heat into electricity for pyroelectric energy harvesting (thermodynamic converse of the EC effect). Similar ideas have also been realized in magnetocaloric materials by exploiting the change in magnetization with temperature to produce electrical energy [2]. Here we developed a macroscopic pyroelectric harvester using 42 g of active PST-MLCs, which produces 11.2 J of energy per thermodynamic cycle [3]. One PST-MLC can generate an electrical energy density of 4.4 J cm^{-3} during one cycle. In addition, we also built an autonomous pyroelectric harvester comprising of microcontrollers, low-voltage converter, and temperature sensors which is powered by the energy harvested from 0.3 g of active PST-MLCs. Finally, we show that 40% of Carnot efficiency could be achieved in PST-

MLCs for a temperature span of 10 K near their phase transition temperature.

[1] Torelló, A., et al. "Giant temperature span in electrocaloric regenerator." Science 370.6512 (2020): 125-129.
[2] Waske, Anja, et al. "Energy harvesting near room temperature using a thermomagnetic generator with a pretzel-like magnetic flux topology." Nature Energy 4.1 (2019): 68-74.
[3] Lheritier, Pierre, et al. "Large harvested energy with non-linear pyroelectric modules." Nature 609.7928 (2022): 718-721.

11:45 AM EN03.04.08
How Highly-Efficient Power Electronics Transfers High Electrocaloric Material Performance to Heat Pump Systems Stefan Moench[1], Richard Reiner[1], Patrick Waltereit[1], Michael Basler[1], Rüdiger Quay[1,2], David Bach[3], Roland Binninger[3] and Kilian Bartholomé[3]; [1]Fraunhofer IAF, Germany; [2]Universität Freiburg, Germany; [3]Fraunhofer IPM, Germany

Electrocaloric heat pumps are an emerging solution for emission-free cooling and heating with high performance. The material performance of some known electrocaloric ceramics or polymers can exceed that of today's vapor compression systems. However, the system performance of published prototypes still lacks significantly behind. This talk presents ultra-efficient power electronics as a solution to this fundamental problem: First, a simple half-bridge switched-mode power converter topology based on gallium nitride transistors is used to demonstrate 99.3% efficient charging of capacitors. Second, an advanced multilevel and partial-power-processing approach is demonstrated, which achieves over 99.7% charging efficiency. This is a significant reduction of electrical charging losses (by multiple 10-times) compared to a resonant circuit approach previously used for electrocaloric prototypes. It is shown how the combination of low-loss electrocaloric materials and highly-efficient power electronics, both existing already today, will enable a high electrocaloric heat pump performance. For example, for available PMN material data, a best-case relative system coefficient of performance COPr (including the external charging losses) over 50% for Carnot-like cycles and over 75% for Ericsson cycles with temperature regeneration is projected, which is close to the material limit of over 80%. The flexibility of the proposed power electronics is demonstrated: The switched-mode approach allows to efficiently charge also very large capacitive loads which are required for future large-scale heat pumps. On the one hand, over 99% efficient charging of 384 commercial capacitors with a very low cycle frequency below 0.02 Hz is demonstrated, which allows heat transfer between thick electrocaloric elements. On the other hand, over 1 kHz cycle frequencies are efficiently realized, which is useful for characterization of the samples' dielectric losses but is beyond the usable thermal time constants of today's prototypes. The trade-off between performance and power density is analyzed. To increase the system efficiency (COPr), but at the expense or reduced power density, it is shown how an offset-field significantly reduces the effective electrocaloric capacitance while the temperature effect is only reduced slightly. The effect of increasing system frequency is discussed. It is discussed how it improves the power density of the system by reduction of electrocaloric material required for the same cooling power. However, it is also shown that it does not reduce the required power rating of the charging circuit and thus does not reduce the size of the electronics. The control system has an inner current-control for adjustable constant-current charging, and an outer voltage-control for waveform generation (arbitrary field variation). A trigger signal allows synchronization of for example servo-control signals, which are useful to realize complete heat pump prototypes. While maintaining a high charging efficiency, the voltage waveform generation is used with an electrocaloric heat-pump prototype to experimentally demonstrate Carnot-like cycles, further verified by temperature and heat flux measurements. Finally, it is shown how the highly-efficient power electronics will be applied to an electrocaloric prototype in the ongoing Fraunhofer lighthouse project "ElKaWe – Electrocaloric heat pumps", which is targeting a high cycle frequency by using a heat-pipe system approach. The discussed multi-disciplinary approach combines ideas from material research, mechanical engineering and electrical engineering. This allows to accelerate the development of electrocaloric heat pumps, and the transition towards emission-free heat pumps for efficient cooling and heating applications.

SESSION EN03.05: Magnetocaloric Materials and Devices II
Session Chairs: Sakyo Hirose and Julie Slaughter
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2003

2:00 PM *EN03.05.02
Room-Temperature Polymer-Assisted Additive Manufacturing of Microchanneled Magnetocaloric Structures Radhika Barua, Vaibhav Sharma, Eddie Goldworthy, Hong Zhao and Ravi Hadimani; Virginia Commonwealth University, United States

Magnetic refrigeration is an energy-efficient, sustainable, environmentally-friendly alternative to conventional vapor-compression cooling technology.[1] There are several magnetic refrigerator device designs in existence today that are predicted to be highly energy-efficient, on condition that suitable working materials can be developed.[1] This challenge in manufacturing magnetocaloric devices is unresolved, mainly due to issues related to shaping the mostly brittle magnetocaloric alloys into thin-walled channeled regenerator structures to facilitate efficient heat transfer between the solid refrigerant and the heat exchange fluid in an active magnetic regenerator (AMR) cooling device.[2]

To address this challenge, we have developed a novel low-temperature extrusion-based additive manufacturing (AM) method to 3D print microchanneled magnetocaloric structures.[3] The printing ink consists of magnetocaloric powders, a polymer binder, and multiple solvents to achieve desirable shear-thinning property, which is critical for a robust printing process. Acting as a sacrificial binding agent for the magnetic powders, the polymer binder holds the 3D printed structures in place and is subsequently removed using a two-step heat-treatment process. Research efforts pertaining to AM process development using three precursor magnetocaloric powders will be presented - **(1)** $La_{0.6}Ca_{0.4}MnO_3$ powders prepared by a patented modified Pechini sol-gel wet chemical method[4] **(2)** $AlFe_2B_2$ powders manufactured by a unique molten salt sintering method[5] and **(3)** $La(Fe_xCo_ySi_{1-x-y})_{13}$ powders produced via gas-atomization. The effect of various process parameters, such as powder-binder ratio, the viscosity of printing ink, powder size, shape and internal porosity etc., on the geometrical and mechanical characteristics of green parts will be discussed. In addition, the effects of sintering and printing parameters on the quality of the densified magnetocaloric structures will be deliberated upon. Last, the feasibility of 3D printing magnetocaloric structures with spatially designed microchannels of minimum dimensions of 150 µm will be demonstrated. Overall, this study provides strategies for realizing low-cost functionally graded magnetic regenerators, thus potentially eliminating one of the main barriers to commercialization of magnetic cooling technology.

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2:30 PM DISCUSSION TIME

2:45 PM EN03.05.05
Improving Performance of Active Magnetocaloric Regenerators Agata M. Czernuszewicz[1], Lucas Griffith[1], Julie Slaughter[1] and Vitalij K. Pecharsky[1,2]; [1]Ames National Laboratory, United States; [2]Iowa State University, United States

Heat pumping based on the magnetocaloric effect has the potential to become a more environmentally benign and sustainable replacement for vapor-compression technologies commonly used in air conditioning and refrigeration. The cost of producing high magnetic field changes and the necessity of using large amounts of magnetocaloric materials are known limitations that hinder the adoption of this technology. One way to boost performance of Active Magnetic Regenerators (AMRs) without investing in stronger magnetic fields or larger mass of working materials is optimizing the AMR shape; specifically tailoring aspect ratio, which is defined as the ratio of the regenerator length to the square root of its cross-sectional area. This parameter strongly influences viscous dissipation and axial conduction losses inside the regenerator. High aspect ratio AMRs are more susceptible to viscous dissipation losses, however, low aspect ratio AMRs suffer from more significant axial conduction losses [1].

Using CaloriSMART [2] and a moderate maximum magnetic field of 1.13 T, we experimentally demonstrate how a simple change in shape greatly impacts AMR performance. Five different aspect ratios ranging from 1.0 to 3.8 were tested across a wide range of operating conditions. Regenerators were filled in with 16.6 ± 0.3 g of Gd spherical powders. The results show that increasing the aspect ratio positively impacts temperature spans, however, shortening regenerators helps to maximize the cooling power. Maximum exergetic cooling power [3] and maximum exergetic power quotient [2] varied with aspect ratio, respectively, by as much as 37 and 21%, with a clear optimum.

This work was performed with joint funding from the Advanced Manufacturing Office and the Building Technologies Office of the Office of Energy Efficiency and Renewable Energy of the United States Department of Energy. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University of Science and Technology under Contract No. DE-AC02-07CH11358.

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3:00 PM BREAK

SESSION EN03.06: Multicaloric Materials and Measurements
Session Chairs: Radhika Barua and Tino Gottschall
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2003

4:00 PM EN03.06.01
Giant Multicaloric Effects in Charge-Transition Oxides Yuichi Shimakawa, Yoshihisa Kosugi and Masato Goto; Kyoto University, Japan

Some transition-metal oxides containing cations with unusually high valence states show charge transitions to relieve the electronic instabilities. Such compounds often release significant latent heat by the first-order charge transitions. We found that the large latent heat and the corresponding isothermal entropy changes can be utilized through caloric effects by applying pressure (barocaloric effects) and/or magnetic fields (magnetocaloric effects). The A-site-ordered quadruple perovskite $NdCu_3Fe_4O_{12}$ containing the unusual high valence $Fe^{3.75+}$ shows the large entropy change of 84.2 $J\ K^{-1}\ kg^{-1}$ by the intersite charge transfer transition ($NdCu^{2+}{}_3Fe^{3.75+}{}_4O_{12} \leftrightarrow NdCu^{3+}{}_3Fe^{3+}{}_4O_{12}$) near room temperature. This entropy change can be utilized by applying pressure through the barocaloric effect. The analogue quadruple perovskite $BiCu_3Cr_4O_{12}$ containing $Cr^{3.75+}$ also shows the large entropy change by the charge disproportionation transition ($BiCu_3Cr^{3.75+}{}_4O_{12} \leftrightarrow BiCu_3Cr^{3+}Cr^{4+}{}_3O_{12}$) at 190 K. Because the charge disproportionation yields a ferrimagnetic phase below the transition temperature, the observed entropy change can be controlled by applying magnetic fields as well as pressure. The compound is thus demonstrated to show the multicaloric effects. The charge transitions, where the charge, spins, and lattice degrees of freedom are strongly correlated, are crucial to the observed novel giant caloric properties.

4:15 PM EN03.06.02
Multicaloric Effect Studied in High Magnetic Fields—Dissipation Losses Limiting First-Order Phase Transition Materials for Cryogenic Caloric Cooling Timo Niehoff[1,2], Benedikt Beckmann[3], Tino Gottschall[1], Catalina Salazar-Mejia[1], David Koch[3], Lukas Pfeuffer[3], Andreas Taubel[3], Esmaeil Adabifiroozjaei[3], Olga Miroshkina[4], Stefan Riegg[3], Nagaarjhuna Kani[3,3], Markus Gruner[4], Leopoldo Molina-Luna[3], Konstantin Skokov[3], Oliver Gutfleisch[3] and Joachim Wosnitza[1,2]; [1]Helmholtz-Zentrum Dresden-Rossendorf, Germany; [2]Technische Universität Dresden, Germany; [3]Technische Universität Darmstadt, Germany; [4]Universität Duisburg-Essen, Germany

With the world's increasingly affluent population demanding more comfortable living and working conditions and rising global temperatures, leading to an ever growing demand for cooling [1], which is predicted to exceed the energy consumption for heating in this century [2], it is vital that we address the development of much more efficient cooling technologies as an urgent priority. A promising alternative approach is based on solid-state refrigeration by one of the caloric effects – electrocaloric, magnetocaloric, barocaloric or elastocaloric - where the material's temperature is changing under the application of an electrical, magnetic, or mechanical field [3]. However, there is also the possibility to combine these different effects in a beneficial way, in the so-called multicaloric cooling cycle. Magnetic Ni-Mn-based Heusler alloys are ideally suited for multicaloric applications due to their coupled magnetostructural transformation between martensite and austenite [4].

Ni-Mn-based Heusler alloys, are highly promising materials for solid-state cooling, because large multicaloric effects can be achieved across their magnetostructural martensitic transformation over a broad temperature range, which is possibly also relevant for cryogenic applications such as the liquefaction of hydrogen. In this work, we simultaneously measured the responses of the magnetic structural and electronic subsystems to the temperature-and field-induced martensitic transformation of Ni(-Co)-Mn-Ti at low temperatures, showing an abnormal increase of hysteresis and consequently dissipation energy at cryogenic temperatures [5]. Simultaneous measurements of magnetization and adiabatic temperature change in high pulsed magnetic fields up to 50 T [6] reveal a positive and irreversible adiabatic temperature change as a consequence of increased dissipation losses and decreased heat capacity. This is in contradiction to the expected negative adiabatic temperature change, which was determined indirectly by heat capacity measurements. Most importantly, this irreversible phenomenon was also observed in other material systems and is universal to any first-order material with non-negligible hysteresis, effectively limiting the utilization of their caloric effects for gas liquefaction at cryogenic temperatures.

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[2] M. Isaac er al., Energy Policy 37 (2) (2009).
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[5] B. Beckmann et al. submitted for publication.
[6] T. Gottschall et al., Phys. Rev. B **99**, 134429 (2019).

4:30 PM EN03.06.03
Thermal Switch Capacitor in a Magnetocaloric Device Nada Petelin[1], Katja Vozel[1], Katja Klinar[1], Matej Šadl[2], Hana Uršič[2], Barbara Malic[2], Mitjan Kalin[1] and Andrej Kitanovski[1]; [1]University of Ljubljana, Slovenia; [2]Jozef Stefan Institute, Slovenia

The quest for better performance of magnetocaloric devices has led to the development of thermal management devices such as thermal switches, thermal diodes, and thermal capacitors. These types of devices are capable of controlling the heat in a manner similar to how their electrical counterparts control electrical current. Most existing caloric devices use active caloric regeneration, in which the working fluid oscillates through the caloric regenerator compose of caloric material. The unavoidable, irreversible viscous and heat-transfer losses, associated with the active caloric regeneration principle limit the operating frequency (number of thermodynamic cycles per unit of time), which is directly related to the power density of a caloric device. Thermal management devices offer a new way to control the intensity and direction of heat flow between the magnetocaloric material and the heat source or heat sink, and therefore could improve the performance of caloric devices during high-frequency operation, which is crucial for increasing in the power density (compactness) and energy efficiency.

A thermal switch relies on a control parameter such as an electric field, magnetic field, or pressure to change the thermal conductance of the device. The switching ratio between the highest thermal conductance achieved (the on state) and the lowest thermal conductance achievable (the off state) represents a figure of merit for a thermal switch. Thermal switches can be either static or motional. Motional thermal switches change their thermal conductance by changing their position and making and breaking thermal contacts. Static thermal switches are always in physical contact with adjacent interfaces. The thermal capacitor, on the other hand, is a single-pole element because the other side of this element is always “grounded,” i.e., connected to a heat reservoir. It acts as a temporary heat-storage device, similar to the “self-capacitance” of an insulated electrical conductor in the electrical analogy. The operation of a thermal switch (TS) and a thermal capacitor (TC) can also be combined in a so-called thermal switch capacitor (TSC).

In this work, we have analyzed a novel thermal switch capacitor made of silicon operating as a solid heat transporting device. The thermal switch capacitor first stores energy and then releases it by means of the transport of heat caused by the motion of the material. We studied the impact of different design parameters and operating conditions on performance of magnetocaloric device, and based on this, established guidelines for an optimal design for further experimental studies. The proposed design provides a compact cooling solution that can be attached directly to the heat reservoir, making it attractive for a variety of applications.

4:45 PM EN03.06.04
Digital Microfluidic Thermal Switch in Magnetocaloric Cooling Urban Tomc[1], Hana Uršič Nemevšek[2], Victor Regis[2], Blaz Velkavrh[1,2], Lluis Mañosa[3], Jens Freudenberger[4], Bruno Weise[4] and Andrej Kitanovski[1]; [1]University of Ljubljana, Slovenia; [2]Jozef Stefan Institute, Slovenia; [3]University of Barcelona, Spain; [4]Leibniz Institute for Solid State and Materials Research Dresden, Germany

Among the related technologies, magnetocaloric energy conversion represents one of the most promising alternatives to vapour compression. Despite the fact that this technology has made substantial progress over the last two decades, there are unfortunately still unsolved and strongly relevant challenges regarding the use of rare-earth materials, energy efficiency, and the competitive cost of potential future devices.

Namely, today’s state-of-the-art devices are based on the so-called Active Magnetic Regeneration, which is moderately efficient at low operating frequencies (up to 5 Hz). To achieve considerable cooling power and magnetic fields at such low frequencies, a significant amount of magnetocaloric and permanent magnet material is required, which also affects the cost. Therefore, a new research direction has emerged in recent years in which researchers are trying to develop devices that operate efficiently at much higher frequencies (up to 20 Hz or more). This would increase the power density, which in turn would allow miniaturization of the devices and the use of drastically less magnetocaloric and magnetic material. There are two major challenges to be solved. One concerns the application of new magnetic field sources that can generate a fast and efficient alternating magnetic field at high frequencies. The other one deals with the application of new thermal management principles in a form of thermal control devices. One particular sub-domain of thermal control devices are thermal switches.

An interesting field, to look for thermal switch mechanisms, is microfluidics, which has enabled the development of integrated lab-on-chip devices. Although most microfluidic devices are based on a continuous flow of liquids in microchanells, there has been an increasing interest for the past couple of years in devices that rely on manipulation of discrete droplets using surface tension effects. One such technique is ElectroWetting On Dielectric (EWOD), which is based on wettability of liquids on a dielectric solid surface by varying the electrical potential. EWOD system’s similarity to the digital microelectronic systems has led to the term digital microfluidics.

In this contribution we will present a new concept of magnetocaloric device which couples magnetocaloric effect and EWOD droplet actuation as thermal switch mechanism. We will show different potential designs of such a devices and their operation. Furthermore, the materials and its properties, which constitute the whole device will be discussed.

SESSION EN03.07: Barocaloric Materials and Devices
Session Chairs: Xavier Moya and Jaka Tusek

Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2003

8:30 AM *EN03.07.01
Barocaloric Effects from Hydrocarbon Order–Disorder Transitions Jarad A. Mason, Jinyoung Seo, Adam Slavney, Selena Zhang, Faith Chen, Vidhya Dev, Ryan McGillicuddy, Rahil Ukani and Jason Braun; Harvard University, United States

Efficient barocaloric cooling requires materials that undergo reversible phase transitions with large entropy changes, high sensitivity to hydrostatic pressure, and minimal hysteresis—the combination of which has been challenging to achieve in existing barocaloric materials. Here, I will describe how hydrocarbon order-disorder phase transitions in organic and metal–organic materials can be manipulated to induce large, reversible barocaloric effects at moderate pressures. In particular, I will discuss the structural and chemical factors that contribute to entropy changes, sensitivity to hydrostatic pressure, and hysteresis for two classes of layered materials that undergo structural transitions associated with the disordering of hydrocarbon bilayers. Additionally, I will highlight the important role the pressure-transmitting medium plays in directing these barocaloric effects.

9:00 AM *EN03.07.02
Reversible Colossal Barocaloric Effects at Low Pressures in Disordered Materials Pol Lloveras[1], Junning Li[2], Maria Barrio[1], David J. Dunstan[3], Richard J. C. Dixey[3], Xiaojie Lou[4], Anthony E. Phillips[3], Kartik Sau[5,5], Sangryun Kim[6], Shigeyuki Takagi[5], Tamio Ikeshoji[5], Shin-ichi Orimo[5,5], Claudio Cazorla[1] and Josep-Lluís Tamarit[1]; [1]Universitat Politècnica de Catalunya, Spain; [2]Luxembourg Institute of Science and Technology, Luxembourg; [3]Queen Mary University London, United Kingdom; [4]Xi'an Jiaotong University, China; [5]Tohoku University, Japan; [6]Gwangju Institute of Science and Technology, Korea (the Democratic People's Republic of)

Materials undergoing order-disorder first-order phase transitions are attracting interest for thermal management because they can act as heat sinks or sources due to the energy stored in the disordered phases. Moreover, the application of pressure on these materials may allow an active control of the heat exchange, which leads to conceive barocaloric methods for solid-state cooling and heat pumping [1]. Interestingly, they promise a more environmentally friendly and efficient alternative to harmful vapor compression. Fast progress on materials research has allowed the identification of some organic plastic crystals as outstanding barocaloric agents, with colossal barocaloric effects much above 100 J K^{-1} kg^{-1}. However, typical moderate or large hysteresis and a moderate sensitivity of the transition to pressure make these colossal barocaloric effects be obtained reversibly upon pressure changes above 100 MPa, which limits their potential applicability. Here we present two recently investigated materials that exhibit relatively little-hysteretic phase transitions releasing strong disorder in the high temperature phase and accompanied by large volume changes. These features allow to obtain reversible colossal barocaloric effects below 100 MPa in both compounds, with simultaneously large values for isothermal entropy changes ΔS and adiabatic temperature changes ΔT. One material is a layered hybrid organic-inorganic pseudoperovskite [2] whose disorder is associated with the melting-like process and rotation of the organic chain linked to the inoganic octahedra. It displays reversible $\Delta S \sim 230$ J K^{-1} kg^{-1} under low pressure changes of 50 MPa, and reversible $\Delta T \sim 10$ K under pressure changes of 80 MPa. The other material is a fast-ionic conductor [3] displaying strong molecular orientational disorder of anions coupled to diffusion of cations. In that case, the material undergoes reversible $\Delta S \sim 170$ J K^{-1} kg^{-1} and $\Delta T \sim 10$ K under pressure changes of 84 MPa. Here, the high transition temperature suggests that it could be also used for solid-state barocaloric waste heat recovery [4].

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[3] K. Sau et al., Sci. Rep. **11**, 11915 (2021).
[4] H. Tokoro et al., Nat. Commun. **6**, 7037 (2015).

9:30 AM EN03.07.03
Microstructural Observations of Reversible Phase Transformations in Barocaloric Plastic Crystal Systems Chase Somodi, Denali Ibbotson, Alex Foncerrada and Patrick Shamberger; Texas A&M University, United States

Plastic crystals exhibit a degree of structural order between an ordered crystal, in which molecules have fixed position and orientation, and liquid, in which molecules can rotate and translate in every direction. Small molecules within plastic crystals are fixed on a rigid lattice, but still maintain rotational degrees of freedom. Such plastic crystals typically crystallize in cubic systems (FCC or BCC) at high temperature, and undergo a first order phase transition associated with a large entropy change to lower symmetry phases upon cooling. The transition between ordered crystals and plastic crystals are associated with introduction of rotational degrees of freedom and thus, large changes in entropy, with a pressure-dependent T_{cr} due to the Clausius-Clapeyron coupling between pressure and volume change at the transition. This pressure and volume change dependence forms the basis for giant barocaloric effects, which can be used in heat pump or refrigeration cycles, and can also be considered to represent a tunable thermal energy storage media, where pressure is used as an independent variable to control the temperature at which heat is stored or discharged. In both cases, the overall efficiency of the refrigeration cycle or the energy storage scheme is dominated in large part by the reversibility of the plastic crystal transition. Thus, understanding the origin of the undercooling in plastic crystal transformations and developing strategies to reduce undercooling is a critical element of advancing these systems towards practical use.

Here, we use calorimetry and optical microscopy to investigate the reversibility of the plastic crystal transformation, and its microstructural evolution through the heating and cooling transformations. We demonstrate that the transformation on heating (low to high symmetry) exhibits a dense concentration of nucleation points and significant phase coexistence, which remains stable when held under isothermal conditions. In contrast, the transformation on cooling is nucleation-limited, resulting in abrupt propagation of a phase boundary throughout the sample volume after nucleation of an under-cooled volume. This cooling transformation does not appear to conserve the original microstructure of the rotationally ordered plastic crystal phase. We report specifically on the role of plastic crystal chemical structure and the impact of introducing small concentrations of other plastic crystal molecules below the solubility limit (<5 wt%) on the degree of undercooling and microstructure of the system. These results reveal the fundamental mechanisms occurring during the transition, including its asymmetric nature, and demonstrate a pathway towards dramatically decreasing undercooling and thereby increasing efficiency in plastic crystal systems.

9:45 AM EN03.07.04
Overcoming Hysteresis in Barocaloric Materials Jinyoung Seo, Adam Slavney and Jarad A. Mason; Harvard University, United States

From air conditioning to refrigerators to heat humps, cooling technologies have played critical roles in enabling access to improved living conditions. Yet, ironically, the very technologies that helped us beat the heat are now making the planet warmer. Current cooling systems rely on volatile hydrofluorocarbon refrigerants, the majority of which are potent greenhouse gases. As demand for cooling continues to increase, the direct emission of volatile refrigerants is predicted to dramatically increase—well above 10% of greenhouse gas emissions by 2050. In the face of an increasingly warming world, new technologies are urgently needed to provide sustainable cooling. Solid-state cooling through barocaloric effects—pressure-induced thermal changes in a material—offers an environmentally-friendly alternative to conventional cooling technologies. Unlike gaseous refrigerants, solid refrigerants have zero global warming potential as well as a variety of potential advantages, including increased efficiency, reduced system size, and greater recyclability. Importantly, barocaloric materials are particularly well suited to providing cooling at scale. This is, in part, because pressure is easy to generate, can be applied to materials regardless of their form factor, and, due to the dominance of vapor-compression technology, extremely amenable to scaling.

To produce useful barocaloric effects at low pressures, phase transitions that feature large entropy changes, high sensitivity to pressure, and minimal hysteresis are needed. In particular, hysteresis—which represents the dissipated energy during a pressure-driven phase change—plays a central role in determining the cooling performance. In addition to increasing the operating pressure, large hysteresis compromises efficiency, cooling power, and cyclability. Despite the range of barocaloric materials that have been studied to date, it has proven challenging to manipulate—and understand—hysteresis in barocaloric materials. Because existing classes of barocaloric materials are often difficult to manipulate synthetically in a systematic fashion, it is challenging to establish structure–property relationships needed to inform efforts to overcome hysteresis. As such, strategies to reduce—and, ideally, eliminate—hysteresis in barocaloric materials have yet to be developed.

Here, we present systematic studies on hysteresis in barocaloric materials. We leverage the new classes of tunable barocaloric materials recently discovered in our laboratory—including two-dimensional hybrid perovskites [1] and molecular spin-crossover complexes [2]—to elucidate key molecular factors that govern the hysteresis of pressure-driven transitions. In particular, we characterize the compositionally diverse library of barocaloric materials using advanced calorimetry and operando X-ray diffraction techniques, as well as direct temperature measurements under variable-pressure conditions. These efforts are complemented by molecular modeling and microstructural analyses. Finally, we describe our efforts to understand the impact of hysteresis at the device level. By evaluating the performance of select barocaloric materials in our recently developed cooling prototype, we directly probe materials losses—especially those that originate from hysteresis—in a wide range of driving conditions. Bridging the gap between materials discovery and prototype development, this work represents a crucial step toward the development of barocaloric materials for practical solid-state cooling. We envision that our approach to understand barocaloric effects across length scales—ranging from molecular to device levels—will provide new insights and opportunities for studying phase transitions and thermal behaviors in materials.

[1] *Nature Communications* **2022**, *13*, 2536.
[2] *J. Am. Chem. Soc.* **2022**, *144*, 6493.

10:00 AM BREAK

10:30 AM *EN03.07.05
Exploring Atomic Structure and Dynamics in Barocalorics for Solid-State Cooling with Neutron Scattering Helen C. Walker; Rutherford Appleton Laboratory, United Kingdom

Conventional vapour-compression refrigeration relies on refrigerants that contribute both to global warming and ozone depletion. Barocaloric materials, in which a large isothermal entropy change is associated with a pressure-induced phase transition, offer an eco-friendly solid-state alternative. While an increasing number of materials are being identified as barocalorics, a microscopic understanding of what drives the entropy change is often lacking, negatively impacting the opportunity to create a roadmap for developing new optimised barocaloric materials.
We have used a range of neutron scattering methods: total scattering, quasielastic neutron scattering and inelastic neutron scattering to investigate both the structure and dynamics in two barocaloric systems: ammonium sulfate [1,2] and adamantane [3]. Combining our data with density functional theory and molecular dynamics simulations we have obtained an insight into the significance of configurational and dynamic entropy, providing ideas for crystal engineering better barocalorics for applications in both cooling and heat pumps.
[1] S. Yuan et al., *Adv. Funct. Mater.* 2022, 2207717
[2] B.E. Meijer et al., *Phys. Rev. B* 2022, **106**, 064302
[3] B.E. Meijer et al., *submitted* 2022

11:00 AM *EN03.07.06
Key Parameters for Barocaloric Cooling and Heating Enric Stern Taulats[1,2], Pol Lloveras[3] and Xavier Moya[2]; [1]Universitat de Barcelona, Spain; [2]University of Cambridge, United Kingdom; [3]Universitat Politècnica de Catalunya, Spain

Heating and cooling markets sum up a 70% share of energy consumption worldwide and urge the shift towards more efficient and low-carbon solutions [1, 2]. Heating market heavily relies on fossil fuel-dominated technologies. Cooling market relies on the use of refrigerant gases that have been severely in the spotlight of environmental protocols and EU regulations in view of their high Global Warming Potential and ozone-depletion properties.

In the last decades, substantial research effort has been concentrated on the development of alternative, more sustainable technologies based on caloric materials [3], which can exhibit a giant thermal response in the vicinity of a phase transition under the influence of a magnetic field, an electric field, or mechanical stress. Particularly, barocaloric materials are blossoming into calorics with the outbreak of new classes of materials displaying colossal thermal effects that compare to those of refrigerant gases [4, 5].

However, implementing these promising materials still remains preliminary, which poses a challenge from both the materials science and engineering viewpoints. In this regard, I will review the state-of-the-art caloric materials and the conditions yielding enhanced thermal responses. I will discuss the key parameters related to materials cyclability and heat transfer phenomena to be addressed to match applications' demands and design constraints.

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[4] Li, Bing, et al. "Colossal barocaloric effects in plastic crystals." *Nature* 567.7749 (2019): 506.
[5] Lloveras, Pol, et al. "Colossal barocaloric effects near room temperature in plastic crystals of neopentylglycol." *Nature communications* 10.1 (2019): 1803.

11:30 AM EN03.07.07
Device-Level Thermodynamic and Heat Transfer Model for a Barocaloric Solid State Refrigerator Naveen D. Weerasekera, Kameswara Pavan Kumar Ajjarapu, Kavish Sudan, Gamini Sumanasekera, Kunal Kate and Bikram Bhatia; University of Louisville, United States

Solid state refrigeration based on caloric materials has demonstrated the ability to replace existing vapor compression cooling systems that are inefficient, difficult to scale and have a high global warming potential. Unlike solid state cooling based on electrocaloric, magnetocaloric and elastocaloric effects, barocaloric refrigeration – based on the entropy change due to applied hydrostatic pressure – have received comparatively less attention but have recently demonstrated significant potential in material-level studies. However, device-level numerical and experimental studies are still missing in the literature. This work presents a thermodynamic and heat transfer model for a barocaloric refrigerator comprising commercially-available nitrile butadiene rubber (NBR) and operating between a hot and a cold thermal reservoir. We combine experimentally-validated barocaloric properties of NBR with transient heat conduction modeling to evaluate the performance of a reverse Brayton refrigeration cycle. Specifically, we evaluate the coefficient of performance (COP), energy density and power density of the device, and quantify the contributions of device geometry, operating frequency, heat transfer coefficient, and applied pressure. We show that a barocaloric refrigerator operating with a 2.3 K temperature span, 10 mHz cycle frequency and 0.1 GPa applied pressure change can achieve a COP as high as 8 – exceeding that of traditional vapor compression-based refrigerators. Additionally, we show that increasing the thermal conductivity of the elastomeric solid-state refrigerant can substantially improve performance – increasing the COP by 67% when the refrigerant's thermal conductivity was raised from 0.2 W m^{-1} K^{-1} to 1 W m^{-1} K^{-1}. This work demonstrates the promise of solid state cooling devices based on soft barocaloric materials and provides a framework to quantify its performance at the device-level.

11:45 AM EN03.07.08
TCCbuilder: an Open-Source Tool for the Design and Evaluation of Thermal Circuits in Calorics and Other Applications Katja Klinar, Katja Vozel and Andrej Kitanovski; University of Ljubljana, Slovenia

Thermal management as control of the temperature, as well as the intensity and the direction of heat flow between components of a system, is crucial for high energy efficiency, optimized performance, high reliability, and safety. Thermal management is also the key challenge of modern technology in the whole energy chain: energy production, conversion, transport, and utilization.

It is becoming more and more evident that thermal management methods like conventional thermal resistors (i.e. thermal insulation) and capacitors (i.e. thermal storage) cannot meet thermal control requirements of advanced, especially small-scale systems with higher power densities or potentially transient, fluctuating, or migrating hot or cold spots, as well as for temperature-sensitive equipment. The newly emerging thermal control devices (TCDs), including thermal conduits, thermal resistors, thermal switches, thermal regulators, thermal diodes, and thermal capacitors, allow nonlinear, switchable, and active control of the heat, just as their electrical counterparts control the electrical current.

We wanted to take a step forward in the development of these novel thermal management techniques, which led us to this project, whose main goal is to provide researchers and broader society with the world's first open-source numerical tool for simulating thermal control circuits (TCCs). Therefore, we present here the TCCbuilder tool and its associated library – a large database of appropriate materials and TCDs already published in the literature. The tool will also serve as a solid foundation for sharing knowledge in the field of thermal management.

The implementation of nonlinear and switchable TCDs, together with a heat source and a heat sink, forms TCCs and leads to qualitatively better thermal capabilities, including better regulation or stabilization of temperature, rectification, heterodyning, amplification, regulation, redirection, and stabilization of heat flux density, temporary storage of excess heat, heat scavenging, thermal computation, etc. The output of the TCCbuilder will be demonstrated with several examples, where TCDs have been implemented and have improved the operation of conventional devices, e.g. temperature doubler, peak detector, and load shifter.

One of the most important areas of investigation in thermal management are caloric devices. It has already been demonstrated that thermal switches and/or thermal diodes can enable the operation of magnetocaloric, electrocaloric, and elastocaloric devices at higher frequencies. To increase the cooling power density of caloric devices, breakthrough ideas are needed, which can be tested, accepted, or disproved with the TCCbuilder.

SESSION EN03.08: Elastocaloric Materials and Devices II
Session Chairs: Ray Baughman and Huseyin Sehitoglu
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2003

1:30 PM *EN03.08.01
Multi-Mode Elastocaloric Cooling Systems Based on Superelastic Shape Memory Alloys Ichiro Takeuchi; University of Maryland, United States

Elastocaloric/thermoelastic cooling based on superelastic shape memory alloys uses the large latent heat associated with the martensitic transformation to pump heat. Elastocaloric cooling has been recognized by DOE as one of the most promising alternative cooling technologies. We have been developing prototypes of elastocaloric cooling systems using superelastic NiTi. Our effort started with tension-based coolers using NiTi wires. Because of the fatigue issue associated with wires, we have since been focusing on compression-based devices. Key features of our cooling devices include tube-bundle-based heat exchangers and a work-recovery system which is necessary for high-efficiency operation of the systems. We have developed a multi-mode elastocaloric system, where operational modes can be switched between the high-utilization mode and the active regenerator mode. The high-utilization mode allows delivery of maximum cooling power, while the active regeneration mode can build a large temperature lift across the regenerator. In the current 4-bundle system, our system can deliver over 100 W of cooling power in the high-utilization mode, while the active regenerator mode can generate larger than 20 K in the temperature lift. I will also discuss our effort in development of new materials for elastocaloric cooling. Comparison of recent advances in elastocaloric cooling with other caloric cooling technologies will be discussed. This work is carried out in collaboration with Suxin Qian, David Catalini, Nehemiah Emaikwu, Jan Muehlbauer, Yunho Hwang, Huilong Hou, Jun Cui, Kenjiro Fujimoto, and Reinhard Radermacher. Our work is funded by the DOE EERE BTO BENEFIT project.

2:00 PM *EN03.08.02
Miniature-Scale Elastocaloric Cooling by Rubber-Based Films Manfred Kohl; Karlsruhe Institute of Technology, Germany

The elastocaloric effect associated with the strain-induced crystallization and entropy elasticity in elastomers is of special interest for environmentally friendly and low-cost solid-state cooling applications and may provide an alternative for vapour compression technology. One material candidate is natural rubber, which has the potential to meet the various challenges associated with elastocaloric cooling, including large adiabatic temperature change and

extraordinary fatigue resistance under dynamic load. For miniature-scale cooling applications addressed in this work, the focus is on rubber-based films having a large surface-to-volume ratio to enable rapid heat transfer. Target applications are on a small scale including microelectronics, micro-electro-mechanical systems (MEMS) and lab-on-chip systems. Yet, larger scales are accessible by massive parallelization.
Elastocaloric materials should fulfil a number of key properties including (i) a large adiabatic temperature change ΔT, (ii) minimum fatigue, (iii) high materials efficiency and (iv) sufficient thermal conductivity for efficient heat transfer. Though the thermo-mechanical properties of natural rubber are well investigated, the key properties (i)-(iv) required for elastocaloric cooling are not examined systematically. A series of laser-cut and cast samples based on cured natural rubber foils and prevulcanized natural rubber latex concentrate is presented for various thicknesses in the range (50 – 900) µm. The samples are characterized by uniaxial tensile tests in combination with infrared thermography to determine suitable elastocaloric materials. Among the investigated materials, laser-cut cured natural rubber foils exhibit the highest elastocaloric temperature changes of +7.4/-10 K and a material's coefficient of performance of 3.6.
Elastocaloric cooling devices require an appropriate actuation mechanism to meet required strain levels up to 700 % and rates up to 5 s^{-1}. Separation of heat and cold can be achieved via directional heat transfer by alternating mechanical contact of the film sample to heat sink and source elements. Engineering issues comprise sample fixations and the designs of thermal and mechanical interfaces for efficient heat transfer as well as force recovery to enhance the COP on the system level. First demonstrators will be presented that address the various design issues. The design studies are complemented by lumped-element modelling to understand the dynamics of heat transfer and resulting cooling capacity.

2:30 PM BREAK

3:30 PM EN03.08.03
Experimental Regenerative Elastocaloric Heat Pump Using Natural Rubber Gael Sebald[1], Giulia Lombardi[2,1], Gildas Coativy[3], Jacques Jay[4], Laurent Lebrun[3] and Atsuki Komiya[2,1]; [1]ELyTMaX IRL3757, CNRS, INSA Lyon, Centrale Lyon, Université Claude Bernard Lyon 1, Tohoku University, Japan; [2]Institute of Fluid Science, Tohoku University, Japan; [3]Univ. Lyon, INSA Lyon, LGEF EA682, France; [4]Univ. Lyon, CNRS, INSA-Lyon, CETHIL, UMR5008, France

In the search of refrigeration alternatives for performance optimization and environmental sustainability/friendly issues, caloric materials may offer several advantages, such as a high coefficient for performance (COP) and low global warming potential. Refrigeration prototypes using magnetocaloric, electrocaloric and metallic elastocaloric materials were proposed in recent years with particularly promising performances. Elastocaloric polymers may offer additional specific advantages, such as their low CO_2 footprint, their abundancy and their low cost, as well as low actuation stress. However, such materials require large deformations to obtain significant adiabatic temperature change DT_{ad} (i.e. elongation >400% for DT_{ad}>3 K), and exhibit a low thermal conductivity (~0.2W/(m K)), one or two decades lower than ceramics and metals.
In this work, taking into account the above-mentioned limits, we developed an experimental proof of concept of a refrigeration device using natural rubber tubes. An active regenerative configuration was used, which consists basically of activating the caloric material cyclically, and circulating a fluid at the same frequency with a phase shift of 90°. Such technique is known to provide large temperature span and cooling power for other caloric materials. The thickness of the rubber walls was ensured to be lower than that of the harmonic thermal boundary layer in the rubber for typical operating conditions, thus solving the low thermal conductivity issue. The large required deformation issue was solved by working from a pre-elongation of 400% and by imposing cyclic deformations between 400% and 600%. Finally, a technique for the grip of the natural rubber materials was proposed. Two geometries were tested using natural rubber tubes-based regenerators.
The natural rubber tubes were first stretched cyclically without fluid, an adiabatic temperature variation of ~3.5 K was measured for an elongation varying between 3.5 and 5.5. Heat exchangers were then added on both sides of the regenerators, the fluid circulation in the natural rubber tubes was provided by a piston pump, and the hot heat exchanger was maintained at room temperature by a dedicated fluid circulation. The cold heat exchanger comprised a heating source for determining the cooling power for a given temperature span.
Different operating conditions were tested and the maximal temperature span, cooling power, and COP was determined for each condition. It was obtained temperature span as high as 10 K, a cooling power in the Watt range and COP above 5. The corresponding specific cooling power ranged 100~200W/kg. For regenerative systems, from the literature, the displacement of the fluid strongly influences the temperature span and the cooling power, where an optimum displacement is observed. In the devices using natural rubber, it was found that the temperature span and cooling power were monotonic functions of the displaced volume. It was interpreted in the light of the low thermal conductively of natural rubber, which contributed to maintain a large temperature span even for low cooling power.
Finally, the proposed design is fully scalable: it is straightforward to increase the number of natural rubber tubes to meet a given targeted cooling power.

3:45 PM EN03.08.04
Fatigue Resistant Elastocaloric Regenerative Cooler / Heat Pump Showing High Performance Stefano Dall'Olio, Ziga Ahčin, Andrej Zerovnik, Parham Kabirifar, Luka Porenta, Jan Cerar and Jaka Tusek; University of Ljubljana, Faculty Of Mechanical Engineering, Slovenia

Due to the high global warming potential of refrigerants in the short and long term, the refrigeration community is looking for a reliable alternative technology that could replace the current dependency on vapor compression systems. A valuable alternative technology should be highly efficient and environmentally friendly. Recently, devices based on the elastocaloric effect (eCE) proved to be one of the most promising candidates to replace vapor compression cooling and heating systems in the following years. The elastocaloric cooling is based on the elastocaloric effect (eCE), which is closely related to the superelasticity of shape memory materials. In the specific case of shape memory alloys, which are the most studied elastocaloric materials (eCM), the eCE occurs due to a stress-induced martensitic transformation. When an external force is applied to an eCM, the transformation from an austenitic to a martensitic phase occurs. This is an exothermic transformation that leads to the release of latent heat and thus to the heating of the eCM under adiabatic conditions. During unloading, the endothermic reverse martensitic-austenitic transformation occurs, leading to the absorption of the latent heat, causing the material to cool below its initial temperature, under adiabatic conditions.
In our recent work [1] we developed an elastocaloric cooling and heat-pumping device that showed outstanding specific performance compared to the existing caloric devices. It is based on the concept of an active elastocaloric regenerator made of Ni-Ti tubes loaded in compression. It has the shape of a shell-and-tube heat exchanger and consists of eighteen 56 mm long tubes, equivalent to only 13.7 g of eCM. The regenerator can operate in both cooling and heat-pumping modes and shows durable operation and record performance with a maximum temperature span of more than 31 K at zero thermal load and a heating power of more than 60 W, equivalent to 4,400 W per kg of eCM at a temperature span of 10 K. The best performance was obtained at a frequency of 2 Hz and a stress level of 825 MPa.
In this talk we will present the performance of our elastocaloric regenerator, its main characteristics and the research behind the development of the device. In particular, we will focus on the optimization process of the critical areas of the regenerator: the flow distribution inside the regenerator, the displaced fluid volume ratio, the dead volume and the heat transfer losses to the ambient. Moreover, motivated by the excellent results we have obtained with a single elastocaloric regenerator, we are designing a more complex and compact prototype device with four phase-shifted regenerators including a force recovery mechanism, to increase the total cooling/heating power with respect to a single regenerator and to reach a performance comparable to that of a small conventional cooling/heat-pumping unit.

Acknowledgments
This work was supported by European Research Council under Horizon 2020 program
(ERC Starting Grant No. 803669). Jaka Tušek would also like to acknowledge the support of Slovenian research agency (Core funding No. P2-0422).

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SESSION EN03.09: Electrocaloric Materials and Devices II

Session Chairs: Neil Mathur and Qibing Pei
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2003

4:00 PM *EN03.09.01
Richness of Ferroelectrics for Caloric Cooling Brahim Dkhil; Univ. Paris-Saclay, CentraleSupélec, France

The search for alternative solid-state refrigeration materials to hazardous gases in conventional and cryogenic cooling devices is a very active field of condensed matter. The use of phase transitions is a powerful tool to achieve giant caloric effects in ferroic materials in which magnetization, polarization, strain and/or volume can be strongly tuned under a moderate external stimulus. Here, we explore various features of ferroelectric materials to reveal their potentialities as solid state coolers. This includes their phase transitions, the multiphase and critical points, their stress-sensitivity, their inverse electrocaloric effect, the asymmetry in non-ergodic states, the use of dual-stimuli multiferroics or intentionnally introduced defects. These aspects will be put in perspective of the recent works in the literature.

4:30 PM *EN03.09.02
Electrocaloric Materials for Practical EC Heat Pumps Qiming Zhang; The Pennsylvania State University, United States

More than a decade of active electrocaloric (EC) material research has produced several EC materials that exhibit a giant electrocaloric effect (ECE) at high electric fields which is assured by direct measurement. These EC materials have enabled the demonstration of EC cooling devices, which exhibit temperature lifts of more than 10 K at thermal non-loading. These research and development efforts have revealed the critical importance of electrical breakdown, which is common in all electric and dielectric materials and devices under high voltages and electric fields, in developing EC materials and their use in EC devices. This talk will present general considerations in developing EC materials for EC coolers that generate large temperature span with significant cooling powers. Recently reported large ECE at low electric fields (fields much below the electric breakdown) in the P(VDF-TrFE-CFE-FA) tetrapolymers creates opportunities for practical EC coolers. We will present materials studies related to the phase transition behavior in this new class of relaxor polymers. We will also present the associated electromechanical actuations of the materials which may be utilized for heating pumping from the cold load to heat sink.

SESSION EN03.11: Virtual Session I

Session Chairs: Sakyo Hirose, Xavier Moya, Julie Slaughter and Jaka Tusek
Wednesday Morning, April 26, 2023
EN03-virtual

10:30 AM *EN03.05.01
Magnetic Shape Memory Heuslers for Caloric Applications—The Crucial Role of Microstructure in the Martensitic Transformation Franca Albertini[1], Milad Takhsha Ghahfarokhi[1], Simone Fabbrici[1], Francesca Casoli[1], Lucia Nasi[1], Giovanna Trevisi[1], Greta Cavazzini[1,2], Lorenzo Gallo[1,2], Francesco Cugini[1,2] and Massimo Solzi[1,2]; [1]Consiglio Nazionale delle Ricerche IMEM-CNR, Italy; [2]Università degli Studi di Parma, Italy

The vast family of Ni-Mn based Heusler alloys provides an extended playground of physical properties. The interplay between a martensitic transformation and magnetically ordered states gives rise to a series of functional properties that can be exploited in different technological sectors, among which remote actuation, solid state refrigeration and thermomagnetic generation. Their excellent responsiveness to external fields, i.e. magnetic field, pressure and stress and their combined application, makes them promising for multifunctional exploitation. On the other hand the hysteretic character of the martensitic transformation cripple the performance of these materials in cyclic operations.

In my talk I will present some recent results on NiMn-based Heuslers, including nano/microscale materials obtained by different fabrication methods, i.e. epitaxial thin films [1], patterned micro/nanostructures [2], mechanically-milled particles [3]. Thin films and micro/nanostructures are of particular interest not only for the realization of miniaturized new-concept devices, but also for providing insights into the magneto-structural coupling at the different length scales, suggesting possible strategies for the optimization of material performances.
The talk will focus on microstructure tuning and microstructure-related effects on the martensitic transformation, in view of the possible exploitation of this class of materials in smart and caloric applications.

[1] M. Takhsha Ghahfarokhi et al., Acta Mater. **23** (2021), 117356.
[2] M. Takhsha Ghahfarokhi et al., Appl. Mater. Today **23** (2021), 101058.
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11:00 AM *EN03.05.03
Magnetic Refrigeration – A Materials Challenge Max Fries and Falk Muench; MagnoTherm Solutions GmbH, Germany

Magnetocaloric materials change their temperature when a magnetic field is applied or removed. At MagnoTherm Solutions GmbH, we develop magnetic cooling devices based on our many years of experience in the field of synthesis and characterization of magnetocaloric materials. In the talk, we will present the performance of our latest developed prototypes and compare them to conventional vapor compression devices. We will present possible setbacks when integrating materials into a magnetic cooling machine and give an overview of our lessons learned and some insight on future roadmaps of material development.

11:30 AM EN03.04.03
Large Electrocaloric Effects in Lead-free $BaTiO_3$ Multilayer Capacitors Junning Li[1], Alvar Torelló[1], Veronika Kovacova[1], Sakyo Hirose[2] and Emmanuel Defay[1]; [1]Luxembourg Institute of Science and Technology, Luxembourg; [2]Murata Manufacturing Co., Ltd., Japan

Electrocaloric (EC) materials, presenting large adiabatic temperature change or isothermal entropy change under the application (or removal) of electric fields, hold the potential to offer more efficient alternatives to caloric heat pumps for replacing hazardous gases used in traditional vapour-compression systems. Recently, large EC effects with 5.5 K have been reported in $Pb(Sc_{0.5}Ta_{0.5})O_3$ multilayer capacitors (MLC) [1] thanks to its strong first-order phase transition, and then a 13 K of temperature span is reported in a prototype based on these MLC [2]. However, the toxicity of lead forces researchers to find eco-friendly materials exhibiting EC performances competitive with lead-based. Here, we study the EC effects in lead-free $BaTiO_3$ (BTO) MLC using an infrared camera. Unlike the commercial BTO MLC, we prepared our sample without scarifying the feature of first-order transition in BTO. The adiabatic temperature variation versus temperature profile shows two peaks, which matches with two first-order phase transitions of BTO in the same temperature range, as observed by Differential Scanning Calorimetry. We measured a temperature drop of ~ 0.9 K with a temperature span of 70 K under 170 $kV\ cm^{-1}$, starting at 30 °C near the tetragonal-to-orthorhombic transition. Under the same electric field, a larger temperature change of ~ 2.4 K was recorded above 126 °C, the Curie temperature of BTO. Our findings suggest that further optimized BTO MLC can offer a path for designing lead-free caloric cooling prototypes with promising results.

[1] Nair, Bhaskaran, et al. "Large electrocaloric effects in oxide multilayer capacitors over a wide temperature range." Nature 575.7783 (2019): 468-472.
[2] Torelló, A., et al. "Giant temperature span in electrocaloric regenerator." Science 370.6512 (2020): 125-129.

SESSION EN03.10: Virtual Session II: Multicaloric Materials
Session Chairs: Sakyo Hirose, Xavier Moya, Julie Slaughter and Jaka Tusek
Thursday Morning, April 27, 2023
EN03-virtual

8:30 AM *EN03.10.01
Giant and Durable Electrocaloric Effect in Polar High-Entropy Polymers Xiaoshi Qian and Donglin Han; Shanghai Jiao Tong University, China

For a practical electrocaloric (EC) device, a $\Delta T > 5$ K is required for its solid-state working body. Although giant ECEs have been observed for more than 15 years, the large temperature change ($\Delta T > 5$ K) still requires large electric fields, *e.g.*, 5.5 K under 29 MV/m for PST ceramic MLC (Nature 575, 468, 2019) and 5.1 K under 83.3 MV/m for P(VDF-TrFE-CFE) polymeric MLC (Science 357, 1130, 2017). These two materials represent the best EC material in inorganics and organics, but the fields applied were too close to the breakdown field (E_b) of respective materials, raising issues in reliability and practical deployment of the technology. In this work, we developed a high-entropy EC polymer by incorporating C=C double bonds in the polymeric main chain to induce localized nano-scale structural modification. Compared to state-of-the-art polymers, this new polymer tripled the cooling effect under ultra-low electric field of polymer, *i.e.*, the ΔT was enhanced from below 2 K to over 7.5 K (3.75-fold) under ultra-low field of 50 MV/m, which is merely 14% of its breakdown field. For the first time, we show that the large ECE ($\Delta T > 5$ K) can operate with fatigue resistance for more than one million cycles.

9:00 AM *EN03.10.02
High-Performance Elastocaloric Materials via Novel Design and Advanced Fabrication Daoyong Cong; University of Science and Technology Beijing, China

Elastocaloric refrigeration, which employs the large latent heat associated with stress-induced martensitic transformation, has been considered as one of the most promising non-vapor-compression cooling technologies. Development of high-performance elastocaloric materials is central for the implementation of elastocaloric refrigeration. After a short review of the elastocaloric research field, this talk will introduce our recent endeavour on developing high-performance elastocaloric materials via novel design and advanced fabrication. The concept "the larger the unit cell volume change across phase transition, the larger the transition entropy change" was used to design a novel alloy with a colossal elastocaloric effect. The "high-entropy alloy" concept was employed to design elastocaloric alloys with a wide operating temperature window. Advanced fabrication techniques, including directional solidification and additive manufacturing, were applied for microstructure control to increase the magnitude of elastocaloric effect and enhance its long-term cyclic stability. Perspectives on future directions for advanced elastocaloric materials development will be given.

9:30 AM *EN03.10.03
Multicaloric Effects and Additively Manufactured Elastocaloric Materials with Tailored Transformations Huilong Hou[1], Bin Wang[1], Kai Wang[1], Yongzhong Lai[1], Suxin Qian[2], Xinqing Zhao[1] and Ichiro Takeuchi[3]; [1]Beihang University, China; [2]Xi'an Jiaotong University, China; [3]University of Maryland, College Park, United States

The field of caloric cooling has undergone a series of transformations in the past decade bolstered by the advent of new materials and devices, and yet there remain challenges that need to be overcome before they can enjoy widespread commercialization. An exciting new direction in the field is multicaloric materials systems, which inherently display several first-order transitions and thus can be cooled using multiple fields. In this talk, we survey the emerging field of multicaloric cooling and explore state-of-the-art caloric materials systems responsive to multiple fields. We show that all caloric cooling processes fall into one of the four schemes of multicaloric cooling modes depending on whether a material is a single-phase or a composite and whether a single field or multiple fields are required for pumping heat. We examine the physics of multicaloric cooling concerning intrinsically coupled ferroic order parameters in multiferroic materials. We will also discuss the key factors governing the overall system efficiency of multicaloric cooling devices.

Because the mechanocaloric effect plays an important role in multicaloric cooling configurations, we revisit the definition of the mechanocaloric effect and expand its scope beyond the limited two members of elastocaloric and barocaloric effects. Further, we employ additive manufacturing to design highly-reversible superelastic transition pathways at a microscopic level in elastocaloric Ni–Ti-based alloys. Through rapid cooling and high-precision compositional tuning, we have fabricated Ni–Ti binary nanocomposites with unique curved nano-interfaces, which give rise to quasi-linear stress-strain behaviors with unusually narrow hysteresis, resulting in an enhancement in the materials coefficient of performance by a factor of four to seven. Our nanocomposite NiTi is stable over 1 million cycles of superelastic transitions. In addition, we have fabricated Ni–Ti-based ternary alloys whose transformation temperature and latent heat can be tailored in a large range.

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10:00 AM *EN03.10.04
Lock-In Thermography as a Tool for Investigating Caloric Effects Ken-ichi Uchida; National Institute for Materials Science, Japan

Thermal measurement techniques play an important role in pioneering new thermal management principles. We have investigated various physical phenomena and heat control functionalities through active thermal measurement techniques based on the combination of non-contact temperature measurements and lock-in detection. Specifically, we have mainly used the lock-in thermography (LIT) method, in which thermal images are acquired by an infrared camera while periodically applying thermal excitation to a sample. In the LIT method, only the temperature change components that follow the periodic excitation are selectively extracted by Fourier analysis, which makes it easy to achieve highly sensitive temperature measurements with sub-mK-order resolution. There are various choices of excitation sources, such as a charge current, heat current, magnetic field, and light, and a variety of heat generation phenomena responding to the excitation sources can be precisely measured. The main application of the LIT technique has been nondestructive failure analysis of semiconductor devices, since the path of a charge current can be visualized by measuring Joule heating distribution associated with periodic current application. Recently, it has been used for fundamental studies on spin caloritronics and thermoelectrics [1-4].
In this talk, we will summarize the measurement principles and features of the LIT method and present recent experimental results on magnetocaloric [5,6], electrocaloric [7], and elastocaloric [8] effects obtained by this technique. The LIT method not only enables non-contact, simultaneous measurements of adiabatic temperature changes induced by the caloric effects for a large number of samples, but also leads to the demonstration of their new functionalities. This technique will thus be useful for material exploration and application research of the caloric effects.

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SYMPOSIUM

April 11 - April 26, 2023

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SESSION EN04.01: Catalysis I
Session Chairs: Hong Li and Xiaolin Zheng
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2004

10:30 AM *EN04.01.01
Top-Down Production of Macroscopic Monolayers For Study of Static and Dynamical Properties Fang Liu; Stanford University, United States

Two dimensional (2D) materials and their artificial structures hold great promises for electronic, optoelectronic, and electrochemical applications. The best quality monolayers for exploring the exotic quantum properties so far are mostly produced by scotch tape exfoliation, which is stochastic and often yields microscopic sized monolayers. On the other hand, bottom-up growth techniques such as chemical vapor deposition often produces monolayers with higher defect densities. Beyond the Scotch tape exfoliation, a few new scalable and controllable top-down processes have been developed to exfoliate a variety of van der Waals (vdW) single crystals into monolayers and monolayer nanoribbons with high yield, high quality, and macroscopic dimensions. High-quality and large-area crystals will allow us to further assemble them into artificial heterostructures. The monolayers and other 2D structures have been demonstrated to achieve enhanced nonlinear optical responses, and integrate into multiple pump probe techniques as electron diffractions to explore the key static and dynamic properties in these low dimensional systems. Obtaining high quality materials with enhanced yield will not only facilitate the basic research, but also take us one step closer to mass production and commercialization of the 2D devices in the future.

11:00 AM EN04.01.02
Energy Level Alignment at 2D Semiconductor/Electrolyte Interfaces for Photoelectrochemical Energy Conversion Justin Sambur; Colorado State University, United States

The fundamental problem that limits the solar energy conversion efficiency of conventional semiconductors such as Si is that all absorbed photon energy above the band gap is lost as heat. The critical question that our research addresses is: *Can we avoid energy losses in semiconductors*? Hot-carrier systems that avoid such losses have tremendous potential in photovoltaics and solar fuels production, with theoretical efficiencies of 66% (well above the detailed-balance limit of 33%). Ultrathin 2D semiconductors such as monolayer (ML) MoS_2 and WSe_2 have unique physical and photophysical properties that could make hot-carrier energy conversion possible. The specific knowledge gap in the field is how the energy levels of 2D semiconductors move with applied potential and/or illumination, making the driving force for charge transfer ($\Delta G^{0'}$) unclear. Since $\Delta G^{0'}$ governs the hot-carrier extraction rate (k_{ET}), understanding how and why $\Delta G^{0'}$ changes under solar fuel generation conditions is critical to controlling k_{ET} relative to the cooling rate. Absence of this critical information is limiting our ability to perform hot-carrier photochemistry. Our research team has employed photocurrent spectroscopy, steady-state absorption spectroscopy, and in situ femtosecond transient absorption spectroscopy as a function of applied potential to characterize underlying steps in a ML MoS_2 photoelectrochemical cell. The rich data set informs us on the timescales for hot-carrier generation/cooling and exciton formation/recombination, as well as the magnitudes of changes in exciton energy levels, exciton binding energies, and the electronic band gap. These findings open the possibility of tuning the hot-carrier extraction rate relative to the cooling rate to ultimately utilize hot-carriers for solar energy conversion applications.

11:15 AM EN04.01.04
Large-Area Triazine-Based Covalent Organic Framework Nanofilm on Cu for Electrochemical CO_2 Reduction Yusik Oh and Hye Ryung Byon; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Carbon dioxide (CO_2) emission from the combustion of fossil fuels causes global warming and climate change. Much attention has been paid to converting CO_2 gas to high-value fuels, and electrochemical CO_2 reduction reaction (*e*-CO_2RR) is one of the promising methods operated at ambient pressure and room temperature. Indeed, the *e*-CO_2RR successfully generated carbon monoxide (CO) with >90% Faradaic efficiency (FE) using Ag and Au catalysts.[1] In comparison, ethylene (C_2H_4), ethanol (C_2H_5OH), and propanol (C_3H_7OH) production, called C_{2+} species, remained challenging due to complicated reaction pathways and low selectivity. Copper (Cu) is the sole catalyst facilitating these multicarbon formations but also allowing H_2 and CO evolution.[2] Thus, it is necessary to suppress these undesired reactions while enhancing CO coverage for the C-C dimerization.
Here, we developed a large-area covalent organic framework (COF) nanofilm on the Cu substrate to enhance the C_{2+} selectivity. Triazine, as a well-known CO_2-capturing moiety, was used as the main motif in the COF. A photo-assisted Schiff-base reaction assembled triazine and linkage building blocks and formed ~3.3 nm diameter of hexagonal pores and well-ordered eclipse structure by the reaction at solution/air interface. Then, a floating COF film was transferred to the Cu substrate. The resulting seamless COF nanofilm can provide a consistent local condition for triazine moieties, thus being distinguished from previously studied powdery and polymeric organic layers.[3] For the *e*-CO_2RR, the COF/Cu provided 52.2% FE of C_{2+} at -1.1 V vs. RHE, which was twice higher than the bare Cu (23% for C_{2+}). In particular, C_2H_4 was predominant and occupied ~25% of FE. The hydrophobic COF film was significantly suppressed in H_2 evolution (17.8% vs. 35.1% FE for triazine-COF and Cu, respectively). In addition, the porous nanochannels provided high local pH in the confined COF/Cu interface, causing further mitigation of H_2 evolution. The COF film also helped perform stable *e*-CO_2RR and was preserved on the Cu substrate after 2 hours, although some torn holes appeared. This result was in contrast with the rapid deactivation of the bare Cu (<1 h). We also separately prepared triazine-free COF by replacing triazine with benzene and detected 30.5% of FE_{C2+} and 18.7% of FE_{C2H4}. It suggested better CO_2 and CO interaction at triazine and promoted the C-C dimerization at the COF/Cu interfaces. Compared to the ~4 nm thickness of triazine-COF films, a thick one (~27 nm) showed significant CH_4 conversion efficiency at the expense of C_{2+} production. It revealed the competitive CO conversion reaction to hydrogenation and the C-C coupling at a thicker organic film. In the presentation, I will discuss the detailed role of triazine-COF and highlight the pivotal material design to understanding electrochemical reactions and optimizations in the presentation.

[1] *ACS Catal.* **2021**, *11*, 4530−4537
[2] *J. Am. Chem. Soc.* **2014**, *136*, 14107−14113
[3] *ACS Catal.* **2018**, *8*, 4132−4142

11:30 AM EN04.01.05
Effects of Nitrogen Functionalities and Metal Ions in Defect Engineered Low Dimensional Carbon Catalysts on Carbon Dioxide Electroreduction
Soumyabrata Roy[1], Ram Manohar Yadav[2,1], Zhengyuan Li[3], Jingjie Wu[3] and Pulickel Ajayan[1]; [1]Rice University, United States; [2]VSSD College, CSJM University, India; [3]University of Cincinnati, United States

Renewable electricity powered reduction of carbon dioxide (CO_2) to fuels and chemicals has extensive potential to close the anthropogenic carbon cycle. The large spectrum of CO_2 electroreduction (eCO_2R) products offers great opportunity from an electro-synthetic standpoint, although its potential is still limited by low catalytic selectivity for specific key products. Metal catalysts majorly dominate the state-of-the-art scenario in eCO2R. Copper (Cu) leads the way with its ability to produce hydrocarbons and oxygenates beyond the 2e-reduction process, but unfortunately with a wide product distribution. On the other hand, Ag/Au and Sn/Bi produce C1 products like carbon monoxide (CO) and formate ($HCOO^-$) respectively, with >90% Faradaic efficiency (F.E.). Methane (CH_4), which is a kinetically hindered 8e- electron eCO_2R product, can be used both as a fuel and hydrogen carrier. Thus, the challenging CO_2-to-CH_4 conversion pathway has received considerable attention in the past few years as an important step in the carbon capture and utilization roadmap.[1,2] Interestingly, low dimensional carbon matrices provide a reasonable alternative to metal-systems as tunable catalysts for eCO_2R. Over the years our group has systematically investigated several avenues of defect engineering, nitrogen (N) doping, amine functionalization etc. to develop important structure-activity correlations in carbon nanocatalyst (quantum dots, carbon nanotubes, graphene etc.) for eCO_2R.[3-7] In our current study, we present a general molecular tuning strategy- in-situ amine functionalization of nitrogen-doped graphene quantum dots (N-GQDs) for CO_2-to-CH_4 conversion at high efficiencies.[8] N-GQDs achieve a CH_4 Faradic efficiency (FE) of 63% and 46%, respectively, at CH4 partial current densities of 170 and 258 mA cm^{-2}, matching to or even surpassing the performance of the state-of-the-art Cu-based catalysts.[9,10] The N-GQDs also produce C_2 products comprising primarily ethylene (C_2H_4) and ethanol (C_2H_5OH) with a maximum FE of ~10%. Detailed structure-activity relationship studies reveal that the

CH_4 yield varies linearly with amine group content, whereas the C_2 production rate shows a positive dependence on the pyridinic N dopant content. A holistic analysis of our collective studies on carbon nanocatalysts provides meaningful insights into the routes and effects of controlled N-defect doping strategy (defect nature and density) with specific N configurations, variable local chemical environments, and functionalization on eCO_2R outcomes. These works can guide the rational design of defect-engineered carbon nano-catalysts with CO_2-to-C1 product conversion efficiency at the industrially relevant level.

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SESSION EN04.02: Catalysis II

Session Chairs: Hong Li and Xiaolin Zheng
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2004

1:30 PM *EN04.02.02
A Platform of 3D Printed Devices to Power Wearable Sensors Cecilia Mattevi; Imperial College London, United Kingdom

3D-printing is regarded as a sustainable manufacturing technique with applications in different industries, from automotive to aerospace, medicine, and energy.
At small scale, 3D printing can enable the fabrication of miniaturized electrodes with free form factors and high mass loading over small footprint areas. 2D materials with outstanding electrochemical properties are particularly suitable to serve as functional materials in energy harvesting, conversion and storage devices.
In this talk, I will present our work on 3D printed miniaturized electrodes in the form of supercapacitors, rechargeable batteries beyond lithium, and energy harvesting systems. We use earth-abundant electrode materials and water-based electrolytes or gel electrolytes to manufacture energy storage and harvesting devices to meet the growing energy demand to power wearable and portable electronic devices.
I will discuss the materials challenges in formulating inks of nanomaterials and different architectural design to optimize the electrochemical performance. I will then show how these devices can power wearable sensors.

2:00 PM EN04.02.03
Intermediate Temperature Alkaline Fuel Cells Enabled by Using Inorganic Layered Double Hydroxides as Solid Electrolyte Leanna Schulte, Jarrett Dillenburger, Zahra Fakhraai and Thomas Mallouk; University of Pennsylvania, United States

Layered double hydroxides (LDHs) are a class of two-dimensional material whose nanosheets are comprised of metal cations octahedrally coordinated to hydroxides. LDHs typically exist as micron wide hexagonal crystallites, and within each crystal, tens of nanosheets are vertically stacked together, forming inter-sheet regions that contain water, hydroxides, and other anions to balance charge. Unique among inorganic layered materials, LDH nanosheets have a positive charge which facilitates impressive hydroxide conductivity on the order of 10^{-2} – 10^{-1} S/cm, competitive with state-of-the-art polymer ion-exchange membranes that are employed as solid electrolytes in alkaline fuel cells and electrolyzers. LDHs also excitingly preserve water content in their inter-sheet galleries well beyond the boiling point of water, up to 200 °C in some cases, a temperature range in which polymer electrolytes experience critical loss of humidity and thermal degradation. Therefore, LDHs are a promising candidate for solid electrolyte in alkaline fuel cells and electrolyzers as they could enable higher operating temperatures (100-200 °C) leading to faster kinetics of desired redox reactions and higher energy conversion efficiency.

In my presentation, I will describe my work in implementing LDHs as inorganic solid electrolyte in alkaline fuel cells to access to an elevated range of operating temperatures at and above 100 °C. First, I will discuss the fundamental relationship between hydroxide conductivity and LDH interlayer anion identity under ambient pressure conditions and over a temperature range up to 140 °C that has not yet been explored for this two-dimensional material. I will then share fabrication strategies to transform crystalline LDH powders into gas impermeable, mechanically robust, and chemically stable membrane architectures. Lastly, fuel cell polarization behavior of LDH alkaline fuel cells will be presented, and *in operando* three electrode characterization of the anode and cathode will be used to understand kinetics of the hydrogen oxidation and oxygen reduction reactions in this new class of inorganic fuel cell.

2:15 PM EN04.02.04
Defect-Modified Two-Dimensional Carbon Nitride for Solar Energy Storage and Hydrogen Production Li-Che Chueh and Jih-Jen Wu; National Cheng Kung Univ, Taiwan

Cyanamide-functionalized potassium poly(heptazine imide) (CFKPHI) which exhibits the abilities of light harvesting and photoelectron storage for solar energy conversion is a new class of two-dimensional (2D) carbon nitrides. In this work, CFKPHIs were synthesized by ionothermal treatment of supramolecular complexes of various nitrogen-rich organic compounds. Solid-state nuclear magnetic resonance characterizations reveal that in addition to the cyano defect in CFKPHI, intrinsic defect modified CFKPHIs, including C-H group-functionalized and carbon vacancy-modified CFKHPIs, can be tailored by the compositions of the supramolecular complexes. The C-H group-functionalized and carbon vacancy-modified CFKHPIs demonstrate comparable photocatalytic activities for hydrogen evolution under AM 1.5G (100 $mWcm^{-2}$) illumination in the presences of the Pt nanoparticle cocatalyst and the hole scavenger of triethanolamine (TEOA), which are 3-fold enhanced compared to the photocatalytic activity of CFKPHI. The dark photocatalytic performances of the two defect-modified CFKPHIs were also examined in this work. The CFKPHI photocatalysts in TEOA aqueous solution were irradiated using AM 1.5G (100 $mWcm^{-2}$) for 2 h, the Pt precursor was injected into the solution as soon as the irradiation was turned off. The delayed H_2 productions over the C-H group-functionalized and carbon vacancy-modified CFKPHIs are 14-fold and 194-fold higher than that over CFKPHIs. The photophysical properties of light-storing carbon nitrides are variable by modifying the microstructure of CFKPHIs towards efficient solar energy storage and conversion. The influences of chemical and electronic structures on the solar energy storage and photocatalytic activity of KPHIs will be discussed in this presentation.

2:30 PM BREAK

3:00 PM EN04.02.06
Electrodeposited Single-atom Coupled with CoFe Layered Double Hydroxides for Enhanced Oxygen Evolution Jaehyun Kim[1] and Ho Won Jang[1,2]; [1]Seoul National University, Korea (the Republic of); [2]Advanced Institute of Convergence Technology, Korea (the Republic of)

To address the global energy crisis, hydrogen production from electrochemical water electrolysis is one of the most promising strategy for obtaining a sustainable and eco-friendly energy source without emitting carbon dioxide. For industrial large-scale hydrogen production from water electrolysis, current densities larger than 1 A cm-2 at low overpotentials less than 300 mV should be acquired to reduce the price of hydrogen and substitute the fossil fuels. However, the oxygen evolution reaction (OER) in water electrolysis requires a four-electron transfer process, which leads to the sluggish kinetics with high activation barriers and overpotentials. Ir or Ru-based electrocatalysts has excelled at decreasing the overpotential of OER but these scarce elements are expensive and also suffer from the poor stability. Therefore, developing active and durable electrocatalysts with abundant elements or ultralow noble metal usage is urgent for industrial hydrogen production. In this research, we atomically dispersed Ir and Ru metal atom on the iron–cobalt layered double hydroxide (FeCo-LDH) with unsaturated coordination sites using facile two-step electrodeposition. Ir and Ru single-atoms facilitate the electron transfer of FeCo-LDH by balancing the adsorption and desorption behavior of the intermediates for the four-electron transfer process of OER. First-principle calculations revealed that the energy barrier of deprotonation intermediate step from *OH to *O was dramatically lowered in FeCo-LDH with Ir and Ru single-atom compared to pristine FeCo-LDH and metal oxides. By using X-ray absorption spectroscopy, it was confirmed that Ir and Ru single atoms coupled with unsaturated surface oxygen atoms of FeCo-LDH exist at a low valence state, which hinders the oxidation of Ir and Ru single-atom and prevent the metal dissolution into the electrolyte during OER. With less than 1 wt.% loading of Ir and Ru, FeCo-LDH with Ir and Ru single-atom achieved the current density of 10 mA cm-2, 100 mA cm-2, and 1000 mA cm-2 at the overpotential of 187 mV, 210 mV, and 270 mV, respectively, with a small Tafel slope of 31 mV dec-1. We further investigated other transition metal elements as atomically dispersed on FeCo-LDH by density functional theory (DFT) based graph neural network (GNN) model and predicted that non-noble element as Cr, W, and Ce single-atom on FeCo-LDH might show ideal adsorption and desorption behaviors of the intermediates for OER. We believe that synergetic coupling between metal single-atom and FeCo-LDH supports is the key for developing a superior OER electrocatalysts and the practical large-scale hydrogen production from water electrolysis to substitute fossil fuels and facilitate a green global energy ecosystem.

3:15 PM EN04.02.07
Ultrathin 2D-Pt/NiFe-LDH/2D-Pt Sandwiched Catalyst toward Synergistically Enhanced Electrocatalytic Hydrogen Evolution Reaction SunWoo Jang; Pohang University of Science and Technology, Korea (the Republic of)

The search for efficient Pt electrocatalysts in hydrogen evolution reaction (HER) from alkaline water is noteworthy, but the obtained HER activity is hugely relies on synergistic catalysis with its accompanying oxophilic component responsible for water dissociation. In addition, the exfoliation of Pt into atomic level and their precise electronic modification could play pivotal role for achieving superb HER performance. Herein, a surfactant-free, facile, wet-chemical protocol is established to develop nanometre-thin, two-dimensional Pt nanosheets (2D-Pt) through 'surface-surface confined growth' on 2D-nickel iron layered double hydroxides (LDHs) template. Under an optimized reaction condition, a 2D-Pt/LDH/2D-Pt sandwich structure were realized, where the close proximity of the two 2D-catalytic entities i.e., Pt and oxophilic LDH are recognised to maximize their electronic interaction in the strongly bound nanohybrid. Thus, through judicious installation of layered LDH/2D-Pt interface for the water dissociation and combining with the fast and efficient hydrogen evolution from the on-bound thin and porous 2D-Pt layers, an well-organized interfacial synergy endows the HER performance to reach 6.1 times superior Pt mass utilization than commercial 20% Pt/C at -0.07 V vs RHE, whereas their sandwiched nature of the catalytic entities promote a record-high HER stability over 50 h long electrochemical study. This work highlights the opportunity for merging the exfoliated Pt into atomic level and their strong integration with catalytic in-house LDH surface to challenge remarkable electrochemical HER activity and excellent durability.

3:30 PM EN04.02.08
Electrode Material based on 2D MoS$_2$ and rGO Aerogels for Supercapacitor Applications Glaura G. Silva, Daniel E. Lippross, Felipe Medeiros and Rodrigo L. Lavall; Universidade Federal de Minas Gerais, Brazil

Supercapacitors are of great interest as they bridge the gap of energy density versus power density between conventional capacitors and batteries. The development of new materials for electrodes of supercapacitors is the challenge addressed in this work. The semiconductor phase of MoS$_2$ (H-MoS$_2$) is the stable phase while the metallic conducting phase (T-MoS$_2$) is metastable and will transition to H-MoS$_2$ with heating and ageing. However, when layers of MoS$_2$ contact rGO they may transition and remain in the T-MoS$_2$. In this work, a composite of 2D MoS2 and an rGO aerogel was investigated to produce an effective supercapacitor electrode. Aerogels have potential in this application as their porous morphology give the material a high surface area in which electrolyte can diffuse and electric double layers can form. MoS2 monolayers were prepared by intercalating MoS2 with lithium and exfoliating with sonication, this produced a suspension of monolayer MoS2 with a mean diameter of 500 nm. The rGO aerogel was produced in a self-assembly reduction reaction of GO with ascorbic acid. The MoS2 suspension could be dripped onto the aerogel's sponge-like structure that effectively soak up the suspension, depositing the MoS2 on the rGO surface. The obtained materials were examined by scanning electron microscopy with element mapping, transmission electron microscopy, atomic force microscopy in contact mode, X-ray diffraction and Raman spectroscopy. Cyclic voltammetry was used to determine the electrochemical window of the electrode, galvanostatic charge-discharge to determine the specific capacitance and electrochemical impedance to analyze the charge transfer kinetics, all experiments were conducted using a three-electrode flooded cell in a 1M solution of Li$_2$SO$_4$. The tested devices showed capacitance of 140.4 F g^{-1} at 0.5 A g^{-1} for the supercapacitor with rGO-MoS$_2$, which is 60% higher than the device using only rGO in the electrode. Moreover, the rGO-MoS$_2$ electrode based supercapacitor evidenced great cyclability maintaining 85% efficiency after 5000 cycles. Its superior performance over a pure rGO aerogel electrode can be attributed to the increase in surface area of the porous electrode and the increase of interaction with the electrolyte.

3:45 PM EN04.02.09
Trimetallic Oxides/GO Composites Optimized with Carbon Ions Radiations for Supercapacitive Electrodes Adil Alshoaibi; King Faisal University, Saudi Arabia

Hydrothermally synthesized electrodes of Co3O4@MnO2@NiO/GO were produced for use in supercapacitors. Graphene oxide (GO) was incorporated into the nanocomposites used for electrode synthesis due to its great surface area and electrical conductivity. The synergistic alliance among these composites and GO enhances electrode performance, life span, and stability. The structural properties obtained from the X-ray diffraction (XRD) results suggest that nanocomposites are crystalline in nature. The synergistic alliance among these composites and GO enhances electrode performance, life span, and stability. Performance assessment of these electrodes indicates that their characteristic performance was enhanced by C2+ radiation, with the uttermost performance witnessed for electrodes radiated with 5.0 1015 ions/cm2.

4:00 PM EN04.02.10
Crumpled Graphene-MoS_2-Graphene Heterostructure for Flexoelectric Energy Harvester Yeageun Lee[1], Hyungjong Bae[1], Farhadul M. Haque[1] and SungWoo Nam[2]; [1]University of Illinois at Urbana-Champaign, United States; [2]University of California, Irvine, United States

Flexoelectric effect induces an electric polarization from strain gradient. Theoretically, since the size of the strain gradient grows quadratically as the material's length scale decreases, the flexoelectricity-induced polarization grows quadratically as the material's length scale decreases as well. Consequently, the flexoelectric-induced electric polarization can be maximized in atomically thin two-dimensional (2D) materials. In this study, we demonstrate flexoelectric energy harvesters by utilizing crumpled 2D molybdenum disulfide (MoS_2) as an active material to generate power output from strain gradient. We assembled graphene-MoS_2-graphene vertical stack on a pre-stretched very high bond (VHB) substrate followed by a release of the stretch to create a crumpled heterostructure. The fabricated flexoelectric energy devices showed 1 V of open circuit voltage (OCV) and 10 nA of short circuit current (SCC) under repetitive bending motions. However, the devices showed limited capability on harvesting energy from the translational motion. To overcome this challenge, we employed an asymmetric device configuration. The asymmetric device configuration was achieved by two-step stamping-crumpling methods and resulted in a periodic contact between one graphene electrode and the MoS_2 active layer while maintaining a full contact between the other graphene electrode and the MoS_2 active layer. As a result, the device with asymmetric device configuration showed 3 mV of OCV and 0.01 nA of SCC under repetitive translational motions. Furthermore, the crumpled structure allowed high deformation endurance, and the devices demonstrated robust energy harvesting ability up to 100 % and 50 % stretching strain for symmetric and asymmetric configurations, respectively.

SESSION EN04.03: Poster Session I: Catalysis
Session Chairs: Hong Li and Xiaolin Zheng
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN04.03.01
Universal Platform for Robust 2D Dual Atom Catalysts with Superior Hydrogen Evolution in Wide pH Media Laud Anim Adofo[1,2], Seon Je Kim[1,2], Soo Ho Choi[2], Young-Min Kim[1,2], Soo Min Kim[3] and Ki Kang Kim[1,2]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Institute for Basic Science (IBS), Korea (the Republic of); [3]Sookmyung Womens' University, Korea (the Republic of)

Layered two-dimensional (2D) transition metal dichalcogenides (TMDs) have been suggested as efficient substitutes for Pt-group metal electrocatalysts in hydrogen evolution reaction (HER) during water electrolysis. While scalable synthesis of TMDs is available by chemical vapor deposition (CVD), it is often required to transfer on the electrode, degrading the long-term durability due to the weak adhesion. Furthermore, poor catalytic activities in neutral and basic medium retard the practical applications. Here, we report the universal platform for direct synthesis of superior 2D TMD electrocatalysts (MoS_2, WS_2, ReS_2) for HER in a wide pH. Catalytic activity was further boosted by the incorporation of V-Co dual atoms in ReS_2 for highly efficient wide pH water electrolysis. It shows the ultralow overpotentials of 31 mV, 83 mV, and 35 mV at a current density of 10 mA/cm^2 in acidic, neutral, and alkaline medium, respectively, with high unperturbed durability of more than 70 hours in all media at 200 mAcm^{-2}. These recorded values are the best milestone among TMD catalysts without Pt group metals. The high intrinsic HER performance is explained by the robust catalyst-support synergy, lower energy barrier for water adsorption/dissociation, and the thermoneutral Gibbs free energy after V-Co dual doping. This study holds great promise for scaling up TMDs for industrial water splitting.

5:00 PM EN04.03.02
Surface Active Self-Reconstruction of Ni-Fe Thiophosphate to Core-Shell Oxyhydroxide Nanosheets for Efficient Oxygen Evolution Reaction Ki Kang Kim[1], Balakrishnan Kirubasankar[1,2], Yoseob Won[1], Soo Min Kim[2], Soo Ho Choi[1] and Jae Woo Kim[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Sookmyung Women's University, Korea (the Republic of)

Designing a high efficient, robust oxygen evolution electrocatalyst is an essentially important process in water splitting. Two-dimensional (2D) layered transition metal thiophosphate (MTPs or MPX_3) are evolving as potential candidates for wide-range of applications. In this work, we chose a dual cationic and anionic 2D layered van der Waals Ni-Fe thiophosphate ($NiFePS_3$) ultrathin nanosheets as an OER electrocatalyst rather than conventional Ni-Fe oxides, layered hydroxide and oxyhydroxide. During the electrochemical activation process the abundant dual anionic edge P/S sites react with OH^- ion to form an oxyhydroxide (OOH^*) layer over the surface of $NiFePS_3$. The surface reconstructed NiFe oxyhydroxide (OOH^*)/$NiFePS_3$ can efficiently acts as ultimate catalytic center for oxygen evolution reaction (OER) and trigger dual cationic sites OER mechanism rather than conventional adsorbate evolution mechanism (AEM). As a result, the surface reconstructed NiFe(OOH)/$NiFePS_3$ delivers overpotential of 278 mV at a current density of 20 mA cm^{-2} and better stability over 50 h in alkaline electrolyte. The assembled NiFe(OOH)/$NiFePS_3$||Pt/C full cell water splitting delivers 10 mA cm^{-2} at 1.53 V with excellent stability in alkaline medium and outperformed most NiFe based electrocatalysts. This work provides a valuable fundamental insight toward surface reconstruction of $NiFePS_3$ and the role of dual species involved in dual-site OER mechanisms for constructing efficient OER electrocatalysts.

5:00 PM EN04.03.04
The Atom-level Understanding on the Role of a Transition Metal Heteroatom in the Hydrogen Evolution Reactions on Transition Metal Dichalcogenides Sangjin Lee, Sujin Lee and Young-Kyu Han; Dongguk University, Korea (the Republic of)

Hydrogen has attracted tremendous attention as a sustainable and renewable energy source, and for the last decade, a clean generation of hydrogen has been extensively studied. Since the expected demands for hydrogen will keep increasing up to about 12% of the total energy sources until 2050, establishing clean and feasible hydrogen generation methods from water-splitting is essential because the hydrogen generation still depends largely on fossil fuels, producing massive amounts of greenhouse gases. To effectively generate hydrogen from water, the use of catalysts is considered crucial, boosting the hydrogen evolution reaction (HER) with reduced energy consumption. For effective HER catalysts, the hydrogen adsorption free energy, ΔG_{H^*}, has been considered one of the most significant descriptors to predict the hydrogen generation performance.
Two-dimensional transition metal dichalcogenides (TMDs) are among the most noteworthy catalyst materials for HER because of their earth abundance, high stability and controllable electronic structures. Since Pt catalysts have shown the most superior HER catalytic performances with the near-zero ΔG_{H^*}, intensive research efforts have been carried out to realize new catalyst materials with zero ΔG_{H^*}. Doping of TMD with TM heteroatoms have been

considered promising strategies to optimize the ΔG_{H^*} because doped heteroatoms may provide optimal hydrogen adsorption process and H_2 generation expediting the HER catalytic activity. For examples, Co, Zn, Pd, and Pt were used to reduce the ΔG_{H^*} of MoS_2 by activating its inert basal plane, and doping of Co, Ni, Cu, and Zn into $MoSe_2$ dragged the high ΔG_{H^*} of non-doped structure into the near-zero values. However, although lots of doped TMDs have been suggested for enhanced HERs with optimal ΔG_{H^*}, the atomic-scale process and appropriate general rules explaining the overall relation between the dopant TM and the ΔG_{H^*} have not yet been fully understood.
In this presentation, the universal trends and underlying mechanisms observed in the ΔG_{H^*} on the TM heteroatom doped TMDs are provided. Using first-principles calculations, the electronic and structural analyses were carried out on the 3*d*, 4*d* and 5*d* TM doped MoS_2 catalysts, and we found a distinctive difference between the early and the late TM dopants with respect to the position of Fermi levels on their *d* bands. While the group 9-12 dopants were expected to show an optimal HER performance with the near-zero ΔG_{H^*}, we revealed that the hydrogen adsorption process in those late TM doped MoS_2 is mainly regulated by the strain relaxation from the dopant heteroatom. On the other hand, a structural deformation is barely observed in the early TM doped MoS_2 but the charge in the charge of the chalcogen atom plays a key role to govern the hydrogen adsorption. In addition, we validated that other TMD systems such as $MoSe_2$, $MoTe_2$, CrS_2, and WS_2 had also the similar trends on TM heteroatom doping as found in MoS_2 system.

SESSION EN04.04: MXene and Other Applications
Session Chairs: Damien Voiry and Zongyou Yin
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2004

8:30 AM *EN04.04.01
MXenes for Electrochemistry and Electrocatalysis Yury Gogotsi; Drexel University, United States

The ability of transition metal atoms to reversibly change the oxidation state enables redox energy storage. Catalytic properties of some of the transition metals lead to use of their oxides in catalysis and electrocatalysis. A few oxides that are conductive find applications in transparent conductive layers in solar cells, thus contributing to energy harvesting. However, the majority of oxides have a low conductivity, limiting their applications in electrocatalysis, electrochemical energy storage, harvesting, and conversion. Two-dimensional (2D) carbides and nitrides of transition metals known as MXenes, with a thickness of a nanometer or less, have their surfaces terminated by oxygen or OH, forming compounds like Mo_2CO_2, $Ti_3C_2(O,OH)_x$, or $Nb_4C_3O_2$ with the surfaces resembling that of oxides or hydroxides. They are hydrophilic, form stable colloidal solutions in water, and work well with aqueous, ionic liquid or polar organic electrolytes. They chemically behave very much like the corresponding oxides/hydroxides; however, the fundamental difference is that electrons of the transition metal give them metallic conductivity, thus compensating for the key limitation of oxides and eliminating the need for conductive carbon additives. Moreover, the conductivity of titanium carbide MXene with O, OH, and/or F terminated surface is outstanding and can exceed 20,000 S/cm. A combination of high electronic conductivity with hydrophilicity and 2D structure facilitates electronic and ionic transport, allowing extremely fast charge/discharge with the electron transfer. Naturally, this opens new opportunities in energy storage, electrocatalysis, and other fields where a combination or surface redox with electrical conductivity is required. The family of 2D transition metal carbides and nitrides (MXenes) has been expanding rapidly since the discovery of $Ti_3C_2T_x$ (T stands for surface terminations) in 2011. Close to 50 different MXenes have been synthesized, and the structures and properties of numerous other MXenes have been predicted using density functional theory (DFT) calculations. Furthermore, the availability of solid solutions on M and X sites, control of surface terminations, and the discovery of in-plane and out-of-plane ordered double-M MXenes (e.g., $Mo_2TiC_2T_x$) offer a potential for synthesis of dozens if not hundreds of new materials. The versatile chemistry of the MXene family renders their properties (conductivity, work function, surface charge, etc.) tunable for a large variety of catalytic and energy-related applications.

9:30 AM *EN04.04.03
Architected 2D Materials for Energy Conversion and Transfer Juyoung Leem; Stanford University, United States

Introducing three-dimensionality to two-dimensional (2D) materials opened new possibilities and novel applications in material system design. Extraordinary intrinsic properties of 2D materials have attracted scientific research communities, and various 2D material-based structures and devices have been proposed and demonstrated for photonics applications, energy conversion, and heat and energy transfer. Given the fascinating electrical, optical, and thermal properties of 2D materials, constructing three-dimensional (3D) structures out of 2D materials makes 2D systems even more interesting by providing means of extrinsic modulation of material properties and morphology controls. In this talk, I will focus on architecting 2D materials for nanoplasmonic applications, which allow for confining light, enhancing absorption, and manipulating light-matter interactions. 2D-0D hybrid materials were mechanically deformed to enhance the plasmonic effect of the hybrid materials, and the enhanced plasmonic effects were demonstrated with optical measurements and enhanced sensing efficiency. Lastly, the implications and future directions toward energy conversion and transfer using architected 2D hybrid materials will be briefly discussed.

9:30 AM BREAK

10:00 AM EN04.04.05
Interfacial Surface Engineering of Nickel-Iron Sulfide Nanosheets on Layer Ti_3C_2 MXenes/Nickel Foam Electrode for Alkaline Water Electrolysis
Debabrata Chanda[1,2], Karthik Kannan[1,2], Jagadis Gautam[1,2], Mikiyas Mekete Meshesha[1], Jang S. Gwon[1], Gee Seong Lee[3], Dae Won Hong[3], Myungsik Choi[4] and Bee Lyong Yang[1,2]; [1]Kumoh National Institute of Technology, Korea (the Republic of); [2]GHS Co ltd, Korea (the Republic of); [3]National Nanofab Center, Korea (the Republic of); [4]SJ Tech Co, Korea (the Republic of)

The growing environmental issues arising from the unchecked use of fossil fuels and energy shortages arising from the growing population mean that there is a need for the development of clean renewable energy technologies. Renewable-energy-driven electrochemical water splitting is a promising route for the sustainable production of hydrogen as an energy carrier, as well as the production of future green energy fuels. The electrochemical water splitting process includes the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER); however, both the HER and OER are conventionally carried out using state-of-the-art Pt and Ir catalysts, respectively. Although highly efficient, economical and environment friendly electrocatalysts for hydrogen and oxygen evolution reactions (HER and OER) need to be explored for sustainable hydrogen production. A novel nickel iron sulfides (NiFeS) nanosheets were immobilized on the electrochemically decorated Ti_3C_2 MXene/nickel foam (Ti_3C_2 Mxene/NF) surface via a simple facial hydrothermal pathway (NiFeS@Ti_3C_2 Mxene/NF). Surface morphology and structural engineering of NiFeS with surface effect of Ti_3C_2 MXene creates electronic coupling that can optimize the adsorption energies of water, hydrogen and oxygen, resulting in more accessible a for HER (20 mA cm^{-2}@180 mV) and OER (20 mA cm^{-2}@290mV) combine to provide excellent structural stability over long-term operation. In addition, the synthesized NiFeS@Ti_3C_2 MXene/NF exhibits remarkable overall water splitting performance in a zero-gap anion exchange membrane water electrolyzer (AEMWE) with the current density of 401 mA cm^{-2} at 1.85 V. It provides performance comparable to the state-of-the-art Pt/C||RuO$_2$ and meets the commercial electrolyzer requirements. From a commercial point of view, our electrolyzers are the best because of their low catalyst loading (ca. 1.25 mg cm^{-2}) and low operating temperatures (50 °C), resulting in low capital and operating costs.This result opens new windows for solar hydrogen production for commercial applications and offers the opportunity to replace the polymer electrolyte membrane water electrolyzer (PEMWE).

10:15 AM EN04.04.07
Vacancy-Rich MXene-Immobilized Ni Single Atoms Enable Remarkable Electrocatalytic Oxidation Reaction Shiqi Zhou and Jiayin Yuan; Stockholm University, Sweden

Single-atom catalysts (SACs) have recently attracted tremendous attention because of their outstanding catalytic performance in the field of heterogeneous catalysis. Building a strong interaction between the single atom and its supporting matrix is pivotal in stabilizing the single atoms. Herein, we reported the successful synthesis of Ni SACs supported by an emerging $Ti_3C_2T_x$ MXene by using a 'self-reduction' strategy *via* the assistance of rich Ti vacancies on $Ti_3C_2T_x$ MXene surface, which act as the trap and anchor sites for individual Ni atoms. The constructed Ni SACs supported by the $Ti_3C_2T_x$ MXene show excellent activity and exceptional operational stability toward the hydrazine oxidation reaction. Density functional theory calculations suggested that this remarkable catalytic performance was attributed to the strong coupling of the Ni single atom and its surrounding C atoms, which optimized the electronic density of states that increased adsorption energy and decreased reaction activation energy, thus boosting the electrochemical activity. Results presented here will encourage a broader pursuit of 2D materials-supported SACs designed by a vacancy-trapped strategy combined with the theoretical calculation.

10:30 AM EN04.04.08
2D Shuttle $Ti_3C_2T_x$ MXene Systems for Enhancing the Performance of Composite Cu_2O/TiO_2 Photocatalysts – Comparison with Graphene Oxide
Gilles D. Berhault, Ziba Roostaei, Frédéric Dappozze and Chantal Guillard; Research Institute on Catalysis and Environment, France

Introduction

The most common semiconductor used in photocatalysis is titanium dioxide due to its high photocatalytic response under UV irradiation. However, the use of TiO_2 remains limited due to its high recombination rate of electron-hole pairs. Different strategies were envisaged to improve its photocatalytic response like cationic or anionic doping, coupling with C allotropes or changing semiconductor morphology. In this respect, previous studies made by our group showed that 1D TiO_2 nanotubes (TNT) provides a better separation of photogenerated charges while the coupling with graphene oxide (GO) allows transfer of photoelectrons to GO making more holes available for photooxidation reaction. However, GO was also found to be unstable when combined with TiO_2 under irradiation through overreduction of oxygen functional groups contained in graphene layers, leading to a complete loss of beneficial effect of adding GO after long photocatalytic runs.
The solution envisaged here is to use a different 2D conductive material, MXene sheets ($Ti_3C_2T_x$), to separate physically the semiconductor (TNT) producing photoelectrons from an electron-acceptor component (herein, copper) to improve both the photocatalytic response and the stability under irradiation conditions. Applications are envisaged for both photooxidation reactions and H_2 production.

Materials and Methods

$Ti_3C_2T_x$ MXene layers were obtained by HF etching of Ti_3AlC_2 MAX precursors to remove aluminium. GO was synthesized according to a modified version of the Hummers method. TNT was obtained under hydrothermal alkaline conditions. Two series of impregnation are performed: first, GO or MXene were impregnated onto TNT while $Cu(NO_3)_2.3H_2O$ was then impregnated onto the resulting materials. Photocatalytic tests were performed for the photodegradation of formic acid (FA) and for the H_2 production.

Results and Discussion

To define the role played by $Ti_3C_2T_x$ MXene layers, several systems combining the TiO_2 semiconductor (TNT as compared to the P25 reference) with Cu and/or MXene were considered.
In the case of Cu doping of TiO_2, the formation of Cu_2O species with well-defined plasmonic properties was evidenced after adequate post-calcination treatment leading to improved photocatalytic activity for both photooxidation and H_2 production.
Adding $Ti_3C_2T_x$ MXene to TiO_2 semiconductors (TNT or TiO_2 P25) was also studied considering several parameters (the MXene loading, the HF concentration during etching or the size of the MXene sheets) showing that an optimized choice of $Ti_3C_2T_x$ MXene layers with adequate sheet size and appropriate etching can lead to high beneficial gain in activity.
In a last step, combining copper to the hybrid $Ti_3C_2T_x$ MXene/TiO_2 system allows an even more efficient separation of charges by beneficiating from the electric conductivity of the MXene layers to transport photoelectrons from the semiconductor to the Cu component with an activity twice higher than without MXene. This last result confirms the beneficial role played by $Ti_3C_2T_x$ MXene as a physical separator between donor and acceptor of electrons allowing a better separation of photogenerated charges.
Finally, comparison to the use of GO instead of $Ti_3C_2T_x$ MXene layers confirms the interest of both systems with their own advantages: higher stability of MXene layers under photocatalytic conditions but better flexibility of GO favoring a higher interaction with each other component.

Conclusion

The interest of using a physical separator between donors and acceptors of photoelectrons has been demonstrated using $Ti_3C_2T_x$ MXene layers as 2D shuttle conductive materials. The physical separation achieved between holes and electrons leads to more active photocatalytic systems for both photooxidation reactions and H_2 production opening the possibility to form a vast family of new, more efficient and more stable photocatalytic hybrid systems.

SESSION EN04.05/NM02.04: Joint Session
Session Chairs: Damien Voiry and Zongyou Yin
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2004

2:00 PM *EN04.05/NM02.04.01

Rapid Energy Sharing at Atomically Thin van der Waals Interfaces During Charge Transfer Archana Raja; Lawrence Berkeley National Laboratory, United States

Charge and energy transfer processes at the junction of atomically thin, two dimensional (2D) materials are an area of burgeoning interest because van der Waals crystals allow for the creation of arbitrary, atomically precise heterostructures simply by stacking disparate monolayers without the constraints of covalent bonding or epitaxy. At a type II heterojunction between two 2D semiconductors, ultrafast charge transfer has been previously determined to occur on the order of 10's of femtoseconds after photoexcitation. However, the coupling between the lattice degrees of freedom of the photoexcited monolayers remains less understood. We use ultrafast electron diffraction to directly visualize lattice dynamics in the individual monolayers at the van der Waals heterojunction of WSe2 and WS2. We are able to track the transfer of energy from one layer to another by following the change in intensity of the Bragg peaks after photoexcitation. With the aid of first principles calculations, we uncover the role of layer-hybridized electronic states in enabling ultrafast charge and energy transport across atomic junctions through bidirectional phonon emission. This work is a result of fruitful collaborations with colleagues at various institutions including SLAC National Laboratory, Stanford, Berkeley Lab, UC Berkeley and NIMS Tsukuba.

2:30 PM BREAK

SESSION EN04.06: Photoelectronics I
Session Chairs: Damien Voiry and Zongyou Yin
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2004

3:00 PM *EN04.06.01
Harnessing Nonlinear Optical and Photocurrent Responses in Two-Dimensional Materials Xiaofeng Qian; Texas A&M University, United States

Two-dimensional materials offer a unique platform with a plethora of novel physical properties and potential applications. Noncentrosymmetric 2D materials allow for second-order nonlinear optical and photocurrent responses that are absent in the centrosymmetric counterparts, suggesting the possibility for harnessing the 2nd-order responses for energy and optoelectronic applications such as bulk photovoltaics and electro-optical modulators etc. In this talk, I will present our recent theoretical effort on understanding and predicting nonlinear responses in 2D semiconductors and 2D quantum materials. First, I will present a theoretical study of second harmonic generation (SHG) in semiconducting 2D materials including monolayer group IV monochalcogenides and Janus 2D materials. SHG polarization anisotropy is strongly correlated with the intrinsic ferroelastic and ferroelectric orders, which leads to non-reciprocal shift and circular photocurrent whose direction can be controlled by both internal ferroic orders and external light polarization. Second, I will present a theory of ferroelectric nonlinear Hall effect in time-reversal invariant layered topological materials, discuss the complex interplay of symmetry, electronic structure, and Berry curvature, and briefly mention the experimental demonstration of Berry curvature memory effect. Our findings suggest the potential applications of 2D materials for bulk photovoltaics and quantum nonlinear electronics by harnessing their nonlinear optical and photocurrent responses.

3:30 PM EN04.06.02
One-Pot Synthesis of a Hierarchical-Octahedral $NiSe_2$ as a Co-Catalyst for Enhanced CO_2 Photoreduction Under Full-Spectrum Light Irradiation Haritham Khan, Hazina M. Charles, Rajendra C. Pawar, Plassidius J. Chengula, Jin-Goo Park and Caroline Sunyong Lee; Hanyang University, Korea (the Republic of)

Excess carbon dioxide emission accompanied by gross fossil fuel consumption has worsened the global warming crisis in recent decades. The photocatalytic conversion of CO_2 into hydrocarbons is a potential solution to mitigate both energy and environmental problems. However, conventional photocatalysts suffer low efficiency in CO_2 conversion with C1 and/or C2 products. Nanostructured perovskite oxides (titanates) have emerged as a class of high-performance photocatalytic materials because of their nontoxic nature, adequate chemical stability, tunable crystal structures, band gaps, and surface energies. Two-dimensional (2D) transition metal dichalcogenides (TMDs) are another emerging group of materials that got high attention due to their light absorption, high conductivity, low cost, and non-toxic properties. The design and fabrication of layered transition metal chalcogenides with high exposure of crystal layer edges is one of the key paths to achieving distinctive performances in their catalysis and electrochemistry applications. Nevertheless, the photocatalytic performance and CO_2 reduction efficiencies are still low due to severe charge recombination and sluggish kinetics. Therefore, the rational design and preparation of dissimilar dimensional materials have been extensively investigated for use to effectively increase photocatalytic performance. In this study, we report an effective strategy to synthesize a unique octahedron-shape $NiSe_2$ nanoparticles from a one-dimensional (1D) $NiTiO_3$ nanofibers (NFs) precursor. Firstly, the 1D $NiTiO_3$ NFs are prepared by electrospinning and then combined with Se powder through the solvothermal method. The 1D $NiTiO_3$ NFs acted bi-functionally, as both the Ni source and the substrate. The combined effect of $NiTiO_3$ NFs and $NiSe_2$ has been optimized by varying the loading amounts of Se powder. The varying amounts of Se powder play a vital role in optimizing the photocatalytic behavior of the $NiTiO_3$ NFs/$NiSe_2$. Among different $NiTiO_3$/$NiSe_2$ products, 0.09 wt.% loading of Se powder shows superior photocatalytic performance because of the unique octahedron-like morphology and enhanced active sites. The as-synthesized sample exhibits lower charge recombination, higher current densities, and outstanding photocatalytic conversion of CO_2 into CO, and CH_4 shows 90% selectivity. This enhanced photocatalytic performance should be attributed to its higher light absorption, efficient charge separation, and transfer as well as a relatively large number of surface-active sites. The structure and morphology of the octahedra with more surfaces endow the $NiSe_2$ favorable for more chemical reactions with exposed active sites. $NiSe_2$ acted as a novel cooperative co-catalyst to trap the electrons and improve charge separation efficiency. Hence, we presume that the synthesized one-dimensional $NiTiO_3$ NFs precursor-derived $NiSe_2$ nanoparticles have excellent potential to replace the noble-metal-based photocatalyst for enhanced photocatalytic activity.

3:45 PM EN04.06.03
Light-Induced Ammonia Generation over Defective Carbon Nitride Modified with Pyrite Judith Zander and Roland Marschall; University of Bayreuth, Germany

Mitigating the effects of climate change caused by continuously rising CO_2-concentrations in the atmosphere is one of the main challenges mankind is currently facing, and one that requires major changes in the energy supply for vehicles and industrial processes. Photocatalysis offers a way of directly employ solar light as an abundant and renewable energy source for the conversion of inert molecules, such as water, or nitrogen into fuels, or valuable chemicals. One of these is ammonia, that is required in large amounts for the production of fertilizers, that are in turn crucial for the nutrition of the world population.[1] Industrially, ammonia is produced in large, centralized power plants from hydrogen and nitrogen gas under elevated temperatures and pressures.[2] Photocatalysts that are able to selectively and efficiently convert atmospheric nitrogen into ammonia are therefore highly desirable. However,

currently known systems are as to yet unable to meet the strident demands, necessitating the development of new photocatalysts and the unveiling of reaction mechanisms and pathways.[3][4]
A promising material for photocatalytic NRR is defective carbon nitride, V_N-C_3N_4.[5][6][7] Carbon nitride is a low cost, non-toxic and easy to synthesize polymeric material with good visible light absorption, but also fast recombination of excited charge carriers.[8][9] Different strategies to improve the activity are widely explored, such as doping, defect engineering, or heterojunction formation.[9][10] Another promising approach for the development of new photocatalysts is based on observations from nature, specifically on the structure of nitrogenases, which are enzymes capable of reducing nitrogen under ambient conditions. The active centers of the different kinds of nitrogenases all have in common, that they mainly consist of sulphur and iron atoms.[11]
One of the simplest iron- and Sulphur-containing compounds is the earth abundant mineral FeS_2, which absorbs a broad wavelength range of visible light.[12] In this contribution we present the fabrication of a composite of V_N-C_3N_4 and FeS_2 that results in a significant activity improvement for the light-induced generation of ammonia, with hydrogen occurring as the only side-product. Crucial for the enhanced activity is the activation of the structure of V_N-C_3N_4 *via* coordination of and π-back-donation to cyano groups at defect sites to iron centers, resulting in an improved reduction of these groups to NH_3, similar to a Mars-van-Krevelen mechanism.[13]

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4:00 PM EN04.06.04
2D MoS_2/BiOBr van der Waals Heterojunctions by Liquid-Phase Exfoliation as Photoelectrocatalysts for Hydrogen Evolution Mengjiao Wang and Teresa Gatti; Justus-Liebig-Universität Giessen, Germany

Photoelectrocatalytic hydrogen evolution from water is a promising topic for producing H_2 efficiently and environmentally friendly. However, the efficiency of hydrogen production in these photoelectrocatalysis systems is still low. Therefore, the discovery of more efficient phototelectrocatalysts has been considered as one of the important directions in the field of clean and renewable energy. 2D BiOBr is emerging as an interesting photoelectrocatalysts because of its unique internal electric field and band structure that facilitate the separation and mobility of the charge carriers[1,2]. However, pure 2D BiOBr suffers from low catalytic efficiency and photocorrosion from the light source. In order to optimize the catalytic efficiency and stability of 2D BiOBr, a 2D BiOBr/MoS_2 heterojunctions with 1 wt%, 5 wt%, 10 wt% and 50 wt% of MoS_2 were fabricated by a simple liquid-phase exfoliation method. Raman spectra prove the existence of strong interactions between the MoS_2 and BiOBr 2D nanosheets in the heterojunctions. The heterojunction containing 1 wt% of MoS2 shows the best performance and stability in photoelectrocatalytic hydrogen evolution than the other samples. The calculation of the heterojuntions shows a better charge transfer inside the heterojunction than the pure 2D materials as well.

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4:15 PM EN04.06.05
Efficient Photoelectrochemical Water Splitting of $BiVO_4$ Nanosheets Vertically Synthesized on WO_3 Nanorods Roshani A. Jayarathna, Dong-Bum Seo, Sung-Soo Bae and Eui-Tae Kim; Chungnam National University, Korea (the Republic of)

$BiVO_4$ nanosheets (NSs) have recently attracted great attention as a promising visible-light responsive photocatalyst for photoelectrochemical (PEC) water splitting. The PEC reactivity of $BiVO_4$ NSs has been further improved by employing heterostructures, such as $BiVO_4/WO_3$ and $BiVO_4/TiO_2$, which enhance the separation and subsequent transfer of photogenerated electron-hole pairs via a built-in junction potential. To fully take advantage of the heterojunction effects of PEC reactions, the size and configuration of $BiVO_4$ NSs on nanostructure matrices, such as WO_3 nanorod (NR) substrates, should be optimized in a controllable manner. In this work, we report the synthesis and PEC performance of vertically-aligned $BiVO_4$ NSs on WO_3 NRs. WO_3 NRs were synthesized via hydrothermal reaction and decorated by $BiVO_4$ NSs through drop casting. The heterostructure of $BiVO_4$ NSs on 1D WO_3 NRs exhibited significantly promoted PEC performance because of beneficial heterojunction effects, improved photoabsorption, and increased reaction surface area. In addition, the heterostructure of $BiVO_4$ NSs/WO_3 NRs formed a desirable heterojunction leading to effective photogenerated charge transfer dynamics. Our study indicates that vertically-aligned $BiVO_4$ NSs on WO_3 NRs are promising candidates as nontoxic, inexpensive, and stable photoanodes for PEC water splitting.

Keywords: photoelectrochemical, tungsten oxide, bismuth vanadate, nanorods, nanosheets
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4:30 PM EN04.06.06
Photoelectrochemical Valorization of Biomass Derivatives by Hematite Photoanodes Modified with Co-Catalysts Irene Carrai; University of Bologna, Italy

The conversion of sunlight into fuels represents one of the possible few solutions to the energy growing demand of the last century and can be considered as a good alternative to fossil fuels. Among all the possible methods to obtain such renewable energy, the photoelectrochemical (PEC) splitting of water into molecular hydrogen and oxygen is a very promising approach, as it allows to capture the intermittent solar energy and to store it in the form of chemical bonds. However, the oxygen evolution reaction (OER), is kinetically very slow and the product -O_2- lacks the economic value. For these reasons, the solar-driven oxidation of biomasses[1] started to be considered as a valid solution to water oxidation. Indeed, valuable chemicals can be obtained, which

can be used as monomers for the synthesis of industrially relevant compounds.
In this work, a PEC cell was employed to perform the photooxidation of 5-hydroxymethylfurfural (HMF) into furan dicarboxylic acid (FDCA). Because of its good stability, cost effectiveness and non-toxicity, a visible band-gap inorganic semiconductor[2] -i.e., titanium-doped hematite (Ti: Fe_2O_3)- was chosen as the photoanode. The experiments were performed in aqueous environments, using a 0.25M borate buffer solutions (pH=9) as the electrolyte. Also, the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) mediator was employed, which resulted to be crucial, allowing the total consumption of HMF without promoting any parasite oxidative pathways. However, because of the highly competitive OER, full conversion into the final product -i.e., FDCA- was not achieved.
To overcome OER competition and to improve the selectivity towards FDCA, co-catalysts were electrodeposited on the surface of Ti: Fe_2O_3 photoanodes. The selected co-catalysts were cobalt-iron(oxy)hydroxide ($CoFeO_x$) [3] and cobalt-phopshate (CoPi)[4]. Then, these electrodes were tested for the HMF PEC conversion, and the results were compared with those of a naked Ti: Fe_2O_3 photoanode. Interestingly, the electrode modified with CoPi showed the best results, giving the highest efficiency and selectivity for the final product -i.e., FDCA. Further studies also revealed that CoPi could enhance the one-electron oxidation process, favouring the TEMPO-mediated HMF photooxidation, at the expense of OER. In the future, the proposed approach can be implemented in a tandem PEC cell, coupling the simultaneous reduction of H_2O or CO_2 at the cathode. In this way, an improvement in the conventional PEC technology can be achieved, providing a green and sustainable alternative for the energy conversion into valuable chemicals.

Citations:

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SESSION EN04.07: Poster Session II: Other Energy Applications
Session Chairs: Damien Voiry and Zongyou Yin
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN04.07.01

Selective, Stable, Bias-Free, and Efficient Solar Hydrogen Peroxide Production on Inorganic Layered Materials Je Min Yu, Jaejung Song, Jang Hyuk Ahn, Hyeonjin Cho, Jiyeon Oh, Hu Young Jeong, Changduk Yang, Jun Hee Lee, Ji-Wook Jang and Seungho Cho; Ulsan Natonal Institute of Science and Technology, Korea (the Republic of)

Hydrogen peroxide (H_2O_2) is one of the most significant chemicals and is in high industrial demand. Further, H_2O_2 is a potential energy carrier. Indeed, H_2O_2 has a comparable energy density (3.0 MJ L^{-1} for 60% aqueous H_2O_2) to that of compressed hydrogen (H_2) gas (2.8 MJ L^{-1} at 35 Mpa). Moreover, it is easily transported, owing to its high solubility in water, and can be produced in a centralized container on a very large scale. Currently, the anthraquinone process has been predominantly applied in industry to supply H_2O_2. However, this process is environmentally harmful and requires multi-step reactions with organic solvents, rare metal catalysts, and high energy inputs for hydrogenation and further oxidation of an alkylanthraquinone.
Alternatively, electrochemical catalysis of metal complexes has been extensively investigated for eco-friendly production of H_2O_2. The key challenge here is the development of oxygen reduction reaction (ORR) catalysts that exhibit high selectivity and activity for a two-electron ($2e^-$) pathway instead of a four-electron ($4e^-$) pathway. Co complexes have an intrinsic advantage of catalyzing the $2e^-$ reduction of O_2 to H_2O_2. This is because Co has high *d*-electron counts and their single Co atom configurations can suppress $4e^-$ ORR, which requires multi-atom sites. Typically, Co porphyrin structures have been used as redox catalytic agents for $2e^-$ ORR. These Co-macrocycles have attracted attention because of their good activity and notable selectivity towards the $2e^-$ ORR. However, these molecular catalysts have the disadvantage of nitrogen ligand degradation in the presence of H_2O_2. Carbon-based materials have also been widely investigated as another type of $2e^-$ ORR catalysts. However, they are limited by their unstable long-term stability, owing to carbon corrosion at high overpotential. On the other hand, metal catalysts such as Pt–Hg, Pd–Hg, and Au–Pd nanoparticles provide adequate stability under harsh reaction conditions, In H_2O_2 generation reactions, metal catalysts with engineered active sites have demonstrated excellent catalytic activity and selectivity. However, the processes are difficult to scale up to an industrial level because of the high cost of the catalysts.
Layered double hydroxides (LDHs) have been extensively investigated as promising electrocatalysts, owing to their unique two-dimensional lamellar structures and abundant constituent cations and anions. LDHs comprise a class of inorganic solids with metal hydroxide layers in which two or more types of metal cations are immobilized by hydroxide anion arrays and exchangeable interlayer anions. These inorganic solids are easily and economically synthesized in high purity and yield. Further, they are characterized by compositional variety, precise control of cation ratios, and the interspersion (rather than segregation) of cations within the hydroxide layers. Therefore, LDHs have great potential to tune active sites in the atomic scale for high catalytic efficiency.
In this study, for the first time, we report a highly $2e^-$ ORR pathway-selective cobalt-containing MgAl [(Co)-MgAl] LDH-based ORR catalyst (near-100% $2e^-$ ORR selectivity), wherein the single atomic Co configuration can be realized by simply controlling the precursor ratios in the synthesis. Moreover, to use an abundant energy source, sunlight for H_2O_2 production, we designed a compartmented photo-electrochemical cell with a membrane separator, in which two catalytic systems (an LDH-based electrocatalyst for H_2O_2 production and an LDH-passivated organic-semiconductor-based photoanode for photovoltage generation) are integrated. The cell generated a concentration of H_2O_2 (~108.2 mM $cm^{-2}{}_{photoanode}$ in 24 h) and a solar-to-chemical conversion efficiency (~3.24%) through sunlight illumination without any external bias. The concentration and solar-to-chemical conversion efficiency are the highest among all reported systems to the best of our knowledge.

5:00 PM EN04.07.03

Investigation of Vibrational and Thermal Properties of γ-GeSe Jinsub Park[1], Joonho Kim[1], Yugyeong Je[2], Joong-Eon Jung[1], Je Myoung Park[3], Hyeonsik Cheong[3], SangWook Lee[2] and Kwanpyo Kim[1]; [1]Yonsei University, Korea (the Republic of); [2]Ewha Womans University, Korea (the Republic of); [3]Sogang University, Korea (the Republic of)

γ-GeSe is a recently identified polymorphic configuration in group-IV monochalcogenides. Despite its great potential for electrical and thermal applications, the experimental confirmation of vibrational modes and thermal conductivity is yet to be reported. Here, we investigate the mechanical properties and thermal conductivity of γ-GeSe using the freestanding sample geometry. The mechanical vibrational modes of doubly-clamped γ-GeSe flakes are measured using optical interferometry. The indentation using atomic force microscopy is also used to measure the mechanical deformation and Young's modulus. By comparison with finite-element simulations, we find that γ-GeSe exhibits Young's modulus of approximately 100 GPa at room temperature. In addition, the laser-irradiation-induced local heating and temperature-dependent Raman peak shifts are used to measure the thermal conductivity of γ-GeSe. We find a low thermal conductivity of approximately 7 $Wm^{-1}K^{-1}$ at 440 K. These results suggest that γ-GeSe has excellent potential for flexible and high-efficient thermoelectric devices.

5:00 PM EN04.07.04
Enhancement of Seebeck Effect Measured in Multi-Stacked Two-Dimensional Film of $PtSe_2$ van der Waals Homo-Structure Jae Won Choi, Yun Ho Kim and Sang Kwon Lee; Chung-Ang University, Korea (the Republic of)

After the properties of graphene and thin film materials are revealed, two-dimensional (2D) film structure become a hot topic of material science. Such as stretchability, portability, variability, and other reasons promise 2D materials to be a candidate for new conformation of thermoelectric device. But the most promising point of 2D materials for thermoelectric device, especially transition metal dichalcogenide (TMDC) is abnormal electric properties that doesn't appear at bulk condition. In our research, electrical conductivity and Seebeck coefficient of TMDC depend on film's thickness, which could be key of break-through of classical trade off at power factor. Additionally, when a 2D material is deposited with a secondary film, the total Seebeck coefficient of the stacked layer is generally represented by a parallel conductor model. Based on the idea, we found the total Seebeck coefficient in the transverse direction may change in a single layer when TE material layers of the same thickness are stacked vertically. We observed an abnormal Seebeck effect in a stacked 2D semi-metallic $PtSe_2/PtSe_2$ homo-structure film, i.e. an extra in-plane Seebeck voltage was produced by wet-transfer stacking at the interface between the $PtSe_2$ layers under a transverse temperature gradient. This abnormal Seebeck effect is referred to as the interfacial Seebeck effect in stacked $PtSe_2/PtSe_2$ homo-structures. We confirmed that the in-plane Seebeck coefficient increases as the number of stacked $PtSe_2$ layers increase and observed a high Seebeck coefficient exceed approximately 188 mV/K at 300 K in a four-layer-stacked $PtSe_2/PtSe_2$ homo-structure.

5:00 PM EN04.07.05
Two-Dimensional Material Protective Layer for Improving the Electrochemical Stability of Zinc Ion Battery Yunhee Ahn[1], Jueun Baek[1,2], Seulgi Kim[1], Segi Byun[2] and Dongju Lee[1]; [1]Chungbuk National University, Korea (the Republic of); [2]Korea Institute of Energy Research, Korea (the Republic of)

Yunhee Ahn[1], Jueun Baek[1,2], Seulgi Kim[1], Segi Byun[2], Dongju Lee[1*]
[1]Department of Urban, Energy, and Environmental Engineering, Chungbuk National University, Chungdae-ro 1, Seowon-Gu Cheongju 28644, Republic of Korea
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ABSTRACT
Zinc ion batteries (ZIB) with aqueous electrolytes are promising next-generation energy storage systems due to their high safety, environmental friendliness, low cost, and high energy density. However, zinc anode has many issues, including dendritic growth, hydrogen evolution reaction (HER), and passivation. The electrode/electrolyte interface is significantly destabilized by dendritic growth and side reactions, which eventually reduce the electrochemical performance. Many studies are being conducted to overcome these problems by electrode structure design, interface modification, and electrolyte optimization.
In this research, we propose a protection layer of zinc metal anode with two-dimensional nanomaterials. Due to their unique structure and variety of physicochemical properties, zinc anode with two-dimensional nanomaterials protection layers have excellent electrochemical performance and cycle stability by restricting zinc dendrite growth. These results suggest that the protective layer based on two-dimensional nanomaterials for zinc anode can be applied in the highly stable energy storage systems.

Acknowledgement
This work was supported by the National Research Foundation of Korean (NRF) grant funded by the Korea government (Ministry of Science and ICT) (2021R1F1A1058854) and the National Research Council of Science & Technology(NST) grant by the Korea government (MSIT) (No. CAP 22071-000).

5:00 PM EN04.07.06
A Binder-Free Electrode with 2D NiFe MOF/rGO as Bifunctional Catalyst for Rechargeable Zinc Air Battery. Chun-Shuo Huang, Yi-Pin Chan and Che-Ning Yeh; National Tsing Hua University, Taiwan

Zinc air batteries (ZAB) are regarded as a promising candidate for the next generation energy storage device due to its low-cost, high-energy density, and eco-friendliness. However, precious materials such as Pt and RuO_2 are commonly used as catalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), and it is important to find alternative catalysts with high stability, low cost, and outstanding catalytic activity to replace the precious metals. Metal organic framework (MOF) is a promising catalyst candidate which has high surface area and abundant active sites to react with air. MOF generally exhibits relatively low conductivity, which lowers the Coulombic efficiency of the batteries. To solve this problem, MOF is commonly grown on conductive substrates such as Ni foam, reduced graphene oxide (rGO), carbon nanotube (CNT), etc. Previous studies have shown high OER performance of the NiFe bimetallic MOF, which is rarely used for ZAB. Also, catalysts are usually coated on the current collector using binder, which may block the mass transport and decrease the rate of electrochemical reaction. Herein, we used rGO as a conductive substrate for the growth of 2D NiFe MOF to prepare a binder-free electrode and studied the impact of precursor concentrations, reaction temperatures, and reaction times on the growth of 2D NiFe MOF. The OER and ORR performances of the binder-free electrode are remarkably higher than those of the electrodes containing binder. We anticipate that these results could open a new direction for the use of 2D NiFe MOF/rGO for zinc air batteries.

SESSION EN04.08: Photoelectronics II
Session Chairs: Hong Li and Zongyou Yin
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2004

8:30 AM *EN04.08.01
Strain-Exciton Coupling in Two-Dimensional Semiconductors SungWoo Nam; University of California, Irvine, United States

In this talk, I will present our work on deterministic manipulation and confinement of excitons in two-dimensional (2D) semiconductors. I will discuss predictable and reconfigurable strain modulation in 2D transition metal dichalcogenides (TMDs) via wrinkle architectures. Strain exerted on wrinkled 2D

TMDs was periodically modulated to tensile and compressive strain at peaks and valleys of the wrinkles, respectively. Furthermore, owing to the deformable nature of the wrinkle architecture, the applied strain can be tuned reconfigurably with the optical gap of TMDs dynamically modulated. We also observed exciton transport across apex and valley of strained TMDs as well as exciton localization at the apex due to strain gradient induced energy modulation of wrinkled TMDs. Finally, I will discuss an extension of our strain modulation approach to interlayer excitons in TMD vertical heterostructures where strain is used to tune both optical gap as well as interlayer coupling between the heterobilayers. I will share our perspectives on strain-exciton engineering toward quantum and energy devices.

9:00 AM *EN04.08.02
Strong Light-Matter Interactions in Low-Dimensional Excitonic Semiconductors Deep M. Jariwala; University of Pennsylvania, United States

The isolation of stable atomically thin two-dimensional (2D) materials on arbitrary substrates has led to a revolution in solid state physics and semiconductor device research over the past decade. A variety of other 2D materials (including semiconductors) with varying properties have been isolated raising the prospects for devices assembled by van der Waals forces.[1] Particularly, these van der Waals bonded semiconductors exhibit strong excitonic resonances[2] and large optical dielectric constants as compared to bulk 3D semiconductors. .

First, I will focus on the subject of strong light-matter coupling in excitonic 2D semiconductors, namely chalcogenides of Mo and W. Visible spectrum band-gaps with strong excitonic absorption makes transition metal dichalcogenides (TMDCs) of molybdenum and tungsten as attractive candidates for investigating strong light-matter interaction formation of hybrid states.[3-5] We will present our recent work on the fundamental physics of light trapping in multi-layer TMDCs when coupled to plasmonic substrates.[6]

Next, we will show the extension of these results to halide perovskites[7, 8] and superlattices of excitonic chalcogenides.[9] These hybrid multilayers offer a unique opportunity to tailor the light-dispersion in the strong-coupling regime.[9] We will discuss the physics of strong light-matter coupling and applications of these structures. If time permits, I will also present our recent work on scalable, localized quantum emitters from strained 2D semiconductors[10] and control of light in magnetic semiconductors.[11]

Our results highlight the vast opportunities available to tailor light-matter interactions[11] and building practical devices with 2D semiconductors. I will conclude with a broad vision and prospects for 2D materials in the future of semiconductor opto-electronics and photonics.

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9:30 AM BREAK

10:00 AM EN04.08.03
High Electrical Conductivity and Spin-Orbit Coupling Observed in γ-GeSe Joonho Kim[1], Jeongsu Jang[1], Dongchul Sung[2], Jong Hyuk Kim[1], Joong-Eon Jung[1], Sol Lee[1,3], Jinsub Park[1], Chaewoon Lee[1], Heesun Bae[1], Seongil Im[1], Kibog Park[4,4], Young Jai Choi[1], Suklyun Hong[2] and Kwanpyo Kim[1,3]; [1]Yonsei University, Korea (the Republic of); [2]Sejong University, Korea (the Republic of); [3]Institute for Basic Science, Korea (the Republic of); [4]Ulsan National Institute of Science and Technology, Korea (the Republic of)

Group-IV monochalcogenides have recently shown great potential for their thermoelectric, ferroelectric, and other intriguing physical properties. The electrical properties of known group-IV monochalcogenides exhibit a strong dependence on the chalcogen type. For example, GeTe exhibits metallic behavior, whereas S-based and Se-based chalcogenides are semiconductors with sizable bandgaps. In this study, we investigate the electrical and thermoelectric properties of γ-GeSe, a recently identified polymorph of GeSe. γ-GeSe exhibits high electrical conductivity (approximately 10^6 S m^{-1}) and a relatively low Seebeck coefficient (9.4 μV K^{-1} at room temperature) owing to its high p-doping level (5×10^{21} cm^{-3}), which is in stark contrast to other known GeSe polymorphs. Based on first-principles calculations, we attribute the high p-doping level to the abundant formation of Ge vacancies in γ-GeSe polymorphic configuration. The magnetoresistance measurements also reveal weak-antilocalization because of spin-orbit coupling in the crystal. Our results demonstrate that γ-GeSe is a unique polymorph in which the modified local bonding configuration leads to substantially different physical properties.

10:15 AM EN04.08.04
Monolayer Molybdenum Disulfide Photovoltaics with Carrier Selective Contacts for High Open-Circuit Voltage Rachel Tham[1], Cora Went[2], Joeson Wong[3] and Harry A. Atwater[1]; [1]California Institute of Technology, United States; [2]Rewiring America, United States; [3]The University of Chicago, United States

While the efficiencies of ultrathin transition metal dichalcogenide (TMDC)-based photovoltaics have shown significant progress due to their intrinsically strong light-matter interactions, little work has demonstrated that TMDC-based photovoltaics can achieve high photovoltaic performance with technologically useful active areas. In this work, we show that a vertical carrier selective contact architecture combined with gold-assisted exfoliation of TMDCs enables millimeter-area, monolayer molybdenum disulfide (MoS_2) photovoltaics. First, we show that under one-sun illumination, photovoltaic devices with a bulk TMDC active layer result in an open-circuit voltage of 523 mV; however, the non-radiative losses associated with the indirect bandgap in multilayer TMDCs limit the achievable open-circuit voltage. We designed a solar cell that leverages the high radiative efficiency of direct bandgap monolayer MoS_2, combined with the electron- and hole-transport layers, C_{60} and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), respectively, to increase the achievable open-circuit voltage. To synthesize MoS_2 on arbitrary substrates, we develop a photoresist transfer process that minimizes the impact of polymer residues on the device performance. Through Raman and photoluminescence measurements, we show comparable optoelectronic quality between gold-assisted and traditional direct tape exfoliated MoS_2 monolayers on silicon dioxide/silicon, which exhibit similar photoluminescence emission with peaks between 1.84 and 1.86 eV, with a linewidth of 0.13 eV, similar to results seen for MoS_2 monolayers directly exfoliated onto silicon dioxide. Raman measurements indicate a similar E^1_{2g} to A_{1g} frequency difference and peak linewidth of less than 8 cm^{-1}. Our methods and results demonstrate the possibility for high efficiency monolayer photovoltaics and opens the door to large-area scalability.

10:30 AM EN04.08.05
2D Chalcogenide Thermoelectric Materials for Enhanced Solar Collection Lindsey Gray, Gabriel Marcus, Robert Link and David Carroll; Wake Forest University, United States

Even for high efficiency photovoltaics (PVs), a considerable amount of energy is lost as waste heat. One of the largest areas of loss is incoming photons with energy below the photovoltaic bandgap. These photons, not contributing to the performance, only heat up the PV, which has been shown to decrease efficiency. A method of capturing this waste heat is to place a thermoelectric behind the photovoltaic. With one side in contact with the back of the solar cell, and the other exposed to the open environment, this can create a sufficient temperature gradient to produce a voltage, and ultimately power. In this work, we present flexible 2D chalcogenide thermoelectric films adhered to the back of traditional planar photovoltaics as a method of heat management. With the benefit of being both lightweight and requiring minimal post processing, the photovoltaic-thermoelectric devices are suitable for both terrestrial and extraterrestrial environments. Tested films include bismuth telluride and antimony telluride, with increasing amounts of silver and copper doping, to improve thermoelectric performance.

10:45 AM EN04.08.06
First-Principles Study of Low-Dimensional Chalco-Halides for Photovoltaic Applications Cibrán López Álvarez, Edgardo Saucedo and Claudio Cazorla; Polytechnic University of Catalonia, Spain

Low-dimensional chalco-halides (LDCH) with general formula ABX (A=Bi,Sb, B=Se,S and X=Br,I) conform a new family of van-der-Waals materials with great promise for applications in critical energy fields like photocatalytic hydrogen production, thermoelectricity and sunlight energy conversion. However, due to their novelty and very recent synthesis, the physical and functional properties of LDCH have been little characterized thus far. We are interested in exploiting the potential of LDCH in state-of-the-art photovoltaic technologies able to compete with current single silicon junctions in terms of conversion efficiency and solar-cell costs. For this end, we present here an exploratory and comprehensive first-principles study based on density functional theory (DFT) calculations on the structural, vibrational and optoelectronic properties of LDCH. Our theoretical calculations for eight different compounds reveal, among other findings, energy band gaps within the range of 2.1-1.6 eV and remarkably large absorption coefficients of 580000 cm^{-1}, thus confirming the adequacy of LDCH for photovoltaic applications. The obtained theoretical results are compared with recent experimental measurements and complemented by photovoltaic device simulations.

11:00 AM EN04.08.07
Photoelectrochemical Hydrogen Evolution Reaction in Heterojunction TMD Nanoscroll Rapti Ghosh[1], Ya-Ping Hsieh[1], Guang-Yu Guo[2], Mario Hofmann[2] and Yang-Fang Chen[2]; [1]Academia Sinica, Taiwan; [2]National Taiwan University, Taiwan

The photoelectrochemical (PEC) hydrogen evolution reaction (HER) could produce carbon-neutral fuel from two of the planet's most abundant resources – water and sunlight. However, a number of technical and economic challenges prevent the scalable use of conventional catalyst materials. The atomically thin 2D transition metal di-chalcogenides (TMDs) are emerging as promising catalysts because of their tunable electronic structure and unique mechanical properties. In particular, the rolling of 2D TMD nanosheets into 1D scrolls induces bending strain and produces a confinement for electronic and photonic interactions. The resulting heterojunctions produce strong internal fields and enhance photocarrier dissociation. This causes a 3-fold enhanced electrochemical performance compared to planar heterojunctions. Strain-induced modification of the band alignment in this quasi-1D MoS_2/WS_2 heterojunction nanoscrolls leads to a novel hybrid charge transfer process which helps in achieving a reduced Tafel value of 39 mV dec^{-1}, and an exchange current density up to 1.44×10^{-4} Acm^{-2}, outperforming any 2D material catalyst.[1]
Reference:
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SESSION EN04.09: Synthesis and Fabrication
Session Chairs: Hong Li and Xiaolin Zheng
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2004

2:00 PM EN04.09.03
Large-Scale Fabrication of Lateral MoS_2 – MoS_2/WS_2 –WS_2 Heterostructures by Two-Step Chemical Vapor Deposition Majvor Z. Mack, Stephen Boandoh, Yu-Tsung Tsai and Norbert Nickel; Helmholtz-Zentrum Berlin für Materialien und Energie, Germany

In the research on two-dimensional (2D) crystals new directions and possibilities have evolved by combining different monolayer materials to lateral and vertical heterostructures. These new functionalities have opened up the fields that lead to field-effect transistors, *pn*- and Schottky solar cells [1] and light-emitting diodes employing transition metal dichalcogenides (TMDs) heterostructures. In the presented work two-dimensional TMDs are grown on Si – SiO_2 substrates using a chemical vapor deposition (CVD) technique with two separated steps as a simple large-scale fabrication methodology. Despite of its simplicity, the two-step CVD technique presented here allows the fabrication of well-defined interfaces over large areas.
In the first step MoS_2 monolayer triangles are grown and in the second step the heterostructures are formed by growing WS_2 at the perimeter of the MoS_2 triangles. Optical microscopy, Raman scattering and mapping show that the two-step CVD process can be used to grow in-plane heterostructures with three-dimensional growth observed at the MoS_2 – WS_2 interface. The change in growth mode from two-dimensional to layered growth is determined by the change of the chemical potential D*m* of the growing layer. A major contribution to D*m* is the presence of strain at the interface between the two different materials, leading to either Frank-van der Merwe growth or Volmer-Weber growth [2]. The presented work provides a deeper understanding of the growth mechanisms taking place at the interface and gives a good starting point to tune the growth parameters for a large-scale fabrication applicable in the field of energy conversion and photocatalysis [3].

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2:15 PM EN04.09.04
Plasma-Enhanced Atomic Layer Deposition – a Swiss Army Knife for Producing Tailored Molybdenum Sulfide Catalysts for HER Miika Mattinen[1,2,3], Wei Chen[2], Marcel Verheijen[2,4], Rebecca A. Dawley[5], Marta C. Figueiredo[2], Emiel J. Hensen[2], Erwin Kessels[2] and Ageeth A. Bol[5,2]; [1]University of Helsinki, Finland; [2]Eindhoven University of Technology, Netherlands; [3]Stanford University, United States; [4]Eurofins Materials Science Netherlands, Netherlands; [5]University of Michigan–Ann Arbor, United States

Electrocatalytic water splitting is an attractive route to produce clean hydrogen (H_2) for a variety of applications.[1] Its successful realization requires highly active, stable, and low-cost hydrogen evolution reaction (HER) electrocatalysts produced in scalable manner. Molybdenum sulfides in different forms (MoS_x) are promising HER catalysts in acid. Layered MoS_2, a prototypic 2D material, displays high activity on its edges, while MoS_2 basal planes are inactive for HER.[2] Thus, maximizing edge-to-basal plane ratio and activating basal planes for HER via doping, defects, strain, and phase engineering are commonly pursued.[3] In addition, amorphous MoS_x (a-MoS_x), which exists in a range of stoichiometries, is a highly promising HER catalyst due to its excellent activity, stability, and availability of low-cost preparation methods.[4] Yet, improved deposition methods are needed for industrial applicability as well as improved understanding and tunability of the HER activity of MoS_x.

Herein, we present a scalable plasma-enhanced atomic layer deposition (ALD) process producing different kinds of MoS_x catalysts. ALD is a gas-phase method based on sequential self-limiting surface reactions that offers accurate and reproducible thickness control and excellent uniformity on large-area and three-dimensional substrates. We show that by modifying the deposition conditions, such as temperature (100–450 °C) and plasma chemistry, a range of amorphous (a-$MoS_{2.7–4.6}$) and crystalline MoS_2 films of varying morphologies and microstructures can be prepared on glassy carbon. Their HER performance has been systematically evaluated in 0.5 M H_2SO_4.

We demonstrate tailoring of the HER activity of 2D MoS_2 by modifying crystallinity and morphology such that their overpotentials at 10 mA/cm^2 (η10) range from 300 to 500 mV. The MoS_2 catalysts were stable during HER with no changes in the structure, morphology, or composition observed.

All of our a-MoS_x ($2.7 < x < 4.6$) catalysts were highly active with η10 and Tafel slope values of 210–250 mV and 40–50 mV/dec. These values compete with some of the best MoS_x catalysts on flat substrates.[4,5] The stoichiometry of a-MoS_x had only a minor effect on activity. Detailed characterization of the catalysts before and after HER revealed that all the amorphous catalysts lost sulfur under HER conditions until MoS_2 stoichiometry was reached. Following this rapid (<5 min) in-situ electrochemical activation, the a-MoS_2 catalysts showed good stability when applying a constant current density of 10 mA/cm^2 for 24 h. To gain a better view into the activated a-MoS_2 catalysts, "quasi in-situ" X-ray photoelectron spectroscopy measurements avoiding exposure of the catalysts to air were performed. Changes in Mo coordination during the activation were attributed mostly to increased disorder, while sulfur was observed to be lost predominantly in the form of bridging S_2^{2-} species. The structure of the activated a-MoS_2 catalyst was observed to depend on the starting stoichiometry.

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2:30 PM EN04.09.05
Controllable Growth and Defect Tolerance Charge and Thermoelectric Transports in Irregular Architected 2D Conducting Metal-Organic Frameworks Hio-Ieng Un; University of Cambridge, United Kingdom

Two-dimensionally (2D) conjugated metal-organic frameworks that represent an emerging class of materials with rich chemistry and physics have shown great potential in electrochemical, optoelectronic, and catalytic applications. These 2D conducting MOFs can be synthesied in a “solution-processed” mild manner. However, unlike organic semiconductors in which microstructure and ordering can be reconstructed during fabrication, 2D conducting MOFs are neither soluble nor meltable at general conductions once made. Therefore, precise (chemical and positional) structural control in solid state during synthesis at various length scales are of particular importance.
In the first part, we will present a general on-surface synthesis method towards highly conductive thin films of nitrogen-coordinated 2D conducting MOFs. The universality of this method is demonstrated with fours materials systems with different pore sizes and different carrier types (hole and electron). Two of them exhibit record electrical conductivity (100 – 200 S cm^{-1}) and power factor (5 uW m^{-1} K^{-2}) for this nitrogen-coordinated MOF family. Their electronic and thermoelectric stabilities are also investigated. The universal method reported here provides access to understanding the fundamentals and potential in applications.
In the second part, we will focus on the interplay between (chemical and micro) structure, defects, and charge and thermoelectric transports. A range of sulfur-coordinated material systems with different chemical compositions are synthesied through liquid-liquid interfacial method. Unexpectedly, these MOFs exhibit irregular nano- and micro-architecture. The origin and the nature of the chemical defects and their vertical distributions will be discussed. Such chemical defects further lead to structural (positional) disorder. Notably, however, no evidence indicates that these defects may hinder electronic delocalization, which is different from many organic and inorganic (semi)conductors. Lastly, a possible transport mechanism for these 2D conducting MOFs will be discussed.

2:45 PM EN04.09.06
Synthesis, Structure, and Properties of New Solid Solution 2D Transition Metal Carbo-Chalcogenides Ahmad Majed[1], Andrey Krayev[2] and Michael Naguib[1]; [1]Tulane University, United States; [2]Horiba, United States

Two-dimensional transition metal carbo-chalcogenides (TMCCs) is a novel 2D family of materials that can be viewed from the atomic perspective as a merge between the features of two well-known 2D families; transition metal carbides/nitrides (MXenes) and transition metal dichalcogenides (TMDCs). Recently, we reported on 2D Nb_2S_2C and Ta_2S_2C, the first members of TMCCs, and we found that Nb_2S_2C is a superconductor.(1) Herein, we report on expanding the family of 2D TMCC to include continuous solid solutions in the Ta-Nb systems, viz., $Ta_xNb_{2-x}S_2C$ (where $2 > x > 0$). The multilayers $Ta_xNb_{2-x}S_2C$ were synthesized using a large-scale solid-state synthesis approach at ambient pressure. Then, exfoliation was achieved by electrochemical intercalation of lithium followed by sonication in water. The effect of different transition metal on the stability and properties of TMCCs will be discussed. Electrochemical performance of the newly discovered materials as electrodes for energy storage and conversion will be presented. Tip-enhanced Raman spectroscopy was used to study the newly synthesized materials and provide chemical imaging of surfaces at the nanoscale.

(1) Majed A, Kothakonda M, Wang F, Tseng E.N, Prenger K, Zhang X, Persson PO, Wei J, Sun J, Naguib M. Transition Metal Carbo-Chalcogenide "TMCC": A New Family of 2D Materials. Advanced Materials 2022, 34 (26), 2200574.

SESSION EN04.10: Poster Session III: Synthesis and Characterizations

Session Chairs: Damien Voiry and Zongyou Yin
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN04.10.01
In Search of Alternative HER Electrocatalysts - Studies on Mo-P/C Films Mateusz Szczerba, Agnieszka Brzozka, Joanna Kapusta-Kolodziej and Grzegorz D. Sulka; Jagiellonian University, Faculty of Chemistry, Department of Physical Chemistry and Electrochemistry, Poland

In recent years, scientists have been increasingly eager to find safe, clean and efficient energy sources that will be able to reduce the progressive environmental degradation and cope with the growing global energy demand. One of the main candidates for future energy supply is molecular hydrogen (H_2), prized for its high energy density compared to commonly used fossil fuels. Electrocatalysts are currently being sought to efficiently produce gaseous hydrogen in the environmentally friendly water electrolysis. Prominent among these are materials based on transition metal phosphides, including molybdenum phosphide [1,2].
In this work, a method for the electrodeposition of Mo-P films on graphite electrodes is proposed with the aim of finding a catalytic material that reduces the overpotential necessary to drive efficiently the hydrogen evolution reaction (HER). The study is distinguished by the fact that moves away from aqueous solvents and uses a deep eutectic solvent (DES) based on choline chloride and ethylene glycol. Several experiments were carried out to determine the effects of Mo and P precursor concentrations, working electrode potential and electrodeposition temperature on the composition and morphology of the obtained Mo-P/C films. It was noted during the study that the obtained materials have a tendency to crack, and an excessive amount of molybdenum relative to phosphorus is present in the resulting deposits. Preliminary results indicated, however, that the Mo-P/C films possess electrocatalytic properties towards HER.

Acknowledgements
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5:00 PM EN04.10.02
Electrodeposited Mo-Se/C Films as Potential Electrocatalysts for Hydrogen Evolution Reaction Daniel Piecha, Agnieszka Brzozka, Joanna Kapusta-Kolodziej and Grzegorz D. Sulka; Jagiellonian University, Faculty of Chemistry, Department of Physical Chemistry and Electrochemistry, Poland

The production of energy from renewable sources and its efficient storage are very relevant aspects that relate to the problems of the modern world, such as atmospheric pollution from the products of burning fossil fuels. One of the most prospective fuels is gaseous hydrogen. It is a renewable energy source that is widely available in nature. A common method used for production of hydrogen is the electrolysis of water. However, this process requires a large energy input to split water molecules. A reduction of this energy barrier is possible through the use of suitable electrocatalysts [1]. Alternatives to platinum-based materials are being explored for compounds that are able to significantly increase the efficiency of the Hydrogen Evolution Reaction (HER) process. In this work, we explore the synthesis of Mo-Se/C films by the electrochemical constant-potential deposition from a deep eutectic solvent (DES) based on choline chloride and ethylene glycol. The effects of temperature and working electrode potential on the composition and morphology of the deposits were investigated. It was shown that simultaneous electroreduction of Mo and Se on graphite substrates is possible. Appropriate optimization of the electrodeposition process, which was the main objective of the research conducted, makes it possible to obtain a material with a chemical composition close to stoichiometric and an interesting morphology. The performed preliminary tests confirmed the electrocatalytic properties of the obtained films.

Acknowledgements
The research was financially supported by the National Science Centre, Poland (Project no. 2017/26/M/ST5/00715)

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5:00 PM EN04.10.03
Highly Aligned Liquid Crystalline $Ti_3C_2T_x$ MXene Film for High-Performance Supercapacitors and Hybrid Ion Capacitors Seoyeon Yuk, Seo Jin Woo and Dongju Lee; Chungbuk National University, Korea (the Republic of)

Supercapacitors (SCs) have considered significant device for energy storage system due to high power density, fast charge/discharge rates and long cycle life. Recently, hybrid ion capacitors are more attracting attention as next-generation of supercapacitors because of their improved energy density compared to conventional supercapacitors. Two-dimensional (2D) $Ti_3C_2T_x$ MXene with outstanding conductivity, broad surface area, abundant functional group and high flexibility is promising electrode material for electrochemical energy storage. However, the self-restacking problem of MXene nanosheets due to their van der Waals interactions limits the electrochemical performances. To overcome this problem, it is considered to add the spacer materials that improve structural stability of maintaining the large interlayer spacing.
In this work, the effect of addition of catecholamine on film structure and electrochemical performances was investigated. The prepared freestanding composite film exhibit widened interlayer spacing and highly aligned structure in parallel direction enabling to improve electrolyte ion and electron transportation. The optimized film exhibited outstanding supercapacitors performances including high specific capacitance and outstanding cycle stability. Additionally, the film electrode with these structural advantages is expected to storage many multivalent ion for high-energy hybrid ion capacitors. These

results suggest that the structural design of two-dimensional materials have great potential as electrodes for various energy storage systems.

Acknowledgement
This work was supported by the National Research Foundation of Korean (NRF) grant funded by the Korea government (Ministry of Science and ICT) (2021R1F1A1058854) and the National Research Council of Science & Technology(NST) grant by the Korea government (MSIT) (No. CAP 22071-000).

5:00 PM EN04.10.04
Facile and Gram-scale Synthesis of $Cu_{2-x}S$ Nanoplate for Photothermal Application by Sonochemical-assisted Reaction Based on High-concentration Copper Ion Complex Precursor Hee Yeon Jeon[1], MiJeong Park[1], Myeongjun Ji[1], Cheol-Hui Ryu[1], Seungheon Han[1] and Young-In Lee[1,2]; [1]Seoul National University of Science and Technology, Korea (the Republic of); [2]The Institute of Powder Technology, Korea (the Republic of)

Recently, to solve the environmental issue caused by fossil fuels and the global energy crisis, numerous research on the conversion and utilization of solar energy are in progress. Humans mainly benefit from solar power by using solar cells, which mainly use a visible region of solar light. Because infrared ray occupies about half of the total sunlight, however, for efficient use of solar energy, it is important to absorb a wide region of light from solar radiation and convert it into as much energy as possible. Among others, photothermal materials attract a lot of attention and are developing because they provide a platform for low-cost and efficient light-to-heat conversion. This energy conversion occurs by localized surface plasmon resonance(LSPR), especially in nanoscale metallic materials. Generally, LSPR has been studied on noble metals that show LSPR in the visible region and have high carrier densities. However, they can show the photothermal effect only in a specific incident light range, which is determined by the size and shape of noble metal nanostructures. In addition, the application of noble metal photothermal materials is limited to wide applications due to their high cost.
Copper-deficient p-type semiconductors, Copper sulfide($Cu_{2-x}S$) attract attention as new photothermal conversion materials because of the low bandgap(~2.2eV) and strong LSPR in the NIR region. Furthermore, they have not only high photostability and low toxicity but are cost-effective due to their lower prices than other noble metals. Although many studies have been conducted on methods for synthesizing $Cu_{2-x}S$ nanoplate like hydro-solvothermal, hot injection, and electrodeposition, they require harsh synthetic conditions such as high temperature and vacuum, many reactants, and complicated steps. Above all, since nanoplates are synthesized by suppressing the growth using a low concentration of precursor, the final synthesis yield is very poor. The limitations of existing synthetic methodologies with inefficient productive yields act as obstacles to the commercialization of photothermal conversion systems of $Cu_{2-x}S$ nanoplates.
According to the homogeneous nucleation and growth theory, the critical nuclear radius and critical nucleation free energy are inversely proportional to the supersaturation of the system. This means that a small diameter and many nuclei and initial nanoparticles can be synthesized even under low energy by using high-concentration precursors. However, as the supersaturation of the system increases, there is a limit to the control of nucleation reaction, hard aggregation, and growth rate due to thermodynamically high interfacial and surface energy. Therefore, a methodological breakthrough that can achieve mass production of uniform nanoplates is required to solve these problems.
In this study, we suggest the sonochemical-assisted reaction method based on a high-concentration metal ion complex precursor solution at room temperature and atmospheric pressure. The ultrasound energy allows for burst homogeneous nucleation and subsequent growth is controlled by the diffusion of growth species because the concentration of the growth species reduces below the minimum concentration for nucleation by the burst nucleation. And the metal ion complex acts as a dispersant to prevent particle agglomeration and growth. Large-scale synthesis of $Cu_{2-x}S$ nanoplates with controlled size and shape for a photothermal conversion is successfully demonstrated by the facile and versatile method. We systematically investigated the effect of the precursor concentration on the size and shape of the $Cu_{2-x}S$ nanoplates by Field Emission Scanning Electron Microscopy(FE-SEM), Dynamic Light Scattering(DLS), X-ray Diffraction(XRD), X-ray photoelectron spectroscopy(XPS), and UV-vis spectroscopy. Furthermore, the photothermal conversion efficiency of the nanoplates is confirmed under the Xenon lamp and the 808nm laser.

5:00 PM EN04.10.05
Anisotropic Transport Property Study of 2D Layered Heterostructures Yu Wang[1], Hannah Blackwood[2], Steve Cronin[3], David C. Johnson[2] and Arun Majumdar[1]; [1]Stanford University, United States; [2]University of Oregon, United States; [3]University of Southern California, United States

Heterostructures made of two-dimensional materials has been attracting much attention because of their unusual electrical, thermal, and optical properties. While in-plane transport properties of 2d heterostructures has been intensively studied, the physical properties in the cross-plane direction are still underexplored. Here, we measure both in-plane and cross-plane transport properties in 2d heterostructures, revealing highly anisotropic behavior. Furthermore, quantum many-body effects such as charge density wave have also been explored in temperature dependent electrical and thermoelectrical measurements. The findings point out that the interfaces between layers in heterostructures play an important role in transport properties, especially in the cross-plane direction.

SESSION EN04.11: Other Energy Applications
Session Chairs: Damien Voiry and Zongyou Yin
Friday Morning, April 14, 2023
Moscone West, Level 2, Room 2004

8:30 AM *EN04.11.01
2D Materials for Near-Unity-Absorption, Polarization, and Phase Modulation Souvik Biswas, Joeson Wong, Samuel Seah, Melissa Li, Claudio Hail and Harry A. Atwater; California Institute of Technology, United States

van der Waals semiconductors have gained a lot of attention for opto-electronics based multifunctional, energy-efficient devices. To harness maximal benefits, strong interaction of light, on-demand control of optical properties as well as efficient extraction of photo-generated carriers are needed. In this talk, we will discuss how excitons in layered materials can enable such a diverse set of functionalities.
First, we will highlight how 2D semiconductors, up to the monolayer limit, coupled with photonic structures can enable near-unity absorption (>90%) of light at room temperatures. This strategy – primarily enabled by the large optical density of states at the excitonic resonances – to maximize light absorption in the active layer is the basis towards building 2D solar cells and requires careful balancing of the radiative (γ_r) and non-radiative (γ_{nr}) rates of the excitonic transition. Next, we will discuss how in a field-effect heterostructure such rates (γ_r ,γ_{nr}) can be actively tuned, thereby strongly modulating the light-scattering properties of the semiconductor. The first example will illustrate how black phosphorus (a birefringent layered material) can be electrostatically gated to generate tunable dichroism and further coupled with optical cavities to enable a polarization modulator with high-dynamic range across the entire Poincare sphere – from linear-horizontal to vertical and circular. The results inspire future metasurface designs to actively steer beam with polarization selectivity, generate optical vorticity and control Pancharatnam-Berry phase. As a second example, we will highlight how optical cavities,

otherwise needed to enhance light-matter interaction, can be eliminated by making 2D materials “perfect” for active metasurfaces. This is achieved by operating at low temperatures (~5K) to suppress non-radiative (γ_{nr}) decay channels and using local electrostatic gates to define spatially-varying amplitude and phase gradients across a monolayer of $MoSe_2$. Such structures allow large tuning of the complex refractive index at the excitonic frequencies and show one-dimensional beam steering.

9:00 AM *EN04.11.02
Quantum Energy Conversion in 2D Materials from Atomic to Wafer Scale Hari C. Manoharan; Stanford University, United States

We present three examples of energy conversion processes imaged and manipulated in two-dimensional (2D) materials using ultrahigh-resolution scanning probe microscopy combined with atomic manipulation. These examples span length scales in which material structure is controlled from atomic up to wafer scales.

In recent experiments, we have been able to detect a special class of quantum-mechanical forces arising from non-local interactions mediated by a background particle field due to alterations in the zero-point energy. A famous member of this class is the Casimir effect, where the force is mediated by quantum fluctuations of the bosonic field of photons. In condensed matter, forces of this class can be mediated by a fermionic field. We show the detection and quantification of this force in real space, and demonstrate nanostructures in which 2D electrons can interact and exchange energy with a designer potential energy landscape to amplify this force.

To show that such quantum forces and energy conversion processes can be extended beyond the atomic and nanometer length scale, we present a study in which the underlying 2D electron system can be encapsulated with a monolayer of hexagonal boron nitride (hBN) using a new wafer-scale growth process. We show that the electronic states remain homogeneous in energy and spectral weight, and that the hBN overlayer acts as a protective yet remarkably transparent window on low-energy structure and quantum energy conversion processes below.

Finally, we present an ‘artificial atom’ concept via nanopatterning of monolayer molybdenum disulphide, demonstrating that a synthetic superlattice of these building blocks forms an optoelectronic crystal capable of broadband light absorption and efficient funneling of photogenerated excitons to points of maximum strain at the artificial-atom nuclei. Such 2D semiconductors with spatially textured band gaps represent a new class of materials, which may find applications in next-generation optoelectronics or photovoltaics.

9:30 AM BREAK

10:00 AM EN04.11.03
Enhanced Energetic Performance of Metal Nanoparticles and Metal/Polymer Composite Fuel with Multi-Functionalized Graphene Yue Jiang[1], Haiyang Wang[2], Jihyun Baek[1], Dongwon Ka[1], Andy Huynh[1], Yujie Wang[2], Michael Zachariah[2] and Xiaolin Zheng[1]; [1]Stanford University, United States; [2]University of California, Riverside, United States

Metal fuels such as aluminum (Al) and boron (B) have been used for energetic applications ranging from space propulsion and exploration, and materials processing, to power generation for nano- and microdevices due to their high energy density and earth abundance. Recently, the ignition and combustion performance of Al and B particles were found to be improved by graphene-based additives, such as graphene oxide (GO) and graphene fluoride (GF), as their reactions provide heat to accelerate Al and B oxidation, gas to reduce particle agglomeration, and fluorine-containing species to remove native oxide shell. However, GF is not only expensive but also hydrophobic with poor mixing compatibility with metal particles. Herein, we report a multifunctional graphene-based additive for metal combustion, i.e., perfluoroalkyl-functionalized graphene oxide (CFGO), which integrates the benefits of GO and GF in one material. We compared the effects of CFGO to GO and GF on the ignition and combustion properties of Al and B nanoparticles using thermogravimetric analysis, differential scanning calorimetry, temperature-jump ignition, Xe flash ignition, time-of-flight mass spectrometry, and constant-volume combustion test. These experiments confirm that CFGO, with controllable oxygen and fluorine functional groups, generates fluorine-containing species, heat, and gases, which collectively lower the ignition threshold, augment the energy release rate, and reduce the combustion product agglomeration of nanosized Al and B particles, outperforming both GO and GF as additives. Moreover, this multi-functionalized graphene additive was further incorporated into boron/ hydroxyl-terminated polybutadiene composite, which is a typical composite fuel for air-breathing propulsion. The effect of CFGO on the burning and mechanical behaviors of the boron/polymer composite was also investigated. This work shows the great potential of using multi-functionalized graphene as an integrated additive for enhancing the energetic performance of metal nanoparticles and metal/polymer composite fuels for advanced propulsion and energy conversion applications.

10:15 AM EN04.11.04
Effects of Quantum Size on Thermoelectric Properties of Bismuth Lei Sun[1,2], Changyi Wu[3], Haoran Gong[1] and Fei Gao[2]; [1]Central South University, China; [2]University of Michigan, United States; [3]Hunan First Normal University, China

At present, a large number of experimental and theoretical studies have shown that the low-dimensionalization of materials will greatly improve their thermoelectric properties, which will make it possible to reuse a large amount of waste thermal energy. The reason for the high potential thermoelectric capability of two-dimensional materials is still unclear. In this study, from the perspective of quantum size effect, we combined first-principles calculations and Boltzmann transport equations, taking Bi as an example, to analyze the relationship between its size effect and thermoelectric performance. Finally, it was found that only below the nanometer scale can two-dimensional materials have better performance than bulk materials.

10:30 AM EN04.11.06
2D-Pt Nanodendrites with Manipulated Crystal Facets: Intimately Coupled Electrocatalytic Heterointerface for Hydrogen Evolution Reaction Yu-Rim Hong; Pohang university of Science and Technology (POSTECH), Korea (the Republic of)

Despite notable signs of progress in Pt-catalyzed alkaline hydrogen evolution reaction (HER) via hybridizing with oxophilic metal-hydroxide surface, maximization of Pt’s reactivity alongside operational stability are still unsatisfactory due to the lack of well-designed and optimized interface structure. Herein, by devising atomically-flat 2D-Pt nanodendrite (2D-PtND) under the deployment of our strategized 2D-nanospace-confined synthesis, it offers all sorts of Pt features to tackle the poor-and-insufficient interfacial impacts in HER catalysis by simultaneously realizing an area-maximized and firmly-bound lateral heterointerface with NiFe-layered double hydroxide (LDH). In particular, the accompanied well-oriented (110) facet exposure of Pt has recognized a massive electronic interplay that certainly bestows strong LDH-binding. As a result, the charge-relocated interfacial bonds in **2D-PtND/LDH** acted favorably in accelerating the hydrogen generation steps and reaching about one of the highest reported Pt-mass-activity improvements (~11.2 times greater than 20 wt% Pt/C) with a substantially enhanced long-term operational stability. This work uncovers the importance of the shape and facet of Pt in feasible heterointerface creation to strengthen the catalytic synergies for efficient hydrogen production.

10:45 AM EN04.11.07
BiSe(Br,I): New van der Waals Semiconductors for Energy Conversion Applications Edoardo Maggi, Ivan Caño Prades, Alejandro Navarro, Joaquim Puigdollers, Jordi Llorca, Lluis S. Turu and Edgardo Saucedo Silva; Universitat Politècnica de Catalunya, Spain

Emerging quasi-1D (Q1-D) van der Waals materials have the potential to become a breakthrough in photovoltaics (PV) and photocatalysis (PC) applications among others, aiming to overcome some of the main issues affecting even the more mature PV and PC technologies. Despite this family of materials has been rarely investigated for PV and PC implementations, mixed chalco-halide compounds such as BiSe(Br,I) fit the urgent necessity of innovative and renewable sources of energy based on earth-abundant, low-toxicity, thermally stable, and defect-tolerant materials.

This class of material has the peculiarity to present a crystallographic structure in which the atoms along one of their crystallographic directions are held together via strong covalent bonds and via weak van der Waals bonds along the other two directions. This creates a highly anisotropic material formed by nano/micro-ribbons with peculiar conductive properties when properly oriented. The high tuneability of the materials and the results obtained in the present work locate the BiSe(Br,I) semiconductors in the spotlight for a broad number of applications, namely next-gen PV tandem and transparent application, piezoelectric, thermoelectric, and photocatalytic applications.

The nano/micro-ribbon structure together with the extremely uniform single-crystal phases lead to an increased amount of photons that reach the space charge region, and the light trapping effect is reported as a reduction in reflection. This type of morphology not only can boost the optoelectronic properties of BiSe(Br,I)-based solar cells but also enhance the photocatalytic activity of BiSe(Br,I)-based photocatalysts. Indeed, the current state-of-the-art of hydrogen production employing photocatalytic methods is still showing low apparent quantum yields (AQY), which can be boosted by Q1-D systems. The dense coverage of properly oriented nano/micro-ribbons determines an increase in the surface area, one of the key parameters to improving the AQY, allowing the synthesis of an efficient, photoactive, photostable, and nontoxic photocatalyst. Moreover, the estimated BiSe(Br,I) band gap is ~1.9 eV, making BiSe(Br,I) active to visible light and determining a big step forward compared to titanium dioxide (TiO_2), the most studied compound for photocatalytic applications so far, but inherently limited by a ~3eV band gap.

The theory is representative of what can be achieved with this technology, not so broadly investigated yet. Up to date, no mixed chalco-halide compounds have been synthesized through physical vapor deposition (PVD) techniques, due to the complexity of the material and the different vapor pressures involved. The present work presents the very first successful attempt to synthesize and explore Q1-D van der Waals BiSe(Br,I)-based semiconductors, through an innovative methodology implying the co-evaporation of chalcogenides followed by high-pressure annealing under halogen atmosphere. Different characterization techniques (X-Ray Diffraction, X-Ray Fluorescence analysis, Scanning Electron Microscope, Raman spectroscopy) demonstrated the high tunability of the morphology of this family of compounds by modifying the annealing conditions and confirming the possibility to synthesize high-quality single-phase material with PVD techniques for the first time. The versatility of the system allows us to obtain optimal nano/micro-ribbons distribution in terms of height, thickness, density, and orientation, according to the final device use, proving how these novel compounds are a sliver of light in terms of advanced PV and PC applications. The first working devices for both technologies will be presented and discussed.

11:00 AM EN04.11.08
Energetic Characteristics of Exfoliated Magnesium Boride Nanosheet Dongwon Ka, Yue Jiang, Andy Huynh, Jihyun Baek, Rui Ning and Xiaolin Zheng; Stanford University, United States

Boron combustion has garnered much attention due to its extremely high gravimetric and volumetric energy density. However, several inherent characteristics of boron prohibit fast response on heating and complete combustion. In this work, a boron-rich two-dimensional (2D) nanosheet is studied in order to overcome the limitations of boron ignition and combustion. Boron-rich MgB_2 nanosheet is prepared by exfoliation from bulk magnesium diboride (MgB_2) with Mg etching; then, its oxidation behaviors and energetic performances are analyzed by material characterizations in slow heating and fast heating conditions. This work reports that MgB_2 nanosheet is oxidized more favorably in slow heating conditions than bulk MgB_2. Even under fast heating conditions like Xenon (Xe) flash ignition, MgB_2 nanosheet has lower minimum flash ignition energy, higher combustion efficiency, and faster pressurization rate than bulk MgB_2, boron nanoparticle, and boron/magnesium mixture. This result shows MgB_2 nanosheet can be regarded as a promising 2D solid fuel with extraordinary energetic characteristics.

SESSION EN04.12: Characterizations
Session Chairs: Damien Voiry and Zongyou Yin
Friday Afternoon, April 14, 2023
Moscone West, Level 2, Room 2004

1:30 PM *EN04.12.01
Two-Dimensional Energy Nanomaterials Studied by in situ TEM Dmitri Golberg[1,2]; [1]Queensland University of Technology (QUT), Australia; [2]National Institute for Materials Science (NIMS), Japan

Two-dimensional (2D) nanomaterials, *i.e.* graphenes, boron-nitrines, molybdenum and tungsten disulfides, and MXenes, are studied in a high-resolution transmission electron microscope (HRTEM) equipped with various *in situ* TEM holders which allow for probing their structural, electrical, mechanical, thermal and optoelectronic properties. Current-voltage characteristics, elasticity, bending and tensile strength, and fracture toughness, photo-current responses and field-emission properties of 2D nanostructures are evaluated during delicate manipulations with them inside the pole piece of the electron microscope using piezo-driven metal probes and/or optical fibers. Performance of diverse nanomaterials as electrodes of Li- and Na-ion-batteries is also evaluated through constructing the prototype *in situ* electrochemical setups. Electrode swelling, formation of new crystal phases during ion-insertion, and secondary electrolyte layers crystalization during charge-discharge cycles are analyzed. The author is grateful to the Australian Research Council (ARC) for a financial support of the *in situ* TEM projects in the frame of a Laureate Fellowship FL160100089, a LIEF grant LE190100081 (QUT double-aberration-corrected laser compatible HRTEM) and the projects members - Drs. D.M. Tang, X.L. Wei, M.S. Wang, J. Fernando, K. Firestein and C. Zhang for their key experimental contributions.

2:00 PM *EN04.12.02
Aberration-Corrected Scanning TEM for 2D Materials at Ultrahigh Resolution Michel Bosman[1,2]; [1]A*STAR (Agency for Science, Technology and Research), Singapore; [2]National University of Singapore, Singapore

The physical and chemical properties of 2D materials are strongly determined by atomic-scale defects and dopants [1]. The process of characterizing this class of materials therefore often necessitates a tool that can visualize and characterize these materials at the atomic scale. The highest-resolution tool we have available for this is aberration-corrected electron microscopy. The new class of electron lenses called 'aberration-correctors' revolutionized electron microscopy, both transmission electron microscopy (TEM) and scanning TEM (STEM). For the first time, it has become possible to correct focus distortions that were previously considered inevitable. Without these distortions, the details that can be resolved are now several times finer than what used to be the case. Suddenly, it has become possible to visualize the individual atoms in 2D films in real space, making this new generation of microscopes an ideal tool for this rapidly-growing class of materials.

This presentation will introduce recent developments in aberration corrected electron microscopy that are relevant to 2D materials. In particular, aberration-corrected STEM is an experimental platform with an enormous potential for new 2D materials applications. It delivers a resolution well below 0.1 nm, with a high beam brightness and monochromaticity for various types of local spectroscopy.

The local distribution of defects and dopants in 2D films can now be quantified by atomic-resolution, real-space imaging with aberration-corrected STEM. It makes this an invaluable tool for gaining insight into the structure-property relationship of these materials. Advances are currently being made in new and optimized imaging methods. These include differential phase-contrast [2] and 4D-STEM mapping for visualizing the atomic structure as well as local electric, magnetic, and strain fields [3]. Moreover, further improvements in resolution, quantification and spatial accuracy are being developed with electron ptychography in the STEM [4,5]. New scan techniques and fast detectors are also under development for very low-dose measurements. These tools can be combined with a gentle beam energy and dedicated sample holders for in-situ experiments, making it possible to observe sample dynamics at the atomic scale, as they happen.

The enormous versatility, sensitivity, and resolution makes aberration-corrected STEM a critical tool for the study of two-dimensional materials for energy applications. The ongoing developments in observing ongoing chemical and physical changes at the atomic scale, and ongoing rapid improvements in hardware and data processing are also making aberration-corrected STEM an indispensable experimental platform for future research on new materials.

The presented work would not have been possible without the invaluable contributions from Hue Thi Bich Do (National University of Singapore, NUS), Loh Leyi (NUS), Zhang Xinyue (NUS), Jagadesh Rangaraj (NUS), Dr. Ning Shoucong (NUS), Prof. Goki Eda (NUS), Daria Kieczka (IMRE, A*STAR), Dr. Zhao Meng (IMRE, A*STAR) and Prof. Wu Lin (SUTD). Funding from the Ministry of Education (MOE) Singapore, under AcRF Tier 2 (MOE2019-T2-1-179), and AcRF Tier 1 (R-284-000-179-133) is kindly acknowledged.

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2:30 PM BREAK

3:00 PM EN04.12.03
Correlating Induced Defects in 2D MoS_2 with Raman Spectroscopy to its Electrocatalytic Performance Holly Fruehwald and Rodney Smith; University of Waterloo, Canada

The excellent performance of two-dimensional materials such as MoS_2 and WS_2 for electrocatalytic reduction reactions such as the hydrogen evolution reaction (HER) has driven the development of diverse synthetic protocols for 2D electrocatalysts. The bulk structure of materials synthesized by these diverse approaches are often similar, but fine structural details such as the degree of lattice strain or the concentration and identity of structural defects often remain unclear. Such understanding is critically important in understanding the differences between synthetic protocols because strain and defects are known to alter electrochemical properties of 2D materials. Raman spectroscopy is highly sensitive to defects in solid-state materials, but 2D materials exhibit a limited number of peaks in Raman spectra and each type of strain or defect is known to alter each feature in a unique way. Our research attempts to quantify the effect of individual defect types on Raman spectroscopic features by combining systematically varied synthetic protocols with a correlation based analysis. This talk will focus on a series of MoS_2 samples that were post-synthetically modified by swift heavy ion irradiation to introduce pores within individual 2D sheets of the MoS_2. Characterization by techniques such as photoluminescence microscopy, electrochemical measurements, and electron microscopy reveal the influence that these defects have on the structure and properties of the series. Subsequent correlational analysis then links the structural of behavioral parameters to quantitative features in the Raman spectra – namely the width, location and intensity of individual peaks. The overarching goal is to establish sufficient correlational maps that a single Raman spectrum can be used as a map for confident defect analysis. Such capabilities will provide the community with a low-cost and user-friendly analysis tool increases the compatibility of the diverse and varied studies being published – a feature that will greatly expedite the development of 2D materials as electrocatalysts.

3:15 PM EN04.12.04
Seebeck Coefficient Measurement of High Mobility Organic Semiconductors Guantong Wang[1,2] and Paddy K. L. Chan[1,2]; [1]The University of Hong Kong, China; [2]Advanced Biomedical Instrumentation Centre, China

Abstract

Thin film-based organic materials are widely used in field effect transistors (FET), thermoelectric device applications, and solar cells. Recently, small molecule 2,9-Didecyldinaphtho [2,3-b:2',3'-f]thieno[3,2-b]thiophene (C_{10}-DNTT) has drawn a lot of attention in the organic FET (OFET) community due to its high mobility up to 15 $cm^2 V^{-1} s^{-1}$ and ultrathin single molecular layer thickness. To date, the contact resistance between electrode and semiconductor as well as the cross-plane resistance of semiconductors are still the major research directions.

To improve the performance of FET, and explore the intrinsic mobility of organic semiconductors (OSCs), Seebeck coefficient or thermoelectric effect, electromotive force that generate across a material with temperature difference, can provide valuable information on estimating the carrier density, intrinsic mobility and other electric properties of the thin film. By comparing hole mobility and effect mobility measured by field effect measurement, it not only allows us to determine the trap states in OSCs, but also help us to optimize the molecule design for future FET and thermoelectric devices.

In this work, we prepared C_{10}-DNTT monolayer organic field effect transistor (OFET) by solution shearing method on SiO_2 substrates. The Seebeck measurement is performed via providing a temperature gradient from 0.3K to 1.6K along the channel with a length of 135 μm. The results show that Seebeck coefficient of monolayer C_{10}-DNTT reaches 450 μV/K when no gate voltage is applied. With applying gate voltage gradually into -90V, the Seebeck coefficient shows descent trend regularity down to 300 μV/K. We evaluated the carrier concentration and noticed the Seebeck coefficient exhibited a logarithmic decrement dependence as an increase in carrier concentration. Eventually, further improvement in measuring Seebeck mobility and field effect mobility will be done to estimate traps states in OSC, and provide attractive approach for designing OSC materials in FET and thermoelectric devices.

KEYWORDS: Seebeck coefficient, mobility, trap states

3:30 PM EN04.12.05
Assessment of the Electrochemical Stability of 2D MoS_2 for Hydrogen Evolution Reaction Raquel Aymerich Armengol[1], Miquel Vega Paredes[1], Andrea Mingers[1], Rajib Sahu[1], Christina Scheu[1], Siyuan Zhang[1] and Joohyun Lim[2]; [1]Max-Planck-Institut für Eisenforschung, Germany; [2]Kangwon National University, Korea (the Republic of)

2D molybdenum disulfide (MoS_2) is regarded as an excellent Pt-alternative electrocatalyst for hydrogen evolution (HER). Several approaches have been reported to enhance the activity of MoS_2 catalysts, e.g. 1T phase selection, dopant introduction and substrate engineering. Nevertheless, the electrochemical stability of such MoS_2-based materials remains controversial. Herein, we present new development on methods to assess the HER stability of 2D MoS_2-based catalysts. Beyond thorough characterization by high-resolution (scanning) transmission electron microscopy ((S)TEM) and associated characterization techniques, the corrosion of 2D MoS_2 electrodes on different conducting substrates is studied in operando by scanning flow cell coupled to an inductively coupled plasma mass spectrometer (SFC-ICPMS). This method allows us to compare the effect of different conducting substrates and dopants on the stability as a function of HER current and overpotential. To gain further insights on the corrosion mechanisms and the evolution of the phases and morphology of the 2D MoS_2 catalysts, this data is complemented by performing electrochemical measurements in identical location (S)TEM conditions (IL-STEM). Based on the methodology, we provide new perspectives on the stability of 2D MoS_2 catalysts and shed light on their HER degradation mechanisms.

3:45 PM EN04.12.06
Thermoelectric-Mediated Selective Ion Transport in Liquid-Exfoliated Molybdenum Sulfide Thin Films for Applications in Novel Filtration and Energy Devices Gabriel Marcus[1], David Carroll[1], Aisling Baragry[2] and Mary Brooks Hall[3]; [1]Wake Forest University, United States; [2]Trinity College Dublin, The University of Dublin, Ireland; [3]Forsyth Country Day School, United States

Molybdenum sulfide (MoS_2), a member of the widely studied transition metal chalcogenide family of compounds, may play a role in novel applications for water desalination, biomedicine and energy storage thanks to its propensity for ionic transport. By exploiting its thermoelectric capability, and the respective properties of its 1T/2H crystalline phases, liquid-exfoliated MoS_2 can serve as a medium for selective capture and movement of ions from solution. Here, we introduce our work undertaken to synthesize and characterize thin films of this material alongside utilizing it for Seebeck-driven water purification and rechargeable battery technologies. Prototype chambered desalination devices incorporating MoS_2 films were constructed and tested to determine changes in electric potential and solution osmolarity following exposure to temperature gradients. In these systems, two salts (NaCl and KBr) were studied at various concentrations to assess MoS_2's potential for ion transport under different conditions. Furthermore, some analysis of film deterioration and attempts to mitigate this problem using polymers or other chalcogenides were explored. Results from these studies indicate that thermoelectric MoS_2 films can effectively filter ions, thereby generating significant voltages across their surfaces via combined carrier/ionic transport. However, ion contact with the film surface and subsequent movement through the film bulk may lead to destabilization, erratic fluctuations in electric potential and impaired transport. Deposition of PVDF on the film surface provides some protection from this breakdown, and studies of hybrid chalcogenides like molybdenum disulfide/antimony telluride that aid in maintaining film integrity are ongoing. Battery architectures that make use of MoS_2 films as both intercalating storage matrices and separation membranes, and recharge through application of thermal gradients, are under investigation as well. We will discuss some of our recent efforts in this area, specifically, design, construction and testing of thermoelectric batteries. While some hurdles remain, MoS_2-based filtration and energy devices can make a significant contribution to solving problems like freshwater scarcity and increasing energy costs facing the world today.

4:00 PM DISCUSSION TIME

4:15 PM EN04.12.08
Bulk Photovoltaic Effect in Graphene-α-In_2Se_3-Graphene van der Waals Heterostructures Shahriar Muhammad Nahid[1], Edmund Han[1], Gillian Nolan[1], Paolo F. Ferrari[1], Andre Schleife[1], Pinshane Y. Huang[1], SungWoo Nam[2] and Arend M. van der Zande[1]; [1]University of Illinois Urbana Champaign, United States; [2]University of California Irvine, United States

The photoelectric efficiency in p-n junction solar cells is fundamentally constrained by the Shockley-Queisser limit. Ferroelectrics surpass the limit because their lack of inversion symmetry leads to a bulk photovoltaic effect. Van der Waals ferroelectrics, such as α-In_2Se_3 have two features which make them compelling candidates for bulk photovoltaic solar cells. First, the band gap is 1.4 eV, close to the ideal bandgap for utilizing the solar spectrum, and much smaller than most ferroelectric oxides with bandgaps of 2.5-4 eV. Second, they naturally exist at nanoscale dimensions, with thicknesses 10-50 nm, well below the mean free path of hot carriers. The key goals are to characterize the domain structures of α-In_2Se_3 and understand how the ferroelectric domains and switching affects the performance of nanoscale solar cells utilizing the bulk photovoltaic effect in α-In_2Se_3.
Here, we first use scanning transmission electron microscopy (STEM), and piezoelectric force microscopy (PFM) to characterize the domain configuration of α-In_2Se_3. We observe uniform domains of α-In_2Se_3 which possess a net dipole moment due to the crystal asymmetry leading to the out of plane ferroelectricity. In addition, we observe the existence of atomically sharp lateral charged domain walls, where the polarization of opposite direction meets to form head to head or tail to tail domain boundaries. Our PFM measurement indicates that the converse piezoelectric coefficient enhances by 800% in the charged domain wall region due to the electrostatic potential in the wall.
Finally, we fabricate sandwiched graphene-α-In_2Se_3-graphene heterostructures, where the top and bottom graphene serve as the electrodes, to characterize and compare how the ferroelectric domains affect the device transport in dark, and under illumination with scanning photocurrent microscopy. In the absence of light, the current vs voltage curve shows an asymmetric resistance. The value of the resistance is 200 MΩ or 2GΩ as an electric field of 0.05 V/nm is applied along or against the polarization direction. Under the illumination of 532 nm laser, the heterostructures display an open circuit voltage of approximately 400 mV. The short circuit photocurrent density scales as intensity$^{\alpha}$, where $\alpha = 0.73$ and reaches a peak value of 0.8 mA/cm^2 under 1 W/cm^2 power. Moreover, we modulate the polarization of the material by sweeping from -0.1 V/nm to +0.1 V/nm and observe a modulation of zero-bias short circuit current from -0.5 nA to 1.5 nA. Both the short circuit current and open circuit voltage demonstrate considerable bulk photovoltaic effect of α-In_2Se_3. These values are similar to the ones observed in other 2D bulk photovoltaic material. Finally, we observe that the existence of charged domain walls enhances the photocurrent generation by more than an order of magnitude.
Our study demonstrates the potential utilization of bulk photovoltaic effect in van der Waals α-In_2Se_3 to realize next generation solar cells.

4:30 PM EN04.12.09
Interface Structure and Properties of 2D Metal-Graphene Supported on Periodically Poled Lithium Niobate Arturo Medina, Marshall Frye, Ian C. Graham, Lauren M. Garten and Faisal M. Alamgir; Georgia Institute of Technology, United States

In this study, we present on the controlled growth of 2D confined metals (2D-M) under heteroepitaxial relations with single-layer graphene (Gr). Using a ferroelectric material, such as periodically polled lithium niobate (PPLN), as a support, external electric/strain fields can be applied to the surface metal via the Gr conduit. With such external fields, non-Faradaic manipulation of electrocatalytic reactions on the metal-graphene structure can be carried out. We explore the architecture of a 2D metal-graphene (2D M-Gr) on top of the PPLN to determine the impact of polarization orientation on the catalytic response of the 2DM-Gr. We conduct atomic force microscopy (AFM) measurements, piezoelectric force microscopy (PFM) and Kelvin probe force microscopy (KPFM) measurements to determine the surface morphology after graphene transfer onto the substrate as well as the polarized states of the poled domains where graphene allows these polarization effects to propagate. PFM and KPFM show that a clear domain structure propagates through the 2D M-Gr. We further present the effect of the piezo/ferroelectric field on the catalytic and electrocatalytic performance of the 2D M-Gr systems and the efficacy, in general of proximity control of catalytic properties through a graphene interface.

4:45 PM EN04.12.10
Energetic Characteristics of Aluminum/Graphene Oxide Composites with Optical Activation Yue Jiang[1], Sili Deng[1,2], Sungwook Hong[3], Jiheng Zhao[1], Sidi Huang[1], Ken-ichi Nomura[3], Ying Li[4], Subodh Tiwari[3], Rajiv Kalia[3], Priya Vashishta[3], Aiichiro Nakano[3] and Xiaolin Zheng[1]; [1]Stanford University, United States; [2]Massachusetts Institute of Technology, United States; [3]University of Southern California, United States; [4]Argonne National Laboratory, United States

Aluminum (Al), with high specific energy density (31 kJ/g) and earth abundance, is a widely used fuel in solid energetic materials to generate heat, gas, and thrust for applications ranging from space propulsion and pyrotechnics to microelectromechanical systems (MEMS). Al-based energetic materials are typically ignited at a single point by a hotwire, flame, or spark. In comparison to point ignition, optical Xe flash ignition occurs across the illuminated area and provides high heating rates, potentially increasing the energy release rate and changing the reaction dynamics of Al. However, micron-sized Al (μ-Al) particles, which are widely used in practical applications, cannot be ignited by a low-energy Xe flash due to poor light absorption properties and high ignition temperature. In this work, we demonstrate that graphene oxide is an effective additive to enhance the optical ignition and combustion properties for μ-Al particles (3–4.5 μm). The results indicate that 3 wt % of GO addition is sufficient to enable the flash ignition of μ-Al particles, for which the normalized minimum ignition energy can be reduced to 44% with 30 wt % of GO addition. The constant-volume combustion test results also show that 20 wt % of GO addition can optimally enhance the combustion performance after flash ignition. The Al/GO (80/20 wt %) composites are superior to the commonly used Al/nanosized metal oxide in terms of higher Al content, lower minimum optical ignition energy, higher peak pressure, faster pressurization rate, and longer overpressure duration during combustion. The energetic nature and enhancing mechanisms of GO were revealed by thermogravimetric analysis, differential scanning calorimetry, Fourier-transform infrared spectroscopy, and reactive molecular dynamics (RMD) simulation. Optically activated GO was experimentally shown to undergo photothermal disproportionation and oxidation reactions, which release heat to initiate the oxidization of Al by air and generate gaseous products to reduce the agglomeration of the solid-phase oxidation products and promote the pressure rise during combustion. The RMD simulation results further confirm that the addition of GO promotes the oxidation of μ-Al particles by exhibiting catalytic effects on the dissociation of oxygen molecules and providing a direct diffusion pathway for the dissociated O atom to reach and react with Al. Overall, the enhanced effects of GO can be attributed to the coupling heat release, catalytic effect, and gas generation. The low mass density of GO can also effectively advance the application of μ-Al particles as energetic materials via the form of Al/GO composites with the advantage of preserving higher Al content, reducing dead mass, and maintaining the high energy density. All of these results confirm that GO is an effective additive to enhance the energetic performance of Al with optical activation.

SESSION EN04.13: Virtual Session
Session Chairs: Hong Li and Damien Voiry
Wednesday Morning, April 26, 2023
EN04-virtual

8:00 AM EN04.13.01
Ni_xMo_y alloy/Graphitic Carbon Nitride(g-C_3N_4) Composites for Hydrogen Evolution Reaction in Alkaline Electrolyte Yu-Chin Shen[1], Jow-Lay Huang[1,1], Sheng-Chang Wang[2] and Yu-Min Shen[1]; [1]National Cheng Kung University, Taiwan; [2]Southern Taiwan University of Science and Technology, Taiwan

Hydrogen energy is regarded as the most promising renewable and clean energy to replace the fossil energy. The noble metals (i.e. Pt, Ru, Ir) were widely utilized to split the water into H_2 and O_2 due to the low Gibbs free energy, however, the high cost and limited availability hinder the commercialization. Recently, transition-metal-based catalysts were developed and achieved good performance and attracted a lot of attention from many research groups. Although these materials have high abundance, they have poor anti-acid corrosion. The cost and instability of catalysts limited the widespread applications in future. Hence, we study HER (hydrogen evolution reaction) in alkaline electrolytes to develop highly efficient and durable electrocatalysts in alkaline electrolytes. Graphitic carbon nitride has been studied intensively, but, it has poor conductivity and few active sites for HER. Therefore, we synthesized Ni_xMo_y alloy/g-C_3N_4 composites to replace the platinum electrode in 1.0 M KOH electrolyte in this study. A wet chemistry method and calcination were utilized to synthesize NixMoy alloy/g-C_3N_4 composites. Firstly, melamine was polymerized at 550°C, and the yellow product of g-C_3N_4 was fabricated. Secondly, nickel and molybdenum precursors are dispersed into diethylene glycol, DI water, and ammonium hydroxide to synthesize $Ni_xMo_yO_z$ and then reduced at 400°C in Ar-H_2 gas atmosphere to obtain Ni_xMo_y alloy/g-C_3N_4 composites. The result showed that the 5-10 nm Ni_4Mo alloy particles were distributed randomly in the surface of sheet-like g-C_3N_4 forming which the (121), (310), and (312) planes of Ni_4Mo were investigated by high-resolution TEM. In NBED and XRD, we found the preferred orientation was (121) of Ni_4Mo. The electrochemical results showed that the overpotential at -10 mA/cm^2 of Ni_4Mo alloy/g-C_3N_4 is 462 mV and the Tafel slope is 95 mV/dec. According to the above result, the Ni_4Mo has active sites for HER. In (121) of Ni_4Mo, there are Ni atoms and Mo atoms and therefore we presumed that the Ni atoms are the dissociation sites for H_2O and Mo atoms are the adsorption sites of hydrogen. In future, we will study the electrochemistry performance of different Ni/Mo ratios and alloy/g-C_3N_4 ratio composites. Further, we will prove that Ni was the active site and Mo was the absorption site toward hydrogen by in-situ Raman spectroscopy. We will also investigate in-situ TEM for studying the transformation of electrocatalysts during HER.

8:15 AM EN04.13.03
Enhancement of Electrocatalytic Activity of $Ti_3C_2T_x$ MXene by *in-situ* Tunable Interfacial Anion Doping and Structural Modification for Hydrogen Evolution Reaction Anand P. Tiwari, Andrew B. Hamlin, Md Saifur Rahman, Julia E. Huddy and William J. Scheideler; Dartmouth College, United States

2D-layered MXenes have attracted increasing attention as promising low-cost, stable electrocatalysts for hydrogen production through electrolysis. However, poor intrinsic chemical activities, and limited active site densities currently inhibit MXenes as practical electrocatalysts for hydrogen evolution reaction (HER). Herein, these limitations are overcome by *in-situ* tunable interfacial chemical doping and structural modification with nonmetallic electron donors—by nitrosulfurization through simple heat treatment with thiourea as a nitrogen and sulfur source in 2D titanium carbide ($Ti_3C_2T_x$) MXene. Through this process, XPS analysis indicates that the substitution of nitrogen and sulfur occurs at the basal plane with controllable chemical compositions ranging from 2 - 4 at. % (Sulfur), and 5-15 at. % (Nitrogen). It is observed by HRTEM, SEM, and AFM that structure of the MXene is changed from planar nanosheets to hexagonal-nanoplate-decorated nanosheets. Moreover, it is confirmed by XRD that the interlayer spacing is increased after interfacial doping, which is expected to increase the diffusivity of electrolytes into the layers and enhance the electrocatalytic activity. The optimal modified $Ti_3C_2T_x$ MXene exhibits a high concentration of Ti-S and Ti-N bonds as well as the lowest overpotential of –260 mV and a Tafel slope of 85 mV/dec at a current density of 10 mA/cm^2 in 0.5 M H_2SO_4, which is three times lower than pristine MXene (overpotential: -770 mV, and Tafel slope: 247 mV/dec). This strategy to improve the electrocatalytic activity of $Ti_3C_2T_x$ MXene for hydrogen evolution by a simple *in-situ* interfacial chemical doping and structural modification will open the possibility of manipulating the electrocatalytic performance of a broad range of MXenes.

8:30 AM *EN04.13.04
Metallic Phase of 2D MoS_2 for Energy Storage Manish Chhowalla; University of Cambridge, United Kingdom

Batteries based on new chemistries that can store more energy than state-of-the-art lithium-ion devices will play an important role in enabling the energy transition to net zero carbon emission. Our previous work has shown that compact electrodes assembled from monolayered nanosheets of metallic 1T phase MoS_2 are highly conductive, lyophilic, and are catalytically active. I will describe the realization of high-performance lithium-sulfur batteries using metallic 1T phase of two-dimensional molybdenum disulfide as binder-free conducting cathodes for hosting sulfur. The attributes of metallic 2D MoS_2 lead to > 85% utilization of sulfur due to improved adsorption of lithium polysulfides, enhanced Li^+ diffusivity, accelerated electrochemical reaction kinetics and superior electrocatalytic activity for polysulfide conversion. We have translated these properties into practical pouch cells, achieving areal capacities of 8.21 ± 0.07 mAh cm^{-2} and capacity retention in excess of 85% over 200 cycles. The metallic MoS_2-based ampere-hour-scale (1.3 ± 0.05 Ah) pouch cells can deliver gravimetric energy density of 402 Wh kg^{-1} and volumetric energy density of 721 Wh L^{-1}. These metrics compare exceptionally favourably with current state-of-the-art in Li-S batteries. Our results provide unique insights into new designs for Li-S cathodes based on electrocatalytically active and conducting two-dimensional (2D) materials.

9:00 AM *EN04.13.05
CVD Graphene: Growth Frontiers & Mass Production Zhongfan Liu[1,2]; [1]Beijing Graphene Institute, China; [2]Peking University, China

With 18 years history of graphene materials, there still exist lots of technical challenges towards graphene industry, including: 1) Low-cost mass production technology; 2) Batch peeling-transfer technology; 3) Transition from single-layer graphene component to macroscopic materials with retained intrinsic performances; 4) Dispersing technology into matrix materials; 5) Irreplaceable killer applications. Beijing Graphene Institute (BGI), established in 2018 and currently having nearly 300 employees, aims to solve these challenging issues by paying particular emphasis to mass production of high-quality CVD graphene materials and manufacturing equipments. BGI is devoted to providing the best graphene materials and related equipments to the market as well as the graphene-related R&D services to enterprises.
The current R&D emphasis on CVD graphene materials at BGI is laid on three different directions: 1) high-quality graphene films and wafers for general purpose; 2) graphene-skinned materials (GSM); 3) purpose-oriented graphene materials focusing on thermal managements, optical communications and medical applications. The star products into market are A3-size graphene films with mm grain boundaries, 4- and 6- inch single crystal graphene wafers, superclean graphene films with best thermal and electrical performances, graphene-skinned glass & fibers, graphene-skinned aluminum oxide fibers, etc. The graphene-skinned glass fibers have been used for deicing applications with extremely high electrothermal conversion efficiency up to 94%. At BGI, we are also working for the customized graphene growth depending on the special needs and requests from customers. There is a great space in this area, which is particularly important before graphene films and wafers find their practical application market in next ten years.

9:30 AM *EN04.13.06
Maximizing Magnetoelectric Energy Harvesting via 2D Material-Based Layer Transfer Jeehwan Kim; Massachusetts Institute of Technology, United States

Magnetoelectric (ME) energy converters utilize the magnetoelectric coupling effect to generate an electric response from an applied magnetic field, or vice versa. Although there are excellent piezoelectric and magnetostrictive materials with their highest coefficient, they cannot be stacked each other epitaxially due to their inherent mismatch in their crystalline structures. In addition, due to substrate clamping effects, those excellent piezoelectric and magnetostrictive thin film materials cannot outperform. In this talk, I will discuss about my group's strategy to maximize ME coupling efficiency by utilizing a 2D material-based layer transfer technique (2DLT). 2DLT is enabled by growing piezoelectric and magnetostrictive epitaxial films on graphene via remote epitaxy which allows to produce freestanding piezoelectric and magnetostrictive by peeling them off from graphene. Then both clamping-free membranes were bonded each other resulting in the best ME coupling devices. I will also discuss about other application spaces of 2DLT and remote epitaxy.

Conventional memristors typically utilize a defective amorphous solid as a switching medium for defect-mediated formation of conducting filaments. However, the imperfection of the switching medium also causes stochastic filament formation leading to spatial and temporal variation of the devices. Thus, it has been extremely challenging to reliably operate large-scale neural networks made of memristor crossbars. In this talk, I will discuss about our group's material strategies to enhance the reliability of memristor-based crossbar arrays. In addition, I present strategies to utilize small scale crossbar arrays for in-sensor/edge computing. Lastly, will introduce optical heterogeneous integration system that enables seamless 3D stacking of small-scale crossbar arrays to enhance the recognition capability.

Symposium Organizers
Andrea Ambrosini, Sandia National Laboratories
Adrianus Indrat Aria, Cranfield University
Ramon Escobar-Galindo, Universidad de Sevilla
Loreto Valenzuela Gutiérrez, CIEMAT - Plataforma Solar de Almería

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* Invited Paper
\+ Distinguished Invited

SESSION EN05.01: Coatings and Heat Exchange I
Session Chairs: Andrea Ambrosini and Adrianus Indrat Aria
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2010

10:30 AM *EN05.01.01
Advances in Optical Coating Materials for CST Gema San Vicente, Angel Morales, Meryem Farchado and Aránzazu Fernández-García; CIEMAT, Spain

Solar reflectors are the first optical material on which solar radiation is incident in concentrating solar thermal (CST) technologies. They are in charge of reflecting and sending direct solar radiation into the solar receiver that will capture it to convert it into thermal energy. The optimal performance and characterization of this material, including the identification of degradation modes in each constituent layer, is a key point to establish the durability of the component. In this way, it is very important the definition of characterization protocols that might also permit lifetime prediction. Once the radiation is reflected in the reflectors, it reaches the solar receiver. In some cases, as parabolic-trough collectors or high-temperature pressurized gas volumetric receivers, a glass cover that minimizes the thermal losses but increases the optical losses protects the absorber. The application of an antireflective coating on the glass increases the receiver's optical efficiency and then the efficiency of the whole solar system. The design of this coating, usually composed of porous silicon dioxide, has to consider a compromise between its low refractive index to produce the highest transparency of the glass and the highest resistance to weathering (high temperatures, UV exposure, and abrasion). Moreover, these two optical components (glass covers and solar reflectors) have to maintain their surfaces clean to avoid radiation scattering and important optical losses. This implies significant economic investments associated with operation and maintenance work, as well as water consumption for cleaning the components. This is particularly remarkable taking into account that the sites with the highest solar irradiance are also those with arid climates, high concentrations of dust, and low water resources. The application of anti-soiling coatings on both components is one of the strategies to mitigate soiling, which is being studied in many research projects. Finally, the solar absorbers must absorb as much as possible of the radiation that hits them to transfer the thermal energy to the heat transfer fluid, increasing its temperature, without losing it through emission. This is achieved by using so-called selective coatings consisting of layers of different compositions which reflect very little radiation in the wavelength range of the solar spectrum but reflect highly in the infrared wavelength range. Depending on the technology and the operation temperatures, the receivers have different configurations and are made of different materials (316 stainless steel, 310 stainless steel, ceramic materials, etc.). The most common configuration is tubular as used in parabolic-through collectors (i.e. ANDASOL solar plant) or tower receivers that use molten salts as heat transfer fluid (GEMASOLAR solar plant). In the first case, a selective coating coats the tube but in the second one the tubular structure is coated with a back paint as no selective coatings, which withstand the operation conditions, are commercially developed. On the other hand, the next generation of CST technologies are looking to increase operating temperatures to obtain higher efficiencies, and then new concepts of receivers as volumetric receivers or particle receivers are being studied. Within the HORIZON 2020 COMPASsCO2 project, the integration of particle systems into highly efficient-CO_2 Brayton power cycles for electricity production is pursued. These particles are coated with black coatings to increase their solar absorptance and withstand high temperatures. In general, the big challenge is the development of coatings with both high optical properties and high durability at operation conditions.
In this talk, the advances in the development of optical coatings applied in components of CST as well as the development in characterization protocols will be presented.

11:00 AM EN05.01.02
Low-Emissivity Superhydrophobic Solar-Thermal Nanocoatings for Power Line Deicing Wei Ma[1], Yang Li[1], Weihong Li[2], Baoling Huang[1] and Shuhuai Yao[1]; [1]The Hong Kong University of Science and Technology, Hong Kong; [2]City University of Hong Kong, Hong Kong

Every winter in frigid regions, power outages caused by ice accumulation on overhead power lines seriously risk the reliability of electrical transmission. Power line deicing methods, which can completely clean the accumulated ice on the complex cable surface gently and efficiently, are highly desired but more technically challenging than those for flat surfaces. Photothermal superhydrophobic surfaces have demonstrated outstanding passive anti-icing and active deicing abilities in cold environments. However, the compatibility with complex curved surfaces and the solar-thermal conversion efficiency remains insufficient for timely ice and frost removal on power lines.
Herein, we report a low-emissivity solar-driven deicing nano-coating that comprises titanium nitride and superhydrophobic silica layers. Specifically, the solar-thermal layer offers strong resonance-enhanced solar absorption (90% on average) and low mid-infrared emission (6%), yielding boosted solar-thermal effects due to thermal radiation management. Enabled by the cooperation between the record-high solar-thermal performance (temperature rise of 72 °C under 1 sun) and the water repellency (contact angle of 173°), the nano-coating realizes effective deicing/defrosting on power lines at −15 °C. The versatility and mass-produced compatibility of this coating bring solar-driven deicing technologies closer to outdoor exposed surfaces in frigid environments.

11:15 AM EN05.01.03
Effect of Pulsed Bias on the Deposition of Multi-Layered $Cr_xAl_{1-x}N_y/Al_2O_3$ Solar Selective Coatings Tandem for High-Temperature Applications Ramon Escobar-Galindo[1], Miriam Sánchez-Pérez[2], T. Cristina Rojas Ruiz[2], F. Javier Ferrer[3,1], Meryem Farchado[4], Angel Morales[4] and Juan Carlos Sanchez-Lopez[2]; [1]Universidad de Sevilla, Spain; [2]Instituto de Ciencia de Materiales de Sevilla (CSIC-Univ. Sevilla), Spain; [3]Centro Nacional de Aceleradores (Univ. Sevilla, CSIC and Junta de Andalucía), Spain; [4]CIEMAT-PSA, Spain

Multilayered solar selective absorber coatings based on $Cr_xAl_{1-x}N_y$ layers with different stoichiometries were deposited on 316L steel and Inconel 625

using radiofrequency (RF) and high-power impulse magnetron sputtering (HiPIMS) technologies. A simultaneous application of DC-pulsed bias (average -100 V, 250 kHz) was applied to the substrates with the aim of increasing the film density and therefore, improving the oxidation resistance and thermal stability at high temperatures (> 500 ºC in air). By changing the synthesis parameters (i.e. sputtering power and gas flows), the chemical composition of aluminium chromium nitride layers was varied to generate i) an infrared-reflective and UV-Vis-NIR absorber layer (with low Al addition and N vacancies) and ii) two intermediate UV-Vis-NIR absorber layers with medium and high aluminium content (CrAl(Lo)N and CrAl(Hi)N). The stack was completed with a top aluminium oxide layer (Al_2O_3) deposited by radiofrequency (RF) magnetron sputtering to act as antireflective layer.
Microstructural characterization was carried out by grazing angle x-ray diffraction, cross-sectional scanning, and high-resolution transmission electron microscopy, while the chemical composition was assessed by Rutherford Backscattering Spectrometry (RBS) and Energy Dispersive X-Rays Spectroscopy (EDS). The solar absorptance (α) and emissivity (ε_{RT}) of the films were determined by UV-Vis-NIR and Fourier-transform infrared (FTIR) spectrophotometry, respectively. The multilayered stack has been heated in air for evaluating thermal stability, oxidation resistance, and optical changes. Coatings were stable after 200 hours of annealing at 600 ºC with an α = *93 and 92%* for samples deposited on steel and Inconel, respectively. The practical performance has been comparatively assessed with a similar solar selective coating deposited without bias assistance and commercial paint Pyromark as a reference. The additional ion bombardment during film growth provided by the bias assistance has led to an increment in the lifetime, thermal stability, and working limit temperature.

11:30 AM *EN05.01.04
Extremely Robust Photonic Nanostructures Andrej Lenert; University of Michigan, United States

The field of nanophotonics has made it possible to manipulate light from visible to infrared frequencies in unprecedented ways, which has improved our ability to harvest the energy of photons, specifically in solar-thermal and thermal-photovoltaic devices. This nanophotonic control is achieved by interfacing materials that have contrasting optical properties to form structures with varying degrees of complexity, ranging from nanoparticles to plasmonic arrays and three-dimensional photonic crystals. However, stabilizing these structures under the extreme thermal and environmental conditions encountered in thermal photonics has remained challenging.

This talk will describe our recent efforts to develop photonic materials that can tolerate operation at very high temperatures in air. Examples include multicomponent transparent refractory aerogels and epitaxial heterostructures of perovskite and rocksalt oxides. The focus will be on the fundamental design of photonic materials that can accomplish the desired photo-thermal conversion with high selectivity and durability, and the integration of such materials into devices that can achieve high performance.

SESSION EN05.02: Storage
Session Chairs: Andrea Ambrosini and Ramon Escobar-Galindo
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2010

2:00 PM EN05.02.01
Development of Core-Shell Structure Heat Storage Materials and Study of Their Adaptation to Cascade Heat Storage System Shenghao Liao, Seiji Yamashita, Mitsuhiro Kubota and Hideki Kita; Nagoya University, Japan

Reducing carbon dioxide emissions is an important issue that must be solved worldwide. From the perspective of carbon dioxide emissions in various sectors, factories account for the largest proportion and industrial furnaces account for the highest proportion. Therefore, improving the efficiency of industrial furnaces is of great significance for reducing carbon dioxide emissions. For example, in the regenerative burner system widely used in the industry, the heat storage temperature is exposed to a high temperature of over 800°C, and heat recovery is performed by switching between two burner systems in a short period. In addition to heat storage and dissipation characteristics in such thermally non-equilibrium conditions, the requirements are durability against repeated thermal shock, strength, and low cost.

Conventionally, solid alumina balls with a diameter of around 20 mm have been widely used as heat accumulators. In this system, a large number of alumina balls are placed in a heat storage tank to store heat using high-temperature waste heat gas, while the stored heat is used to convert air into hot air. Conventional solid alumina spheres have low thermal diffusivity at high temperatures, and it has been found that a short switching time does not transfer heat to the inside of the sphere, leaving the inside of the sphere as a dead zone with little contribution to heat storage.

To improve heat storage efficiency at high temperatures, we are developing latent heat utilization type heat storage balls using ceramics. It is possible to increase the energy density per unit volume and improve the output compared to the sensible heat type by utilizing latent heat. However, the latent heat-utilizing core-shell phase change material (EPCM, Encapsulated Phase Change Material) that can be used above 800 °C has many problems such as sealing technology, durability, and cost, and there is no successful example yet. we have developed a core-thin shell structure heat storage material with high heat storage density and good durability. Specifically, Using cheap alumina powder as raw material and adding a small number of additives to obtain an Al_2O_3 ceramic spherical shell through slip casting and high-temperature sintering, and using waste silicon as raw material, through injection molding and reaction sintering process, obtained Si_3N_4 ceramic spherical shell. On the other hand, for the core materials constituting the interior, we chose materials with different melting points, especially Al-Si, several copper-based alloys, and inexpensive NaCl. By arranging the EPCM having the melting point corresponding to the temperature gradient in the thermal storage tank (Cascade Heat Storage System), the waste heat can be utilized more effectively.

In this presentation, I will focus on thermal storage systems using NaCl. In the molten state, NaCl is highly wettable to ceramics, so it can leak out even the tiniest of crevices due to capillary action. We have found that even in the molten state, adding small amounts of alumina particles can prevent leakage. It was found that when the mixed powder with NaCl and Al_2O_3 as the core material was treated at a high temperature of 850°C, the Al_2O_3 particles rearranged in the molten NaCl and formed a network structure with each other.

In the present study, we investigated the rapid heat storage and heat release properties of heat storage materials with different compositions of core materials by adjusting the ratio of alumina and observed the microscopic morphology of core materials through microscopic analysis. In addition, the strength and thermal shock resistance were evaluated by three-point bending experiments. Based on these performances and primary durability test results, we plan to explain in detail the challenges and possibilities of EPCM using NaCl-Al_2O_3 as the core material.

2:15 PM EN05.02.02

Application of Type 316L Stainless Steel to High-Temperature Design of 700°C Thermal Energy Storage System Hyeong-Yeon Lee, Hyeonil Kim and Jaehyuk Eoh; Korea Atomic Energy Research Institute, Korea (the Republic of)

Type 316L stainless steel (hereafter 316L SS) has been applied as heat resistant structural material of pressure boundary components and piping in a large-scale 700°C thermal energy storage test facility (called TESET) under construction at KAERI(Korea Atomic Energy Research Institute). The TESET facility uses sodium as coolant with operation temperature of 700°C at atmospheric pressure for thermal energy storage from renewable energy sources such as concentrated solar thermal energy. For the design and construction of 700°C 316L SS thermal energy storage facility, French nuclear design rules of RCC-MRx have been used with supplementation of lack material properties and design coefficients around the temperature of 700°C for the readily available material of 316L SS. In ASME boiler and pressure vessel codes such as ASME Section VIII or Section III Division 5, elevated temperature material properties are not codified for 316L SS, which is why it is not possible to apply ASME codes while RCC-MRx provides codified material properties over high temperature in the creep range. However, because the high-temperature material properties such as creep rupture strength, fatigue strength and material strength are not provided up to the temperature of 700°C for 316L SS, a series of material tests on tension, fatigue and fracture toughness over the temperatures up to 700°C were conducted for the determination of lack material properties and design coefficients of 316L SS in RCC-MRx. Based on those works, feasibility on the application of Type 316L SS to 700°C pressure boundary components and piping in the TESET facility was investigated. The evaluation results based on a number material tests, supplementation works of lack material properties and design coefficients showed that an application of 316L SS to 700°C class thermal energy storage system was shown to be possible.

2:30 PM BREAK

SESSION EN05.03: System and Applications
Session Chairs: Adrianus Indrat Aria and Loreto Valenzuela Gutiérrez
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2010

3:00 PM *EN05.03.01
Electrochemical Control and Galvanic Corrosion Mitigation for Molten Chloride Systems Judith Vidal, Ph.D and Kerry Rippy; National Renewable Energy Laboratory, United States

Commercial deployment of high temperature molten salt thermal energy storage (TES) systems for third generation (gen3) of concentrating solar power (CSP) technologies is challenged by the high corrosion rates of molten chlorides. The ternary MgNaK chloride salt is a prime candidate for the thermal storage media because of its low cost, high thermal stability, and good heat transfer properties but it is very corrosive when in contact with traces of moisture and air. Without proper chemical control of the system, only expensive nickel superalloys can contain those fluids for several years. To reduce the capital cost and maintenance and operation costs of the Gen3-CSP plants, we developed corrosion control processes such as in-line electrolytic purification of the salt and to galvanic corrosion control in dissimilar alloys couples. We developed the use of magnesium as a sacrificial anode to mitigate the galvanic corrosion of alloys including Hastelloy C-276 (C276) and Haynes 230 (H230). Multiple corrosion experiments were run in MgNaK molten chloride salt to determine 1) baseline galvanic corrosion and 2) the efficacy of Mg as a sacrificial anode. These experiments provided preliminary results regarding the galvanic corrosion of alloys such as C276 and H230, and future studies can be conducted to provide further evidence for the effectiveness of Mg salt purification as a galvanic corrosion mitigation method.

3:30 PM *EN05.03.02
Comparative Assessment of the durability of Glass and Polymer Mirrors for Concentrated Solar Thermal Technologies Christopher L. Sansom and Mounia Karim; University of Derby, United Kingdom

Mirror durability is crucial to the overall performance of Concentrated Solar Thermal installations, including Concentrating Solar Power (CSP) plants. The reflecting surfaces in the solar field need to maintain their good performance during the plant's lifetime, which can be considered to be between 25-35 years to ensure good profitability of the project.

Sites for CSP installations require high DNI and are often arid, desert-like regions. These dusty environments mean that particulate soiling and surface erosion phenomena remain the most common problems that affect the mirrors performance during their operational lifetime.
The degradation in reflectance caused by soiling deposition is a reversible degradation that can be fully recovered when adopting an appropriate cleaning process. However, it can sometimes lead to an irreversible degradation caused by erosion (due to the impact of airborne sand or dust particles) or by abrasion (due to contact cleaning).

For both degradation phenomena, the drop in reflectance is highly dependent on the environmental conditions (wind speed, wind direction, and sand/dust particle properties) as well as the surface characteristics of the mirror.

In the present work, a series of both outdoor exposures and experimental indoor simulation ageing tests have been conducted to evaluate the effect of soiling and erosion on mirror durability in order to highlight the impact of different influencing parameters on these degradation phenomena. Surface degradation of both polymer film and back-silvered low-iron glass reflecting solar concentrators have been tested and compared in this work. To simulate the real exposure conditions, sand and dust particles have been collected from different potential sites, prepared, analysed and used for the indoor simulation tests.

In this paper, soiling of solar mirrors is described from both a theoretical and experimental perspective. This includes an understanding of the conditions for particle impact with the surface that may lead to erosion, adhesion, or removal. The elemental composition of soiling particles has been analysed as it's a key variable in determining the adhesion force depending on the surface energy. In addition, some contact cleaning processes have been tested in order to evaluate the potential risk of abrasion due to cleaning using different parameters (different soiling particles, different brushes and different speeds).

In order to analyse the impact of erosion on soiling deposition rate, samples have been eroded in the lab before simulating the soiling deposition under different conditions.

Obtained results show that glass solar mirrors present better performance in comparison to polymer mirrors. This has been observed for both soiling and erosion phenomena and could be explained by the high mechanical properties of glass surfaces compared to the PMMA in the case of the polymer mirrors. Also, it has been shown that eroded surfaces accumulate more soiling deposition and the drop in reflectance is higher. This is because of the increase of surface roughness. Regarding contact cleaning simulation, it has been shown that there is a high impact of the brush properties on the degradation that can be generated during the cleaning process.

4:00 PM EN05.03.04
Efficient Generation of the Morphology of Organic Bulk Heterojunction Solar Cells Based on the Scanning Transmission X-Ray Microscopy Images Wenchao Yang; King Abdullah University of Science and Technology, Saudi Arabia

In organic bulk heterojunction (BHJ) solar cells, the morphology of the donor/acceptor (D/A) blend can significantly impact the charge generation efficiency and recombination losses, thus largely determining the device efficiency. In order to simulate the electronic processes in the working devices, near-exact reproduction of the morphology is very important but the method is still lacking. Here we developed an efficient way to reconstruct the morphologies of the DR3:OIDTBR solar cells under different annealing times by employing the 2 dimensional maps of the compositions (D/A percentage) along the thickness (z-) direction obtained by the Scanning Transmission X-ray Microscopy (STXM) technique. Considering the normalized pixel values in the STXM images as the probabilities for obtaining acceptor sites, the site types along each z-direction column in a 3-d cubic lattice are individually generated, and the same-type adjacent domains are merged to form larger domains. Then the Kawasaki-algorithm is applied to the morphology to smooth it and add lateral correlations to the domains. The average size, anisotropy and tortuosity of the domains are calculated and analyzed. The generated morphologies are further used for Kinetic Monte Carlo simulations of the internal quantum efficiencies, which are found to increase with the annealing time, being consistent with the experimental results. Our method provides an easy-to-implement and efficient mean to obtain a massive esemble of device morphology relative to the expensive ones like electron tomography, which can be used for simulating electronic properties of BHJ solar cells.

SESSION EN05.04: Poster
Session Chairs: Adrianus Indrat Aria and Ramon Escobar-Galindo
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN05.04.02
Searching the Fe-Mn-Ni-Al-Cr Composition Space for Materials with High Strength at High Temperature for Use as Solar Absorbers in Concentrating Solar Thermal Plants Andrew Pike and Geoffroy Hautier; Dartmouth College, United States

In order to increase the maximum efficiency of concentrating solar thermal plants, higher operating temperatures are necessary. One issue that arises when attempting to increase plant operating temperatures is that of finding a proper material for the absorber tube. It must be capable of having a long service life with acceptable levels of creep, tolerance to day/night thermal cycling, and resistance to degradation from the working fluid. The high entropy alloy (HEA) $Fe_{28.2}Mn_{18.8}Ni_{32.9}Al_{14.1}Cr_6$ has shown some promise for this use [1]. We will explore the composition space of this alloy to further optimize it for use as a solar absorber. To investigate any significant fraction of the 5-component composition experimentally is practically impossible. From density functional theory (DFT), we will perform a cluster expansion for the system and use this to account for disordered phases and temperature effects to explore the phase diagram computationally. We will specifically search for phases that are expected to have good performance at high temperatures.

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5:00 PM EN05.04.03
Isovalent Doping Effect on Pd Exsolution in Perovskite-type Oxide for CO_2 Methanation Bonjae Koo; Sungshin Women's University, Korea (the Republic of)

The increase of carbon dioxide (CO_2) in the global atmosphere is a critical problem that accelerates global warming through the greenhouse effect, and a solution is needed to reduce carbon dioxide. Among the various carbon reduction technologies, CO_2 methanation can contribute to reducing CO_2 emissions by chemical reactions with hydrogen (H_2), and synthetic methane (CH_4) gas obtained by the reaction can be stored and transported through an advanced natural gas infrastructure. However, it is necessary to develop catalysts with high catalytic activity and durability in order to maintain methane production for a long time. Exsolution process in which metal ions doped in the perovskite lattice escape from the lattice and become nanoparticles on the surface is a synthetic technique that has been reported to ensure catalyst durability by strong bonding with supports and metal ions.
In this study, we aim to apply the isovalent doping effect in perovskite-type oxide to promote the exsolution of Palladium (Pd), which is known as a representative active catalyst for CO_2 methanation reaction. We evaluated the catalytic activity and durability of Pd exsolved $SrTiO_3$ catalysts by Ba doping in Sr sites against CO_2 methanation .

5:00 PM EN05.04.04
Calculation of Required Coolant Flow Rate for Photovoltaic-Thermal Module Using Standard Meteorological Data and Thermal Analysis Hyo Jae Jeong and Daegeun Park; Korea Institute of Industrial Technology, Korea (the Republic of)

Solar power generation efficiency is affected by weather factors such as temperature and wind speed. Note that the amount of power generation decreases because the module temperature increases in summer and the power generation efficiency decreases. A photovoltaic has been researched since the 1970s and has the advantages of generating heat together with power as well as preventing power generation efficiency and power reduction due to the temperature rise of the module. In this study, the amount of heat collected by season, time, and region for photovoltaic (PVT) modules were calculated using IWEC (International Weather for Energy Calculation) data provided by the American Society of Refrigeration and Air Conditioning. The PVT module applied in this study is installed at an angle of 20 degrees from the ground, and the certified power generation efficiency of the module is 17.83%. Therefore, the heat collection amount of the PVT module was assumed to be 82.17% of the solar radiation amount, and the heat collection amount according to the module angle was calculated using the following equation.
Qsc=Ac[0.8217GβFR(τα) - FR(UL)(TSC - Ta,in)]
where Gα is the total transfer strength, AC is the heat collection area (m2) of the PVT panel, FR(τα) is the heat dissipation coefficient, FR(UL) is the absorption rate (W/m2-K), TSC is the average temperature of the circulating refrigerant (K), Ta,in is the dry bulb temperature (K) of the outside. In this study, Ansys Steady-State Thermal solver was used to predict the PVT module temperature in accordance with the amount of heat collected. The grids of

15,720 were applied for numerical analysis. The external convective heat transfer coefficient was 10 W/m2-K and IWEC data values were applied as external temperatures. As the results, the required cooling load of the PVT module was predicted up to 605 W, and the range of cooling water required to improve power generation efficiency was calculated to be 0 to 217 cc/min.

SESSION EN05.05: Coatings and Heat Exchange II
Session Chairs: Andrea Ambrosini and Adrianus Indrat Aria
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2010

8:30 AM EN05.05.01
Fabrication and Characterization of a Novel Carbon/Carbon Composite with Micro-channels for Concentrated Solar Power Gas Receivers Jose C. Cordeiro[1], Hema Ramsurn[1], Daniel Crunkleton[1], Todd Otanicar[2] and Michael Keller[1]; [1]University of Tulsa, United States; [2]Boise State University, United States

Concentrated solar power (CSP) gas receivers have recently been proposed due to their potentially higher efficiencies when combined with sCO_2 (super-critical CO_2) Brayton cycles. The state-of-the-art of modular micro-channel receivers are made with nickel-alloys. However, these receivers face thermal fatigue issues due to daily start-up operations, limiting their operating temperatures to around 560 °C. To overcome these challenges, a novel modular carbon/carbon (C/C) composite with micro-channels for CSP sCO_2 gas receivers is proposed. These composites offer comparable thermal and mechanical properties while having a significantly lower coefficient of thermal expansion. This mitigates thermal fatigue problems, allowing for much higher operating temperatures to be used (> 800 °C), which in turn can greatly increase efficiency. In addition, their lightweight nature can reduce installation costs.

In this work, the fabrication of the C/C composite modules starts by combining carbon fibers with a resorcinol-modified phenolic resin. Between the layers of carbon fibers, 3D printed PLA (polylactic acid) channels are placed, serving as a template for the desired micro-channel network. The resin is then cured in a vacuum bag and in-house designed and built autoclave setup (up to 150 °C, 160 psi) to produce a void-free prepreg. The novel approach of adding resorcinol allows the resin to be first B-stage cured at 50 °C, which is below the glass transition temperature of PLA (52.4 °C), preventing channel squishing due to the high pressure provided by the autoclave. Next, PLA is depolymerized under vacuum at 290 °C, leaving a cleared channel network in its place. The cured phenolic resin in the prepreg is then carbonized at 1000 °C under a nitrogen atmosphere where gas evolution causes a decrease in density. Due to matrix shrinkage, residual stresses build up between the carbon matrix and the fibers, which are alleviated through graphitization at 2200 °C. To obtain composites with the desired properties, a densification procedure is done by using a novel CVI (chemical vapor infiltration) method with methane above 900 °C and vacuum pressures below 250 mbar with processing times between 20-100 hours. During this process, methane is broken down to deposit carbon in the pores of the C/C composite, increasing the density of the material. The densified composite is then graphitized a second time at 2200 °C under argon, greatly improving its thermal conductivity.

Carbon materials are known to oxidize in air and CO_2 at temperatures above 500 °C. Thus, an anti-oxidative coating is applied to the C/C composite modules to prevent mass loss due to both outside air and the heat transfer fluid (sCO_2). A multilayered coating approach using pure SiC and a mixture of ZrB_2-SiC is shown to be effective due to their high temperature stability. Furthermore, the formation of oxides when exposed to air (SiO_2, ZrO_2, and $ZrSiO_4$) aids in protecting the substrate as well as providing self-healing abilities. The first layer consists of SiC, produced through pack cementation using a powder mixture (Si, C, Al_2O_3, and SiC) in a closed graphite crucible heat treated at 1800 °C. This SiC layer has excellent adhesion and acts as a buffer to alleviate thermal stresses between the C/C composite and the outer ZrB_2-SiC layer, which is in turn applied through a slurry/dip coating process. The slurry, in which SiC coated samples are dipped, consists of a mixture of ZrB_2 powders with a polymeric ceramic precursor. Once heat treated above 1000 °C, the precursor acts as a binder by forming SiC. Isothermal tests at 800 °C for 3 days were done and show that after an initial weight increase of around 3.4 wt% due to oxide formation, the specimens remain stable with no weight loss. A combination of SEM (scanning electron microscopy), SEM/EDS (energy-dispersive spectroscopy), XRD (X-ray diffraction) and TGA (thermogravimetric analysis) are used to characterize the produced C/C composites.

8:45 AM EN05.05.02
Machine Learning Accelerated Discovery of Thermal Energy Storage Materials with High Heat Capacity Ming Hu; University of South Carolina, United States

Existing machine learning potentials for predicting phonon properties of crystals are limited to either small amount of training data or a material-to-material basis, primarily due to the exponential scaling of model parameters with the number of atomic species or elements. This renders high-throughput infeasible when facing large-scale new materials. Unlike previous machine learning models with inherently limited training on small data and global properties, we develop Elemental Spatial Density Neural Network Force Field (Elemental-SDNNFF) with abundant atomic level environments as training data. Benefited from this innovation, we integrate >30 million atomic data to train a single deep neural network without increased expensive ab initio simulations. The effectiveness and precision of the Elemental-SDNNFF approach is demonstrated on a set of >100,000 inorganic crystalline structures spanning 63 elements in the periodic table by prediction of complete phonon properties. We then predicted the heat capacity of >50,000 inorganic crystalline structures with non-zero band gap screened from the Open Quantum Material Database. We gain deep insight into the correlation between heat capacity and structure descriptors such as space group, prototype, lattice volume, atomic weight, etc. Several tens of structures were predicted to possess high heat capacity, and the results were further validated with DFT calculations. We also identified a few special structures that exhibit extremely high heat capacity, even higher than that of the Dulong-Petit limit at room temperature. This study paves the way for accelerating the discovery of novel thermal energy storage materials by combining machine learning with minimal DFT inquiry.

9:00 AM EN05.05.03
Material Candidates for the Heat Exchanger Tubes for Solar sCO2 Brayton Cycles Marta Serrano-Garcia; CIEMAT, Spain

Currently, the research focus regarding CSP technology worldwide is related to the development of systems that can reach temperatures close to 1000°C. The concept of particle-based receiver is regarded as a promising candidate where solid particles are both heat-transfer and thermal energy storage media showing the potential to exceed 1000°C. Meanwhile, supercritical carbon dioxide (s-CO2) Brayton cycles offer advantages of its mass density, low viscosity and favourable heat transfer properties, which reduces the cost of concentrating solar power (CSP). The Horizon 2020 project COMPASsCO2 focuses on the efficient and reliable integration of storable solar energy by solid particles into s-CO2 Brayton cycles. In COMPASsCO2, the key component for such an integration, *i.e.* the particle/s-CO2 heat exchanger, will be validated in a relevant environment. One of the main technological challenges is the selection of the heat exchange tube materials as the operating parameters of s-CO2 heat exchangers are estimated around 700°C and 25

MPa at the internal wall.
In this work, the material selection criteria for the COMPASSCO2 heat exchanger tubes is summarized, the first results of the mechanical properties at high temperature of commercial alloys are discussed as well as the development of novel Cr nickel aluminide (NiAl) and Cr silicides superalloys.

9:15 AM EN05.05.04
Application of Silicone Based Heat Transfer Fluids in Parabolic Trough Collectors Loreto Valenzuela Gutiérrez[1], Guillaume Saliou[1], Christoph Hilgert[2], Kai Schickedanz[3] and Christian Jung[2]; [1]CIEMAT - Plataforma Solar de Almería, Spain; [2]German Aerospace Center (DLR), Germany; [3]Wacker Chemie AG, Germany

Despite leaning toward a lower LCOE [1], a higher operation temperature and less degradation products over time [2], silicone-based heat transfer fluids (HTF) have not yet been used in a commercial Parabolic Trough Collector power plant. In this work, a summary of the proof-of-concept process for the new HELISOL® line of silicone-based HTFs developed by Wacker Chemie AG is presented. Three generations of polydimethylsiloxane (PDMS) HTFs, HELISOL® 5A [3], HELISOL® XA and HELISOL® XLP, were successively operated for a loop scale demonstration at temperatures between 425 °C and 450 °C for 480 hours each at Plataforma Solar de Almeria (Spain). Prior to said qualification activities, the PROMETEO parabolic-troughs test facility, with a mirror surface of 1300 m^2, has been upgraded to withstand temperatures up to 450 °C. For each of the tests the plant was completely drained, cleaned and filled with 7 to 8 m^3 of the corresponding HELISOL® grade. HTF degradation and gas formation were determined, plant performances monitored, and operational behaviour and incidents documented while elaborating a guideline on the application of silicone-based HTFs in parabolic trough solar fields [4], which was the basis for developing and proposing an international standard in the IEC context.

DISCLAIMER
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SESSION EN05.06: Thermochemistry
Session Chairs: Ramon Escobar-Galindo and Loreto Valenzuela Gutiérrez
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2010

1:30 PM *EN05.06.01
Bridging Photoelectrochemical and Thermochemical Approaches for Solar Fuel Processing Sophia Haussener; Ecole Polytechnique Federale de Lausanne, Switzerland, Switzerland

Solar radiation is the most abundant renewable energy source available but it is distributed and intermittent, thereby necessitating its storage via conversion to a fuel or chemical commodity (e.g. hydrogen or carbohydrates) for practical use. Solar thermo-chemical and photo-electro-chemical approaches (and combinations thereof) provide viable, non-biological routes for the direct synthesis of solar fuels and chemical commodities. While solar thermochemical approaches utilize heat at high temperature to support an endothermic reaction, photoelectrochemical approaches utilize the photons (with sufficient energy) to drive the endothermic reactions.
I will review the state of the art of photoelectrochemical and thermochemical solar fuel processing approaches and comment on their specific challenges [1]. I will then highlight various approaches in which photo- and thermos-chemical approaches are combined. Specifically, I will discuss the utilization of concentrated solar irradiation and thermal integration for photoelectrochemical approaches and the potential to increase their performance [2]. As the large kinetic, ohmic and transport overpotentials limit the current density and therefore the power density of these approaches, I will further explore approaches for close thermal integration and high current density operation. Specifically, I will discuss the development of a modeling framework that assesses the possibility of high-temperature operation (temperatures > 400 K) of the photoelectrochemical approach in a solid state equivalent design [3]. Such devices would utilize ceramic electrolytes, earth abundant catalysts with small overpotentials, and high-temperature solar cells utilizing the thermionic emission principle. I will discuss requirements on materials (solid electrolyte, catalysts, semiconductor absorber and barriers, etc.), operating conditions and design for such approaches to be feasible and explore limiting efficiencies. I will then present the experimental implementation of such a solar-driven high-temperature electrolysis approach in a simpler integrational approach [4] before ending with discussing how electrochemistry can help in enhancing the performance of solar thermochemical cycles [5].

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2:00 PM *EN05.06.02
Combined Experiment and Theory for Extracting Solar Thermochemical Material Thermodynamics Steven Wilson, Zoe Liberman-Martin, Ellen Stechel and Christopher Muhich; Arizona State University, United States

The ability for certain metal oxides to reduce at temperatures achievable with solar concentration, and subsequently re-oxidize upon exposure to H_2O or CO_2, thereby releasing H2 or CO, underpins solar thermochemical gas splitting technologies. However, the mere ability for a metal oxide to facilitate these coupled reactions is insufficient to achieve an efficient and commercialized process. Ideal materials should be able to reduce at as mild conditions (temperature and pressure) as possible while still converting as much H_2O or CO_2 to H_2 or CO as possible. This juxtaposition arises from the thermodynamics of the cycle, where the first reaction is favored at low metal oxide reduction enthalpies, while the latter is favored at high reduction enthalpies. Thus, a balance must be struck. In order to assess this balance, detailed thermodynamic properties of candidate active materials must be extracted. To-date this has generally relied upon experimental thermogravimetric analysis (TGA) coupled to van't Hoff or the compound energy formalism (CEF) analysis *or* computationally predicted properties, such as from density functional theory (DFT). Such methods are unsatisfactory for rapid material identification in that TGA + van't Hoff only characterizes one material at a time, while TGA + CEF requires complex fitting of many, often linearly dependent parameters. Additionally, both methods for extracting thermodynamics require extensive TGA data sets which are expensive and tedious to gather and are susceptible to enthalpy/entropy trade-offs when fitting, making the quality of the extracted properties ambiguous. Conversely, DFT methods are automatable and can give high quality enthalpy information, when done carefully. However, it is difficult to extract entropic information and thus predict experimental performance and it is costly to examine a wide range of reduction extents.
In this presentation, we will examine two methods to overcome existing challenges in reducible metal oxide thermodynamic characterization: 1) cross-fitting of the CEF to experimental and theoretical data to alleviate ambiguities and provide characterization across materials families; and 2) a Bayesian approach to selecting which data points should be collected. These methods are examined through the perovskite family ($ABO_{3-\delta}$) of materials where there is interest in knowing partial molar entropies and enthalpies (I.e. $\partial H/\partial \delta$ and $\partial S/\partial \delta$). Our cross-fit model allows both DFT and TGA to be directly incorporated into a CEF model. This development is key as the CEF terms, which are linearly dependent in free energy where TGA measured, are linearly independent in enthalpy, which is accessible by DFT. Thus, a reliable CEF can be constructed. Secondly, we examine the use of a Bayesian approach to selecting data points which should be gathered next. Data points to examine include measuring the non-stoichiometric at a particular temperature and pressure in a TGA and new calculated points, i.e. the energy of a particular composition and δ. The combination of these methods not only provides more reliable thermodynamic characterization, but can *a priori* identify critical points to examine in the temperature, O_2 partial pressure, compositional landscape, thus minimizing the number of points which must be examined.

2:30 PM EN05.06.03
Interacting Defect Equilibria—O Vacancy Formation in Oxides for Thermochemical Hydrogen Anuj Goyal and Stephan Lany; National Renewable Energy Laboratory, United States

First principles calculations of defect formation energies provide the basis for prediction of defect concentrations and equilibria. Previous extensions of the dilute defect model have focused on exchange of electronic charge between defects and the Fermi level, including the resulting attractive forces between oppositely charged defects that lead to the formation of pairs and complexes. In oxides for thermochemical hydrogen production, we encounter high concentrations of oxygen vacancies which are subject to a repulsive interaction. Unlike in case of attractive forces between different defects, this situation does not lend itself to description with a simple law-of-mass-action model. Instead, we formulate an approach that utilizes a statistical enumeration of pair and triplet configurations in supercells of varying size. The distribution of defect energies is then condensed into a temperature-dependent free energy of defect formation capturing both the enthalpies and configurational entropies of the statistical ensemble. In conjunction with ideal-gas chemical potentials for O_2, H_2, and H_2O, this model allows the simulation of the reduction and oxidation processes for solar thermochemical hydrogen production with $Sr_{1-x}Ce_xMnO_3$.

2:45 PM EN05.06.04
Photo-Electrochemical Conversion of CO_2 to Solar Fuels with Concentrated Solar Irradiation Mahendra Patel, Etienne Boutin and Sophia Haussener; EPFL, Switzerland

Photo-electrochemical (P-EC) carbon dioxide (CO_2) reduction can produce fuels and platform chemicals such as carbon monoxide (CO), methane (CH_4), or ethanol (C_2H_5OH) utilizing the energy available from renewable sources like (concentrated) sunlight, CO_2, and water. P-EC devices, i.e. composed of an integrated photovoltaics component (PV) and an electrolyzer component (EC), allow to overcome some of the challenges imposed by the solid-liquid interface in traditional PEC devices such as degradation. The challenges of these P-EC device demonstrations is to achieve higher operating current densities while maintaining high solar-to-fuel efficiencies.[1] We demonstrated that process in a custom-made, heat-managed integrated P-EC CO_2-to-CO conversion device operating with concentrated solar irradiation of up to 450 kW/m^2. That device constituted of a directly integrated concentrated PV triple junction cell and a zero-gap EC cell. An operando activation method was used to infuse the alkali metal cations (CsOH) into the gas diffusion electrode (GDE) to reduce the cathodic overpotential. At optimal conditions, the device operated at a solar-to-fuel and solar-to-CO conversion efficiency of 19 and 17%, respectively, with production rates of CO above 1 NL h^{-1}.[2]

In this contribution, we will present work that uses a similar, integrated and thermally-managed device concept for P-EC CO_2 conversion to the higher-value products CH_4 and C_2H_4. We use a Cu nanoparticle-based catalyst layer in a GDE arrangement. Cu-based catalysts are selective towards CH_4/C_2H_4 at high overpotentials but the selectivity depends on the nano-structure of the Cu nanoparticles. For example, Cu (111) surfaces are selective towards CH_4 production and Cu (100) surfaces towards C_2H_4 production.[3] We investigate if such selectivity tailoring – that is typically observed in H-cell designs – is translated also in solar-driven zero-gap GDE P-EC designs. The newly, implemented device incorporates the design and development of a new photoabsorber component with multiple in-series connected concentrated PV cells, providing a higher voltage for CO_2 reduction during the integrated operation. The device includes a thermal management approach to cool down the photoabsorber while preheating the reactant (water) before it enters the anodic flow stream, where the increasing temperature enhances the EC performance. We utilized the previously developed strategy of operando activation of alkali metal cations in the cathodic GDE to infuse the cations to enhance the overall device performance. The dark and integrated experiments show good performance for CO_2 reduction to C_2H_4 including high current density ~240 mA/cm^2 at 4V and product selectivity ~80%. We will show the detail performance characteristics of the new device, including efficiency, selectivity, and dynamic characterization.

This P-EC device demonstration opens a new efficient pathway towards renewable and economic industrial solar fuel production for various gaseous products at efficiency and power density utilizing concentrated solar irradiation.

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3:00 PM BREAK

3:30 PM *EN05.06.05
Non-Stoichiometric Oxides for Redox Applications in Countercurrent Chemical-Looping Regenerative Reactors Brendan Bulfin and Aldo Steinfeld; ETH Zürich, Switzerland

Chemical redox reactions have thermodynamic limits on species conversion which play a major role in process design and efficiency. Unconverted feedstock often needs to be separated and recycled back to reactors, increasing the energy demand, process complexity and cost. Just as is the case for heat exchangers, countercurrent reactor systems can improve the thermodynamic limits on species exchange and conversion. This work demonstrates a countercurrent redox reactor system, which can be realized in a packed-bed chemical-looping reactor by storing the favorable oxygen chemical potential inclines using the unique properties of non-stoichiometric oxide. The concept is analogous to a regenerative heat exchanger (regenerator), but for oxygen exchange and storage, and so we use the term *regenerative reactor*. We apply this approach to the reverse water-gas shift reaction, which is a critical step in the processing of synthetic e-fuels. Modelling results indicate that the thermodynamic limits on conversion can be approximately doubled via this method. Furthermore, the CO is formed separately from the H_2 flow, allowing for the syngas composition to be finely tuned for downstream processing. The concept is modelled and experimentally validated via a lab-scale demonstration performed with CeO_2 at 1073 K, which resulted in a CO_2-to-CO molar conversion of 88%, compared to a thermodynamic limit of 58% for the conventional process at the same conditions. We discuss the outlook from a materials perspective for further development of this application of non-stoichiometric oxides, with focus on the production of solar fuels from H_2O and CO_2.

4:00 PM EN05.06.06
Solar Thermochemical Ammonia Production Via a Renewable Nitride Looping Cycle Andrea Ambrosini[1], Xiang Gao[2], Ivan Ermanoski[2], Nhu Nguyen[3], Hagan E. Bush[1], Suliman Rashid[2], Peter Loutzenhiser[3], Ellen Stechel[2] and James Miller[2]; [1]Sandia National Laboratories, United States; [2]Arizona State University, United States; [3]Georgia Institute of Technology, United States

Ammonia (NH_3) is an energy-dense chemical and a vital component of fertilizer, as well as a potential candidate for thermochemical energy storage for high-temperature concentrating solar power (CSP) and carbon-neutral liquid fuel. For over 100 years, ammonia has been synthesized by the Haber-Bosch process, which requires pressures of 150- 250 bar and temperatures on the order of 450-550 °C. Combustion of hydrocarbons provides the heat and mechanical energy required to drive the NH_3 reaction, and methane is the main source of hydrogen (H_2) and nitrogen (N_2) feedstocks. Overall, ammonia production via Haber-Bosch accounts for almost 1.5% of global CO_2 emissions. The development of a renewable pathway to ammonia production can greatly decrease, or eliminate altogether, these CO_2 side-products.
The aim of the Solar-Thermal Ammonia Production (STAP) project is to develop an advanced two-stage looping process utilizing concentrating solar heat to separate and shuttle N_2 from air for use in the renewable production of NH_3. In the oxide looping cycle, a redox-active metal oxide is thermally reduced via concentrating solar irradiation. Subsequent exposure to air re-oxidizes the material to its original form, removing O_2 and producing relatively pure N_2. The N_2 serves as a feedstock for NH_3 synthesis in a two-step, low pressure, metal nitride looping cycle. In the first step of the nitride cycle, renewably-sourced H_2 reduces a metal nitride, creating NH_3 in the process and resulting in a nitrogen-deficient metal nitride. In the second step, the purified N_2 from the oxide cycle is used to regenerate the reduced nitride to its original stoichiometry, thus closing the loop. The net result is ammonia produced from sunlight, air, and H_2, employing recyclable metal oxides and nitrides.
A series of ternary and quaternary metal nitrides was synthesized, characterized, and screened for reduction (ammonia producing) and re-nitridation activity. Several candidate nitrides demonstrated cyclic NH_3 production and regeneration at pressures an order of magnitude lower than traditional Haber-Bosch. The results, which will be presented in this talk, show the promise for NH_3 synthesis via the metal nitride looping process. By utilizing concentrating solar as a thermal resource and replacing hydrocarbon-sourced H_2 and N_2 with green alternatives, the large carbon footprint of ammonia production can be vastly reduced or eliminated altogether.

SESSION EN05.07: Virtual
Session Chairs: Andrea Ambrosini and Ramon Escobar-Galindo
Tuesday Morning, April 25, 2023
EN05-virtual

8:00 AM *EN05.07.01
Recent Advances and Challenges in Spectrally Selective Coatings for High Temperature Solar Thermal Applications Harish C. Barshilia; CSIR-National Aerospace Laboratories, India

Solar radiation is an abundantly available clean source of renewable energy. It is estimated that one hour of solar radiation has energy equivalent to the world's annual energy consumption. Therefore, harnessing solar energy is one of the most important technologies in realizing carbon neutrality in the future as per the key goals of the COP26 summit. Solar energy can be harnessed primarily in two ways: (i) photovoltaic and (ii) solar thermal. In the latter case, solar radiation is converted into thermal energy and subsequently to electrical energy by solar thermal concentrating systems. Concentrated solar power systems use solar absorbers to convert sunlight to thermal electric power. Highly specialized coatings with very high absorptance in the solar spectrum region (that is, 0.3-2.5 microns) and low thermal emittance in the infrared region (2.5-50 microns) are required to harness the solar energy and these are called spectrally selective absorbers. No natural surface is an ideal selective surface and these surfaces are fabricated using a variety of deposition techniques. All the solar collectors are coated with solar selective coatings with high solar absorptance and low thermal emittance. From the operational point of view, absorber coatings can be divided into three categories. (i) Low temperature coatings, wherein the process temperature is less than 100 deg. C. These coatings are used for domestic hot water applications. (ii) Mid-temperature coatings, wherein the process temperature is between 100-350 deg. C and are used in industrial heat processes. (iii) High temperature coatings. The process temperature here is 400 deg. C and above and these coatings are used for power generation applications. As stated earlier, the basic requirements of a high temperature solar absorber are: it should have high solar absorptance and low thermal emittance as the radiative losses are proportional to the 4th power of temperature. The other most important requirement, however, is that the compositional stability should be very high at high operating temperatures (>400 deg. C). Due of these stringent requirements, there is a need to develop newer absorber coatings for solar power generation applications. Spectrally selective coatings, which are stable up to temperatures ~400 deg. C (in air and vacuum), have been developed in the past. However, in order to increase the efficiency of solar thermal power plants, solar selective coatings with high thermal stability are required. In recent years, great advances have been made in the field of nanostructured solar selective coatings with high solar absorptance and low thermal emittance at higher temperatures (T >450 deg. C). Amongst these, nanostructured transition metal nitride, oxide and carbide based tandem absorbers have emerged as novel high temperature solar selective coatings, which can be used for solar thermal power plants for electricity generation. Research is currently underway to increase the thermal stability of the coatings and to subsequently improve the efficiency of solar thermal power plants. This talk will present an overview of the sputter deposited mid- to high-temperature solar selective coatings used for solar thermal applications. It will address the usage of novel new generation 1D and 2D carbon- based nanostructures as selective absorbers along with the protocols for service life prediction of various spectrally selective coatings. The presentation will also describe in detail commercially available sputter deposited solar selective coatings for solar thermal power generation applications.

8:30 AM EN05.07.02
Supercooled Sugar Alcohols Stabilized by Alkali Hydroxides for Long-Term Room-Temperature Phase Change Solar-Thermal Energy Storage
Xiaoxiang Li; Shanghai Jiao Tong University, China

Seasonal thermal energy storage within organic phase change materials (PCMs) offers a promising way to solve intermittency of renewable energy, but the charged PCMs tend to undergo spontaneous crystallization and lose the stored latent heat to cold environment during storage. Herein, we report introduction of alkali hydroxides into sugar alcohols to increase the activation energy barrier for liquid-to-solid phase transition and stabilize the supercooling state, thereby realizing long-term phase change thermal energy storage. Owing to increased intermolecular hydrogen bonding interaction, the charged composites can maintain the supercooled state and conserve latent heat (~200 J/g) during storage at room temperature or extremely cold temperatures for months. Further compounding with polydopamine organic pigments, the composites demonstrate high solar absorptance (~91.6 %) and thus enable seasonable storage of solar-thermal energy as latent heat at room temperature. The stored heat can be readily released through adding seed crystals or applying mechanical deformation, which triggers cold crystallization of the supercooled composites and releases latent heat within a suitable temperature range of 40–60 °C. Such phase change composites not only eliminate complicated thermal insulation engineering required in conventional long-term thermal storage processes, but also unlock diverse application opportunities for thermal energy systems.

8:45 AM EN05.07.04
Sustainable Textiles Dying Process using Solar Thermal Energy Sameer Rahatekar[1], Syamala Jayanth Reddy[1] and Vishal Sardeshpande[2]; [1]Cranfield University, United Kingdom; [2]Sarvaay Solutions Ltd, India

The textile industry is one of the largest industries both in production and economically in the world. However, the textiles industry has two major challenges, first, it uses toxic dyes which cause significant river pollution, and second, it uses the water heating process during dying which consumes a lot of energy (typically non-renewable energy). Our current research was focused on addressing these two challenges. To address the challenge of the use of non-renewable energy for the textile dying process, we are using concentrated solar thermal energy to heat water between 70 to 90°C for textiles dying. To address the challenge of reducing pollution during textile dying, we used low-toxicity and sustainable dyes. The initial results indicated that the solar thermal heating process can be successfully used for dying textiles and fibers in a range of textile dyes. The tensile testing of the dyed fabrics showed that there was no damage to the fabric due to the solar thermal dying process. Similarly, Scanning Electron Microscopy analysis showed no damage to the textile fibres due to the solar thermal dying process. Our solar thermal heating process can potentially be scaled up for industrial use for sustainable textiles dying to help reduce carbon emissions from the textiles and the fashion industry.

SYMPOSIUM

April 11 - April 25, 2023

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SESSION EN06.01: Inorganic Solid Electrolyte I
Session Chairs: Valentina Lacivita and Jinhyuk Lee
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2006

10:30 AM *EN06.01.01
Anode Interlayers and Composite Cathodes at Low Stack-Pressures in All-Solid-State Batteries Dominic S. Jolly, Xiangwen Gao, Varnika Agarwal and Peter Bruce; University of Oxford, United Kingdom

Lithium-free so-called anodeless solid-state batteries are attractive for manufacturing. However, at charge rates on the order of 1 mA cm^{-2} and above, plating of Li at the current collector/solid electrolyte interface can be inhomogeneous, and dendrites (filaments of Li metal) are observed to penetrate through the solid electrolyte resulting in cell failure. Recent work has suggested that introduction of an interlayer between the solid electrolyte and current collector can protect the solid electrolyte against dendrite growth whilst promoting more homogeneous deposition of Li metal. We investigate a carbon-based interlayer, revealing the structural changes within the interlayer and Li deposition behaviour during the processes of charge and discharge. We identify the origin of the failure of the interlayer at high rates.

It is a practical requirement that solid-state batteries operate under low stack pressures (≤ 2MPa), presenting challenges for performance including of the composite cathode. We investigate a composite cathode composed of a solid electrolyte, NMC811 active material, and carbon nanofibers at low stack pressures.

11:00 AM *EN06.01.02
Highly Cyclable Deposition-type Li Metal Anode For All-Solid-State Li Batteries Naoki Suzuki, Nobuyoshi Yashiro and Ryo Omoda; Samsung R&D Institute Japan, Japan

Lithium-ion batteries (LIBs) are currently used to power a wide range of portable devices and, in particular, a number of pure electric and plug-in hybrid vehicles. As the capacity of a graphite anode conventionally used in LIBs is approaching its theoretical limit, the use of Li metal anode is receiving serious attention.
Currently there are two major difficulties in using Li metal anode in a conventional lithium-ion battery: dendrite formation and low coulombic efficiency (CE). Although several approaches have been reported to mitigate Li dendrite formation, the phenomenon has not been sufficiently avoided so far. The low CE is induced by not only the dendritic growth of the Li metal, but also the subsequent destruction and rebuild of the SEI layer according to the cycle. The currently reported CE of the Li metal anode is ~99% at most, and it requires a large amount of Li reservoir, leading to the decrease of the energy density and the consumption of the electrolyte.
To overcome these difficulties, we use a deposition-type Li metal anode in an all-solid-state battery (ASSB). Since no SEI forms on the anode in an ASSB, high CE is anticipated. The existing challenge is that the short circuit cannot be prevented even by using a solid electrolyte (SE), because Li-metal is known to grow on the surface of the SE grains and propagates through the grain boundaries.
In this study, we found that such a short circuit phenomenon is largely inhibited by using a metal foil coated with carbon black (CB) as a substrate for the Li deposition. The CB electrochemically reacts with Li, but we set the capacity of the CB layer much smaller than that of the cathode, and hence a large part of the Li ions are to precipitate as Li metal on the anode during the charge, and works as a Li metal anode.
We fabricated the ASSB in the following way. First, we made a slurry of carbon black by mixing it with a PVdF binder in NMP, and coated it on a Ni foil. The SE layer was made from Argyrodite-type Li_6PS_5Cl powders spread over non-woven cloth, and the cathode sheet was made from the mixture of NCM, Argyrodite SE, conductive agent and PTFE binder. They were stacked and enclosed in a pouch cell, comprising an all-solid-state battery.
This CB-based anode effectively suppressed short circuit of the cell, and an ASSB with this anode showed an excellent cycle property of over 150 cycles at 0.5 mA/cm^2 (0.1C) with good capacity retention. From measurements involving cross-sectional scanning electron microscopy, deposited Li metal layer was observed at the CB/Ni interface.
It was also found that the addition of metal particles in the CB-based anode drastically improves cell performance by extending the cycle life. An ASSB with an Ag/CB-based anode is operated over 700 cycles at 3 mA/cm^2 current density (0.5 C) with a capacity retention of ~86% after 700 cycles.

11:30 AM EN06.01.03
Control of Ionic Conductivity by Lithium Distribution in the Cubic Oxide Argyrodites $Li_{6+x}P_{1-x}Si_xO_5Cl$ Alexandra Morscher, Benjamin Duff, Guopeng Han, Luke Daniels, Yun Dang, Marco Zanella, Manel Sonni, Ahmad Malik, Matthew Dyer, Ruiyong Chen, Frederic Blanc, John Claridge and Matthew Rosseinsky; University of Liverpool, United Kingdom

Current battery technology used in electric vehicles could soon reach its physicochemical limit and alternative ‘next generation batteries’ are needed to further increase energy density. By replacing the liquid electrolyte with a solid, All Solid-State Batteries (ASSBs) could provide increased energy densities whilst addressing the safety concerns related to the current use of flammable liquid electrolytes.[1]

The discovery of novel solid electrolyte materials with lithium ion conductivities suitable for application remains one of the main challenges in the commercialisation of ASSBs. Recently, argyrodite materials have attracted attention by displaying superionic Li ion conductivity; *i.e.* $Li_{6+x}Si_xSb_{1-x}O_5Cl$ ($x = 0.6$, 14.8×10^{-3} S cm^{-1}).[2] These superionic argyrodites crystallise in Li site disordered (*F*-43*m*) structures in which the precise control of Li distribution and disorder is crucial in determining their ionic conductivities. However, all highly conductive argyrodites are sulphides and suffer from poor stability to air and moisture and their electrochemical stability against Li metal is limited. Oxide argyrodites could provide a solution to these stability issues. However, the only two reported oxide argyrodites, Li_6PO_5X (X = Cl, Br)[3] and $Li_6SiO_4Cl_2$[4], adopt Li site ordered structures which results in ionic conductivities of ~10^{-9} S cm^{-1} that are below usable levels.

We present a newly discovered cubic Li-rich (where Li content is >6) oxide argyrodite, Li_7SiO_5C, that crystallises with an ordered cubic ($P2_13$) structure at room temperature, undergoing a transition at 473 K to a Li site disordered *F-43m* structure, consistent with the symmetry adopted by superionic sulphide argyrodites. Four different Li tetrahedral sites are occupied in Li_7SiO_5Cl: T5, T5a, T3, and T4. Most sulphide Li argyrodites contain Li on T5 and/or T5a sites and only few materials have been reported with additional occupancy of T2 and T3 or T2 and T4 sites. This is the first time such a simultaneous site combination (T5, T5a T4 and T3) sites has been reported in Li argyrodite materials.

This disordered *F-43m* structure can be stabilised to room temperature via substitution of Si^{4+} with P^{5+} in the $Li_{6+x}P_{1-x}Si_xO_5Cl$ ($0.3 < x < 0.85$) solid solution, which retains the same combination of occupied Li sites. The observed variation of ionic conductivity with composition in $Li_{6+x}P_{1-x}Si_xO_5Cl$ is directly connected to structural changes occurring within the Li sublattice which are characterised by diffraction and NMR methods. These structural changes are closely linked to the distribution of Li over the available sites giving rise to a unique composition-structure-property relationship within the new $Li_{6+x}P_{1-x}Si_xO_5Cl$.

The delocalisation of Li sites through occupation of T3 and T4 sites leads to a maximum room temperature ionic conductivity of $1.82(1) \times 10^{-6}$ S cm^{-1} at $x = 0.75$, which is three orders of magnitude higher than any other oxide argyrodite. These materials present superior atmospheric stability over analogous sulphide argyrodites significantly facilitating ease of handling.

The ability to control the ionic conductivity through structure and composition emphasises the advances that can be made with further research in the underexplored field of oxide argyrodite materials. This talk will describe the synthesis, characterisation and properties of these new materials, providing a complete explanation of how composition control of structure determines ionic conductivity in $Li_{6+x}P_{1-x}Si_xO_5Cl$.

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SESSION EN06.02: Inorganic Solid Electrolyte II
Session Chairs: Santosh KC and Valentina Lacivita
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2006

1:30 PM *EN06.02.01
Lithium-Alloy Anodes in Solid-State Batteries Mauro Pasta; University of Oxford, United Kingdom

The lithium metal anode limits solid-state cell performance because of its intrinsic properties including diffusion kinetics [1], mechanical properties [2], and surface chemistry [3]. Lithium-rich alloys have been proposed as a potential route to address these issues [4,5,6]. Nonetheless, there is little understanding of the impact of alloying on physical properties, electrochemical performance, and especially the link between the two. In my talk I will present an investigation framework to synthesise alloys, quantify fundamental material properties, measure key electrochemical performance metrics, and characterise cells after cycling using the Li-Mg binary system as a model. We intend this framework to be applicable to multiphase alloys going forward, enabling the rapid development of alloy anodes to overcome the challenges in solid-state battery development.

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2:00 PM EN06.02.02
Solution-Processed Non-Crystalline Solid Electrolytes for Advanced Energy Storage Alex Rettie; University College London, United Kingdom

Advanced batteries containing a Li metal anode (LMA) are needed to enable the clean economy and meet ambitious climate targets. Currently, LMA batteries are limited by dendrite propagation due to the non-uniform plating and stripping of Li, which is detrimental to cell performance. The non-crystalline solid electrolyte (SE), lithium phosphorus oxynitride (LiPON) is unique in demonstrating stable Li plating/stripping at appreciable rates, but its synthesis requires costly and slow vacuum deposition methods. We use aqueous precursor solutions which are rapidly condensed during spin coating and gently annealed to produce dense, flat, Li metal oxide films without long-range order. However, such solution-processed SEs typically exhibit ionic conductivities (σ_{ion}) too low for energy storage applications (~10^{-8} S cm^{-1}) and far lower than vacuum-deposited LiPON (~10^{-6} S cm^{-1}).

We will discuss various approaches to increase the σ_{ion} of these non-crystalline Li-containing oxide films, including compositional engineering and controlled processing conditions. Structure-property relationships have been elucidated using pair-distribution-function (PDF) analysis of grazing incidence X-ray total scattering data and interphase formation against Li evaluated by time-dependent electrochemical impedance spectroscopy and in situ X-ray photoelectron spectroscopy. Electrochemical testing of these films deposited onto a current collector in an anode-free cell will be used to evaluate their ability to facilitate stable deposition and stripping of Li.

Initial exploration of processing parameters have yielded σ_{ion} values > 10^{-7} S cm^{-1} [1] and the presence of medium-range order (nanocrystalline domains) in some compositions. As only limited chemical compositions and processing conditions of these glassy SEs have been reported, with no corresponding structural studies, our work provides insight to enable the optimisation and discovery of scalable glassy SEs for advanced batteries.

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crystalline solid electrolytes for Li metal batteries. Under review at *Chemistry of Materials*, **2022**. ChemrXiv Preprint: https://doi.org/10.26434/chemrxiv-2022-hwxhv

2:15 PM EN06.02.03
Origins of the Ionic Conductivity in Amorphous Lithium Phosphorus Oxynitride (LiPON) Solid Electrolytes Rafael B. Nuernberg[1], Annie-Kim Landry[2,1], Racha Bayzou[1], Anass Benayad[2], Olivier Lafon[1], Brigitte Pecquenard Le Cras[1] and Frédéric Le Cras[2,1]; [1]CNRS, France; [2]CEA, France

Lithium phosphorous oxynitride ion-conducting glasses, prepared by radio-frequency magnetron sputtering, were a key constituent for the first all-solid-state (thin film) lithium batteries on the market, thanks to a particular combination of properties. Indeed, this solid electrolyte is compatible with both high voltage cathodes and the lithium metal anode, has negligible electronic conductivity and a good ionic conductivity. In the context of the development of new all-solid-state systems, it can now become a useful tool used to mitigate interfacial electrode/electrolyte reactivity. The origins of its outstanding ionic conductivity compared to their crystalline counterparts as well as the interplay between structure and ionic transport in this electrolyte has remained so far somewhat elusive. In this study, we have applied for the first time to this class of materials a methodology based on impedance spectroscopy (EIS) analyses to isolate the distinct energetic contributions to the ionic conduction process namely, the enthalpies for defect formation and migration. The variation of these enthalpies as a function of the nitrogen content is correlated with structural aspects unveiled by Solid-State Nuclear Magnetic Resonance (SS-NMR) and X-ray Photoelectron Spectroscopy (XPS) depth profiling. Our results indicate that the amorphous structure generates a striking decrease of the enthalpy related to defect formation, while the nitrogen incorporation in the material tends to decrease the enthalpy of migration.

2:30 PM EN06.02.04
Intermediate-Stage Sintered LLZO Scaffolds for Li-Garnet Solid-State Batteries Faruk Okur[1,2], Huanyu Zhang[1,2], Kostiantyn Kravchyk[1,2] and Maksym V. Kovalenko[1,2]; [1]ETH Zurich, Switzerland; [2]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The quest for non-flammable and high-energy-density electrochemical energy storage systems has led to a surge of reports on novel batteries based on garnet-type LLZO solid-state electrolyte. LLZO*, inter alia*, is appealing because of its high thermal stability, high Li-ion conductivity, and wide electrochemical window of 0-6 V *vs*. Li^+/Li, which allows direct use of metallic Li as a negative electrode.[1, 2] While significant progress has been achieved in the field of Li-garnet solid state batteries, their further development, however, is hindered by the formation of cavities (Kirkendal voids) at the LLZO/Li interface at practically relevant current densities and areal capacities exceeding 1 mA cm^{-2} and 1 mAh cm^{-2}. As a result, the cells exhibit limited cycling stability due to the inhomogeneous distribution of the applied current density and therefore the formation of the Li dendrites. Another aspect, which is of high importance, is associated with the development of the fabrication methodology of thin LLZO electrolytes for achieving high energy density of Li-garnet solid-state batteries.[3, 4]
To contribute to these two challenging aspects, in this work, we present the facile intermediate-stage sintering method of thin (*ca*. 50 μm) and porous (*ca*. 40% of open porosity) LLZO membranes with mean pore size of 2.5 μm. The employment of such porous LLZO membranes not only provides an effective means of mitigating the formation of voids at the LLZO/Li interface due to the increased LLZO/Li surface area, but also enables to maximize achievable energy densities. We demonstrate that fabricated porous LLZO membranes measured in Li/LLZO/Li symmetrical cell configuration exhibit a high critical current density of up to 1.15 mA cm^{-2} and demonstrate long cycling stability of over 1480 h at current density of 0.5 mA cm^{-2} with areal capacity limitation of 0.1 mAh cm^{-2}.

2:45 PM EN06.02.05
Unlocking the Hidden Chemical Space in Cubic Phase Garnet Solid Electrolyte for Long-Term Stable Solid-State Batteries Sung-Kyun Jung[1,2], Hyeokjo Gwon[2], Hyungsub Kim[3], Gabin Yoon[2], Dongki Shin[4], Jihyun Hong[4], Changhoon Jung[2] and Jusik Kim[2]; [1]Ulsan National Institute of Science and Technology (UNIST), Korea (the Republic of); [2]Samsung Advanced Institute of Technology, Korea (the Republic of); [3]Korea Atomic Energy Research Institute, Korea (the Republic of); [4]Korea Institute of Science and Technology, Korea (the Republic of)

Solid-state batteries (SSBs) are attracting considerable attention as energy-storage devices for electric vehicles owing to their high safety and potential high volumetric energy density compared to conventional lithium-ion batteries. All these advantages of SSBs are attributed to the development of solid electrolytes, and among solid electrolytes, oxide-based garnet ($Li_7La_3Zr_2O_{12}$, LLZO) is regarded as a promising candidate owing to its high reduction stability against lithium metal in comparison to alternative solid electrolytes (sulfides or halides). However, cubic phase stabilization between two polymorphs of cubic (10^{-4}~10^{-3} S/cm) and tetragonal phases (10^{-7}~10^{-6} S/cm) is essential to achieve high ionic conductivity up to ~10^{-4} S/cm. In particular, the tetragonal phase is thermodynamically more stable than the cubic phase at high concentration of lithium in the garnet (Li≈7) owing to the Li–Li repulsion. The critical vacancy concentration to stabilize enthalpy formation energy of cubic phase has been revealed theoretically and experimentally as $n_{c,vac}$=0.4–0.5. It is generally believed that the formation of Li-vacancy is inevitable for stabilizing the cubic phase so far, therefore, most of the Li-vacancy formation has been introduced by aliovalent substitution in Li ($Li_{7-3x}M_xLa_3Zr_2O_{12}$, M=Al, Ga) or Zr site ($Li_{7-x}La_3Zr_{2-x}M_xO_{12}$, M=Nb, Ta) to surpass the instability of cubic phase by alleviating the Li–Li repulsion.
Here, we successfully stabilized the cubic-phase without vacancy formation at a maintained Li composition of Li = 7 in the garnet for the first time by incorporating various dopants (Hf, Sn, Sc, and Ta) in the Zr site, considering the defect formation energy, site-exchange energy, and charge balance, unlike that in the conventional strategy. Unexpectedly, this cubic phase is stabilized by increased entropy-driven by not the phonon vibrational or configurational entropy that is usually shown in high entropy alloy, but the other entropy such as electronic entropy or electronic configurational entropy. We revealed the effect of lithium/vacancy concentration on structure and ionic conductivity by exploring hidden chemical space (Li>6.6). More specifically, this entropy-driven stabilization exhibited the lowest nucleation temperature of cubic-phase garnet as 400 °C in the solid-state reaction implying potential applicability in practically required low-temperature processing for cost-effective SSBs manufacturing.
Conventional vacancy-driven cubic phase stabilization of garnet is vulnerable against Li metal in terms of reduction stability. The cubic-phase garnet derived from the Li-vacancy formation suffered the inevitable phase transformation to the tetragonal phase at the Li/garnet interface owing to the reduced vacancy concentration below the critical value ($n_{c,vac}$<0.4–0.5) that resulted from the thermodynamic driving force for metal reduction and the lithiation into the garnet structure. Moreover, the metal reduction and the phase transformation from the cubic to tetragonal phase induced sluggish kinetics of the Li transport by increasing the interfacial resistance at Li/Garnet interface. However, our entropy-driven stabilized cubic-phase with high lithium contents (Li=7) exhibited superior reduction stability in kinetics aspect compared to that stabilized by vacancy formation (Li=6.6, $n_{c,vac}$=0.4). Compared to the vacancy-driven cubic phase, the entropy-driven cubic phase displayed a tenth of the reduction kinetic constant for Li metal owing to the high chemical potential of lithium in the cubic phase. Consequently, the SSBs developed using our designed garnet electrolyte delivered remarkable long-term cycle performance with 92% capacity retention after 700 cycles, with high areal capacity of 2.92 mAh/cm^2 at 60 °C. Our discovery can provide an intuition for designing the cubic-phase garnet solid electrolyte with high reduction stability against Li metal for long-term stable SSBs.

3:00 PM BREAK

3:30 PM *EN06.02.06
Understanding and Rational Design of Super-Ionic Conductors by First-Principles Computation and Machine Learning Yifei Mo; University of

Maryland, United States

Super-ionic conductors exhibit exceptionally high ionic conductivities and are highly desired as solid electrolytes or electrodes for energy applications such as batteries and fuel cells. However, while multiple ion-conduction mechanisms are proposed for super-ionic conductor materials, the fast ion-conduction mechanisms are still not fully understood, impeding the capability to rationally design these materials. In this presentation, we will illustrate how we combine atomistic modelling, machine learning, and physics analytics to provide an enhanced understanding of the super-ionic conductors and to rationally design new super-ionic conductor materials, using a number of emerging or newly discovered materials systems as examples. We will demonstrate that the combination of atomistic modelling and machine learning extend and empower conventional physics analytics for unravelling fundamental mechanisms and for guiding material design.

4:00 PM EN06.02.07
Bridging the gap between experiment and computation in LGPS solid electrolyte with machine-learning potentials Gavin Winter and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States

$Li_{10}Ge(PS_6)_2$ (LGPS) is a highly concentrated solid electrolyte, and the Coulomb repulsion between neighboring cations has been hypothesized as the underlying reason for concerted ion hopping, a mechanism common among superionic conductors such as $Li_7La_3Zr_2O_{12}$ (LLZO) and $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP). While first principles simulations using molecular dynamics (MD) provide insight into the Li^+ transport mechanism, historically, there has been a gap in the temperature ranges studied in simulations and experiments. Here, we used a neural network (NN) potential trained on density functional theory simulations, to run up to 40-nanosecond long MD simulations to characterize the ion conduction mechanisms across a range of temperatures that includes previous simulations and experimental studies. We have confirmed a Li^+ sublattice phase transition in LGPS around 400 K, below which the *ab*-plane diffusivity D^*_{ab} is drastically reduced. Concomitant with the sublattice phase transition near 400 K, there is less cation-cation (cross) correlation, as characterized by Haven ratios closer to 1, and the vibrations in the system are more harmonic at lower temperature. Intuitively, at high temperature, the collection of vibrational modes may be sufficient to drive concerted ion hops. However, near room temperature, the vibrational modes available may be insufficient to overcome electrostatic repulsion, thus resulting in less correlated ion motion and comparatively slower ion conduction. Such phenomena of a sublattice phase transition, below which concerted hopping plays a less significant role, may be extended to other highly concentrated solid electrolytes such as LLZO.

4:15 PM EN06.02.08
Understanding Ion Transport and Electrochemical Stability of Sulfide-Based Solid Sodium Electrolytes Varun Shreyas, Sabina Chertmanova, Selim Halacoglu, Hui Wang and Badri Narayanan; University of Louisville, United States

Solid-state sodium (Na) batteries (SSSBs) using sulfide-based solid electrolytes (SEs) has been attracting a lot of attention due to their high theoretical specific capacity, enhanced safety, and abundant resources. Especially, Na_3SbS_4 shows tremendous potential as a SE owing to its good Na^+ ion conductivity of ~1 – 3 mS cm^{-1}. Despite its promise, electrochemical performance of SSSBs based on Na_3SbS_4 SE remain far from commercialization. The major roadblock thwarting progress in SSSBs is the lack of fundamental understanding of atomic-scale mechanisms underlying (a) interfacial reactions with Na anode, and (b) Na^+ ion conduction (especially in the presence of dopants). Here, we employ ab initio molecular dynamics (AIMD) simulations to identify key reactions occurring at the $Na|Na_3SbS_4$ interface. Our AIMD simulations indicate that addition of an ionic liquid interlayer results in a stable solid-electrolyte-interphase (SEI) composed mainly of NaF, in excellent agreement with our synthesis and characterization experiments. Similarly, our DFT studies show that Se doping increases the electrochemical stability window of Na_3SbS_4. In terms of Na^+ conduction, we employ AIMD simulations, and nudged elastic band calculations to understand the effect of (a) valence, and (b) size of cation dopants that partially replace Na in Na_3SbS_4. These cations introduce charge compensating Na-vacancies in the SSE, which in turn, enhance Na^+ ion conduction. However, size of the cation dopant has a profound impact on the extent of increase in Na^+ ion conductivity. For instance, Ca-doped Na_3SbS_4 ($Na_{2.75}Ca_{0.125}SbS_4$) showed Na^+ conductivity of ~10 times that of pristine Na_3SbS_4 (r_{Ca}2+ / r_{Na}+ = 0.98). On the other hand, larger Ba^{2+} as dopant (r_{Ba}2+ / r_{Na}+ = 1.35) in $Na_{2.75}Ba_{0.125}SbS_4$ hinders Na-ion hops owing to local strain, thereby, yielding a Na^+ conductivity ~5 times that of Na_3SbS_4.We will discuss these findings in the context of developing solid-state electrolytes for emerging SSSBs.

4:30 PM EN06.02.09
"Dirt Cheap" Electrolytes for Solid-State Energy Storage Erik D. Spoerke[1], Stephen Percival[1], Martha Gross[1], Leo J. Small[1], Amanda Peretti[1], Ryan C. Hill[2] and Yang-Tse Cheng[2]; [1]Sandia National Laboratories, United States; [2]University of Kentucky, United States

Identifying cost-effective, solid state electrolytes with high ionic conductivity at ambient temperatures would enable a growing number of electrochemical energy storage systems. Here, we describe a "dirt cheap" approach to developing solid state separators, utilizing sodium-based clays as easily-processed, highly-conductive ionic materials. Our clay-based system employs phyllosilicate minerals formed of crystalline sheets, regularly stacked, but separated by hydrated, nanoscale interlayer spacings. Populating these interlayer spaces are mobile, charge-compensating cations, such as sodium. We highlight the sodium ionic conductivity on the order of 0.1mS/cm at room temperature, and we investigate the key structural and chemical properties responsible for this impressive performance. We further assemble functional devices and investigate the feasibility of these materials as solid-state electrolytes for electrochemical storage, demonstrating and assessing ionic shuttling between electroactive electrodes during electrochemical cycling. These studies uncover untapped potential from these earth-abundant, low-cost, easily processed materials and their prospects as a new class of solid-state electrolytes. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

4:45 PM EN06.02.10
Coupling of Ionic Hopping and Anharmonic Phonon Dynamics in Superionic Conductors for Solid State Electrolytes Olivier Delaire, Jingxuan Ding, Mayanak Gupta and Hung-Min Lin; Duke University, United States

The design of new solid state electrolytes (SSEs) hinges on identifying and tuning relevant descriptors. While static structural descriptors have been correlated with fast diffusion, the host framework flexibility and vibrations and their complex dynamic coupling with mobile ions remain less studied. Phonons describe the atomic dynamics in crystalline materials and provide a basis to encode possible minimum energy pathways for ion migration but anharmonic effects can be large in SSEs. Identifying and controlling the pertinent phonon modes coupled most strongly with ionic conductivity, and assessing the role of anharmonicity, could therefore pave the way for discovering and designing new SSEs via phonon engineering. Here, we investigate phonons in Na3MX4 and their coupling to fast Na diffusion, using a combination of neutron sca6ering, ab-initio molecular dynamics (AIMD), and accelerated molecular dynamics based on machine-learned potentials. We identify anharmonic soft-modes of the high-temperature phase that play an important role as precursors to mobile Na hopping. We also show how these strongly anharmonic phonon modes enable Na-ions to hop along the minimum energy pathways. Further, the quasi-elastic neutron sca6ering measurements, supplemented with large-scale molecular dynamics simulations, probe the Na diffusion constant and the diffusion characteristics. These results offer detailed microscopic insights into the dynamic mechanism of fast Na diffusion and provide an avenue to search for further Na solid electrolytes. These results will also be contrasted with studies of coupled dynamics of anharmonic phonons and fast diffusion of mobile ions in other superionic systems.

SESSION EN06.03: Inorganic/Polymer Solid Electrolyte
Session Chairs: Ali Coskun and Naoki Suzuki
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2006

9:00 AM *EN06.03.02
Towards Solid State Zinc-Air Batteries—Enabling Bio-Based Polymer Gel Electrolytes Estíbaliz García-Gaitán[1,2,3], Maica Morant-Miñana[1], Domenico Frattini[1], Daniel Gonzalez[2], Igor Cantero[2] and Nagore Ortiz-Vitoriano[1,4]; [1]Centre for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Alava Technology Park, Albert Einstein 48, 01510, Spain; [2]CEGASA Energía SLU, Marie Curie, 1, Parque Tecnológico de Álava, 01510, Spain; [3]University of the Basque Country, Barrio Sarriena, s / n, 48940, Spain; [4]Ikerbasque, Basque Foundation for Science, María Díaz de Haro 3, 48013, Spain

Electrochemical energy storage technologies can help mitigate the dependency from fossil sources and greenhouse gas emissions, enabling energy storage from renewable sources and their integration into the grid, thus driving energy transition worldwide. Presently, the most commercialized technology is lithium-ion, from small portable devices to electric vehicles, and up to stationary applications at grid level. However, its use in stationary energy storage systems involves a great cost, being necessary to seek new highly competitive technologies at lower cost. Therefore, it is strategically not convenient to rely only on this technology to implement electrochemical energy storage, but few valid alternative candidates can be foreseen considering the electrochemical window and energy density. Zn-air secondary battery is one of these; however, affordable development based on industrially and quantitatively relevant breakthroughs is required.

Zn-air batteries based on liquid electrolyte have been widely investigated but due to the open nature of the technology (cell is open to air), electrolyte leaks and/or evaporates causing a decrease in the performance and subsequent cell failure. As a result, recent research has mainly focused on developing synthetic biodegradable polymer-based gel polymer electrolytes (GPEs) due to their low cost and affordability (e.g., alkaline GPEs such as polyvinyl alcohol (PVA), polyacrylic acid (PAA), polyacrylamide (PAM), polyethylene oxide (PEO)). Much of the early, but also recent, work in metal air batteries (especially in Zn and Na air batteries) has been devoted to the study of biopolymer-based membranes, that act as separators and electrolytes to substitute liquid electrolytes.

In this work, the development of an emerging solid electrolyte, based on a natural, linear, and biodegradable polymer will be presented. The biopolymer is directly jelled in the liquid electrolyte solution to for a stable gel, that not only presents outstanding ionic conductivity, (same magnitude order as 8M KOH solution liquid electrolyte) but also mechanical stability, even after being subjected to a constant discharge until battery failure. The gel does not liquefy, and behaves as an elastic material till up to a certain applied compression load. In this study, its manufacture, mechanical characterization and electrochemical performance will be discussed.

9:30 AM EN06.03.04
Ultrafast-Sintered Self-Standing LLZO Membranes for High Energy Density Li-Garnet Solid-State Batteries Huanyu Zhang[1,2], Faruk Okur[1,2], Kostiantyn Kravchyk[1,2] and Maksym V. Kovalenko[1,2]; [1]ETH Zürich, Switzerland; [2]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Towards building non-flammable and temperature-tolerant Li-ion batteries with high energy density, $Li_7La_3Zr_2O_{12}$ (LLZO) has recently attracted considerable attention as a compelling solid-state Li-ion electrolyte (SSE) due to its high thermal stability, Li-ion conductivity of up to 1 mS cm^{-1} (RT), and a wide electrochemical operation window of 0–6 V *vs*. Li$^+$/Li.[1, 2] Additionally, unlike other Li-ion soft solid conductors such as those based on sulfides, LLZO SSE can be manufactured with a bilayer dense-porous microstructure, which prevents the issues of dynamic volume change of the Li anode and the formation of voids at the Li/SSE interface during cycling and thus eliminates the need for external pressure.[3, 4] Here we report a facile, ultrafast sintering methodology for the fabrication of LLZO solid-state electrolyte in the form of self-standing bilayer dense-porous LLZO membranes. The thickness of the produced dense and porous layers was *ca*. 8 µm and 55 µm, which hypothetically allows to achieve high gravimetric and volumetric energy densities of Li-garnet batteries of 202 Wh kg^{-1} and 715 Wh L^{-1} (in combination with an NMC111/LiFSI-Pyr$_{13}$FSI cathode). Electrochemical measurements confirmed that produced LLZO membranes possess high critical current density up to 1.7 mA cm^{-2} and cycling stability of over 45 cycles at a current density of 0.1 mA cm^{-2}.

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9:45 AM BREAK

10:15 AM *EN06.03.05
NMR Insights into Ion Conduction in Chloride Solid Electrolytes and Polymer Electrolytes Raphaële Clément; University of California, Santa Barbara, United States

Nuclear magnetic resonance (NMR) spectroscopy provides detailed insights into the working principles of ionic and mixed conductors used in rechargeable battery applications. Notably, NMR is sensitive to crystalline, disordered or even amorphous phases that arise during electrochemical cycling, and can provide atomic-level structural information, as well as insights into the dynamics of ion motion. In this talk, I will present our recent work on Li-ion and Na-ion conducting rocksalt halides [1, 2] and Li-conducting polymeric ionic liquids [2]. Using a combination of synchrotron X-ray diffraction/scattering, electrochemical impedance spectroscopy (EIS), solid-state NMR, pulsed field gradient NMR (PFG-NMR), NMR relaxometry, and first principles calculations, we provide a multiscale understanding of ion diffusion processes and link these findings to local structure features, crystallinity, and materials synthesis/processing conditions.

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10:45 AM EN06.03.06
Polyethylene Oxide/$\mathrm{Na_{3.2}Ca_{0.1}Zr_{1.9}Si_2PO_{12}}$ as Gel Electrolyte for Quasi-solid-state Sodium-ion Batteries Hao-Yu Liu, Chia-Ching Lin and Han-Yi Chen; National Tsing Hua University, Taiwan

Recently, solid-state sodium-ion batteries (SSSIBs) have attracted wide attention as a choice for next-generation energy storage systems owing to several advantages. Firstly, the low cost of sodium metal and aluminum current collectors makes SIBs a prospective alternative for large-scale industrial use. Secondly, solid electrolytes possess high thermal stability, wide electrochemical window, and high mechanical strength which can suppress dendrite growth. However, high interface resistance between the solid electrolyte and electrode and low ionic conductivity limit the performance of SSSIBs. Hence, developing a gel electrolyte with low contact resistance and high ionic conductivity is the key to enabling the practical application of next-generation SIBs. In this work, a calcium-doped NASICON-type solid electrolyte, $\mathrm{Na_{3.2}Ca_{0.1}Zr_{1.9}Si_2PO_{12}}$ (NCZSP) was synthesized by a sol-gel method. Then, solvent casting was used to prepare a polyethylene oxide (PEO)/NCZSP film. The PEO/NCZSP gel electrolyte achieved high ionic conductivity of approximately 6×10^{-4} S $\mathrm{cm^{-1}}$ (n = 10) at room temperature. After, quasi-solid-state SIBs were assembled and tested with a high-entropy layered oxide (HEO) as cathode and sodium metal as anode under room temperature. The HEO||PEO/NCZSP||Na cells exhibited excellent electrochemical performance with a high discharge capacity of approximately 120 mAh $\mathrm{g^{-1}}$ under the current density of 0.1C and good retention of 78% after 100 cycles, demonstrating that PEO/NCZSP has a good potential as a gel electrolyte for SIBs.

11:00 AM EN06.03.07
An Experimental Technique for Directly Measuring Ultrafast Ion Hopping and its Inherent Correlations Kim Pham, Kimberly See and Scott K. Cushing; Caltech, United States

Ion hopping times can reach the picosecond timescales in superionic conductors and are a complex interplay of ion-phonon, ion-electron, and ion-ion correlations. In this presentation, we present a new experimental technique that can directly measure ultrafast ion hopping on its inherent timescale. As a result, the relative contributions of the different correlations to the many-body ion hopping Hamiltonian are determined. The technique sweeps a broad-frequency range laser from the UV to THz to perturb AC impedance measurements in the grain boundary and bulk ion hopping regimes. High GHz conduction traces measure the picoseconds change in the ion hopping following the perturbation. With proper renormalization, the changes give the relative ion-electron and ion-phonon coupling terms. We demonstrate the technique on $\mathrm{Li_{0.5}La_{0.5}TiO_3}$ (LLTO). For this material, we measure that the dominant ion hopping route is through a THz rocking mode (matching theoretical predictions). The relative role of ion-electron correlations relative to the ion-phonon correlations is also measured. Finally, we discuss how in the future the technique can be extended to measure ion-ion correlations.

11:15 AM EN06.03.08
Computational Study of Mechanism of Fast Ionic Transport in $\mathrm{Li_3YCl_6}$ (LYC): Role of Anharmonicity & Host Dynamics Ballal Ahammed and Elif Ertekin; University of Illinois at Urbana Champaign, United States

Understanding the mechanisms of ionic transport in solid electrolytes (SEs) is key to further tailoring their ionic conductivity and finding accurate descriptors for high throughput predictions. The link between vibrational dynamics and ionic diffusion offers a promising avenue to explore ion transport beyond static structural descriptors. However, strong anharmonic effects in SEs suggest the potential breakdown of the harmonic phonon picture and the importance of anharmonicity for facile ion migration. In this study, we investigate the role of vibrational modes, soft bonding, and strong anharmonicity in lithium ion migration in $\mathrm{Li_3YCl_6}$ (LYC), a halide lithium ion conductor that has gained interest for its wide electrochemical stability window, low electronic conductivity, and good stability towards oxide cathodes. The crystal structure of LYC is characterized by a rigid hexagonal close packed anion sublattice and a flexible disordered cation sub-lattice. We use a combination of ab initio molecular dynamics (AIMD), lattice dynamics, and nudged elastic band (NEB) methods to reveal strong lattice anharmonicity and vibrational coupling between the modes of the mobile and rigid sub-lattices. Ab initio molecular dynamics (AIMD) simulations are performed over different temperatures in order to understand the diffusive dynamics. By quantifying the similarities between phonon eigenvectors and AIMD trajectories, soft phonon modes that may be associated with lithium diffusion are identified. The anharmonic nature of these phonon modes is confirmed by mapping the potential energy surface. We demonstrate how the lithium dominated anharmonic modes enables in-plane lithium hopping while large amplitude in-plane motion of the rigid sub-lattice assists out of plane lithium migration.

11:30 AM EN06.03.09
Sustainable Production of Metal Sulfide Nanocrystals for Electrochemical Storage Applications via Cascaded Metathesis William Smith, Saeed Ahmadi Vaselabadi and Colin A. Wolden; Colorado School of Mines, United States

Sulfide-based solid-state batteries are among the leading candidates to displace conventional lithium and sodium ion battery technologies. Metal sulfides ($\mathrm{Li_2S}$, $\mathrm{Na_2S}$, $\mathrm{SiS_2}$, $\mathrm{TiS_2}$, etc.) are critical precursors for both the solid state electrolytes and the conversion type cathodes employed in these devices. The high cost of these materials hinders development and deployment of these technologies. Their high cost reflects the high temperature carbothermal reduction and solid state synthesis techniques currently employed. Herein we describe the production of these materials employing room temperature, solution-based metathesis. In the first step $\mathrm{Li_2S}$ is produced through metathesis of two low-cost precursors – LiCl and $\mathrm{Na_2S}$ – at ambient temperature in an alcohol solution, with salt as a byproduct. Trace impurities in metathesis $\mathrm{Li_2S}$ introduced by side reactions with the solvent can be removed by a low temperature purification step that retains the desired nanocrystalline morphology. The quality of $\mathrm{Li_2S}$ was validated through the production of argyrodite ($\mathrm{Li_6PS_5Cl}$) solid state electrolytes with state-of-the-art conductivity (> 4 mS/cm). In the 1970s researchers at Exxon showed that $\mathrm{Li_2S}$ was a powerful reagent that can be used for the metathesis of transition metal sulfides ($\mathrm{MoS_2}$, $\mathrm{TiS_2}$ etc.), but practical implementation of this approach was limited by exorbitant cost and quality of the $\mathrm{Li_2S}$ precursor. These reactions are typically conducted in an aprotic solvent and driven by the precipitation of LiCl. Herein we couple these two reactions in a process we've named cascaded metathesis. The net reaction is $n\mathrm{Na_2S} + \mathrm{MCl_n} \rightarrow \mathrm{MS_n} + 2n\mathrm{NaCl}$. Both the lithium chloride intermediate and the solvents are recovered and recycled in a circular economy. We demonstrate this approach through the cascaded metathesis of $\mathrm{SiS_2}$, which to our knowledge is the first time metathesis has been used to synthesize this compound. It is shown that ethyl acetate is the preferred solvent for conducting this reaction and that the reactivity of metathesis derived Li_2S is superior to its commercial counterpart. Finally, the metathesis-derived SiS_2 and Li_2S were employed as precursors in the synthesis of a glassy electrolyte that exhibited a conductivity of 0.11 mS cm^{-1} at 30 °C with a low activation energy of 20.2 kJ mol^{-1}, validating the promise of this method to enable the synthesis of silicon-based sulfide electrolytes for solid-state lithium-ion batteries.

SESSION EN06.04/EN08.06: Joint Session: Solid State Batteries
Session Chairs: Haegyeom Kim, Cengiz Ozkan, Hui Wang and Hongli Zhu
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2006

1:30 PM *EN06.04/EN08.06.01
Lithium Metal Halide Solid Electrolytes for All-Solid-State Batteries Jürgen Janek[1] and Linda F. Nazar[2]; [1]Justus Liebig University, Germany; [2]University of Waterloo, Canada

All-solid-state batteries (ASSBs) have emerged as promising alternatives to conventional Li-ion batteries for electrical energy storage, owing to their anticipated enhanced safety and higher energy densities. ASSBs are founded on high performance superionic conducting solid electrolytes, where the search for new, advanced materials hinges on determining the factors that dictate facile Li-ion (or Na-ion) transport. Incorporating them into highly functional ASSBs, however, relies on mastering the interface of the solid electrolyte with the electrode materials. While there has been much focus on the relative stability of various solid electrolytes against lithium metal as the negative electrode, the cathode-electrolyte interface has received comparatively less attention.

A fundamental understanding of the interaction of the surface of cathode materials with solid electrolytes is crucial to design practical ASSBs. Although sulfides (i.e., thiophosphates) are widely explored, they lack electrochemical stability above ~ 2.7 V vs Li^+/Li, whereas a new class of lithium metal chloride (Li-M-Cl) solid electrolytes are receiving rapidly growing scrutiny owing to their very high oxidative stability (> 4.2 V) in combination with good ionic conductivity and ductility. Because Li-M-Cl electrolytes typically contain resource-limited metals (M) such as indium or rare earths, work has focused on substituting M with more abundant elements such as zirconium and iron. However, a unified understanding of the materials design principles for such substitutions is still lacking, both with respect to voltage stability and ion/electron transport. This presentation will explore both concepts. It will focus on examination of the dynamic evolution of the interphase (via a combination of theory and experiment, including *operando* impedance measurements) at different upper cutoff potentials and degrees of delithiation at the surface of Ni-rich NCM cathode particles. The cathode is coupled to a range of different Li-(M_1,M_2)-Cl catholytes to assess the role of the central metal and the contribution of partial electronic conductivity in determining both chemical stability and high voltage electrochemical stability. Finally, the effect of crystal structure (layered vs spinel, etc) on ion transport will be presented. Overall, this approach establishes a platform for the metrics that can be utilized to efficiently evaluate new halide SEs in SSB cells.

2:00 PM *EN06.04/EN08.06.02
Enabling High-Rate Lithium Metal Anodes by Tailored Structures and Interfaces Eric D. Wachsman; University of Maryland, United States

Oxide-based solid-state Li-batteries (SSLiBs) have the potential to be a transformational and intrinsically safe energy storage solution due to their non-flammable ceramic electrolyte that enables the use of high-capacity Li metal anodes and high voltage cathodes for higher energy density over a much wider operating temperature range. However, their progress has been limited due to electrode/electrolyte interfacial issues. In particular for Li-metal anodes concerns over dendrite formation/propagation and the requirement for elevated temperature and high stack pressure are still prevalent. To eliminate these concerns a rational design of tailored structures and interfaces in Li-metal anodes will be presented. In addition, progress toward full cells using these tailored structures and interfaces will be presented.

2:30 PM *EN06.04/EN08.06.03
Manufacturing Considerations for Solid-State Batteries based on LLZO Electrolytes Marca M. Doeff, Michael Tucker and Wooseok Go; Lawrence Berkeley National Laboratory, United States

Batteries based on LLZO (variants of $Li_7La_3ZrO_2$) are under consideration for vehicle applications based on promising characteristics such as high room temperature ionic conductivity (up to ~$5x10^{-4}$ S/cm) and good compatibility with metallic lithium. One of the biggest challenges is processing the material into battery components, including thin, dense films and porous scaffolds, which can be infiltrated with active electrode materials and conductive additives. Ideal processing techniques minimize cost, maximize throughput, can be scaled-up readily, and yield robust parts or devices that can withstand handling. For this talk, we will consider the pros and cons of various cell configurations, such as those utilizing thin (~20 um thick) dense LLZO separators with a secondary electrolyte on the cathode side, and bilayer (dense + porous LLZO) or trilayer (porous+dense+porous LLZO) arrangements.

SESSION EN06.05: Poster Session: Solid-State Electrolyte
Session Chairs: Haegyeom Kim and Jinhyuk Lee
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN06.05.02
High-entropy Garnet-type Oxide as Solid Electrolyte for All Solid-state Li-ion Batteries Chun Han Kuo, Ai-Yin Wang, Hao-Yu Liu and Han-Yi Chen; National Tsing Hua University, Taiwan

Li-ion batteries (LIBs) are well-known storage systems owing to their high energy density and long cycling life. However, the potential danger of explosion and fire poses a threat to the user safety of commercial production using LIBs. Therefore, more and more researchers devote themselves to developing all-solid-state Li-ion batteries (ASSLIBs). ASSLIBs are mainly composed of an anode, solid electrolyte, and cathode. The solid electrolyte is one of the key parts to determine the performance of an ASSLIB. Among several kinds of solid electrolyte materials, Garnet-type oxide solid electrolytes have been considerably researched because of their wide electrochemical window, good stability against Li, and high thermal stability.[1] The famous Ta-

doped $Li_7La_3Zr_2O_{12}$ was first reported by Li. et. al..[2] Despite the high ionic conductivity of $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ at 10^{-3} S cm^{-1}, the instability of structure due to the easily reaction with the air causes the decay of ionic conductivity.[3]
In our research, a multi-doped strategy was introduced to apply in garnet-type oxide, $Li_{7-a}La_3(ZrTaNbYW)_xO_{12}$ (LLZTNYWO), to improve the stability against ambient air. LLZTNYWO was successfully synthesized using a conventional solid-state method as a solid electrolyte for Li-ion batteries. With the multi-dopant in the crystal structure of garnet, the material exhibited high ionic conductivity and high air stability. The crystal structure and microstructure of LLZTNYWO was confirmed by X-ray diffraction, field-emission scanning electron microscope, energy dispersive spectroscopy, spherical-aberration corrected high-resolution transmission electron microscopy, and extended X-ray absorption fine structure. In addition, the electrochemical performances were investigated by electrochemical impedance spectroscopy analyses, cyclic voltammetry tests, and galvanostatic cycling tests. The results demonstrated that LLZTNYWO could form a single phase in the garnet structure and deliver high ionic conductivity, exhibiting a promising solid electrolyte in ASSLIBs.

References:

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5:00 PM EN06.05.03

Investigating Significant Bond Character Features in Superionic Metal Halides to Study Their Relationship with Cation Diffusivity Salma Ahmed; San Francisco State University, United States

Solid-state batteries have been a focus of much research because they are safer than batteries with organic electrolytes that are used commercially, but they are less conductive. This computational study focuses on the binary metal (Ag/Cu) halides to find the link between bonding character of the diffusive Ag or Cu with the halide static lattice and Ag/Cu conductivity. Maximally Localized Wannier Functions (MLWFs) are used to analyze the bond character (either polar covalent or ionic) of the system to see whether or not there are bond fluctuations between the mobile cation and the anion lattice. The bond character and diffusivity of the metal halides were analyzed in different crystal structures (alpha, beta, zinc-blende, rock-salt) and at different temperatures. The diffusion coefficient for the metal at each temperature was calculated using the mean squared displacement of the metal, and the diffusion coefficient at three temperatures was used to calculate the activation energy barrier of diffusion. Our calculated values followed experimental trends. The polarization for the halides and bond angle was determined using the MLWFs in order to analyze the abundance of polar covalent interactions and how it correlates to diffusivity. The angle and polarization distributions varied as the crystal structure, metal, or halide changed. These results point towards our hypothesis that bond character affects diffusivity. By systematically varying crystal structure and bonding interactions in superionic conductors, we can learn more about the interaction between the diffusion species and the anion lattice, and therefore better understand solid-state electrolytes.

5:00 PM EN06.05.04

Enhancing Ionic Conductivity by *In Situ* Formation of Li_7SiPS_8/Argyrodite Hybrid Solid Electrolytes Robert Calaminus[1,2], Sascha Harm[1,2], Douglas Fabini[1,3], Lucas Balzat[1,2], Anna-Katharina Hatz[1,2], Viola Duppel[1], Igor Moudrakovski[1] and Bettina V. Lotsch[1,2]; [1]Max Planck Institute for Solid State Research, Germany; [2]Ludwig-Maximilians-Universität München, Germany; [3]Massachusetts Institute of Technology, United States

Solid electrolytes (SEs) with high ionic conductivities are prerequisites to establish solid state batteries on a broad basis. Here we report a novel approach to thiophosphate SEs with improved ionic conductivities based on the in situ formation of LGPS-type *tetra*-Li_7SiPS_8/lithium argyrodite Li_6PS_5X (X= Cl, Br, I) hybrid SEs. Quantitative phase analysis reveals the formation of halogen-poor argyrodites $Li_{6+y}PS_{5+y}X_{1-y}$ next to the *tetra*-Li_7SiPS_8 majority phase and an amorphous side phase. EIS measurements indicate ionic conductivities of up to 7 mS cm^{-1}, which exceed those of the parent *tetra*-Li_7SiPS_8 and Li_6PS_5X (X = Cl, Br, I) phases as well as those of simple physical mixtures whose conductivities are well described by the effective medium approximation. In contrast to previous reports, no evidence for halide substitution of the PS_4^{3-} anions in *tetra*-Li_7SiPS_8 was found. Instead, the observed increase in ionic conductivity along with reduced grain boundary resistance is attributed to the directed growth of the *tetra*-Li_7SiPS_8 majority phase in the presence of an argyrodite side phase. As a result, a substantially increased isotropic Li diffusion radius is observed by PFG NMR, consistent with both more bulk-like Li transport within secondary particles and with reduced grain boundary resistance through more benign argyrodite interphases as compared to pristine *tetra*-Li_7SiPS_8. The microstructural changes induced by hybridization thus provide access to the bulk properties of *tetra*-Li_7SiPS_8.

5:00 PM EN06.05.05

Engineered Segmental Mobility in a Family of Solvent-free Single-ion Conducting Borate Network Polymer Electrolytes for Li-metal Battery Applications Jingyi Gao, Jiaming Zhou, Xiaoting Ma and Dong-Myeong Shin; The University of Hong Kong, Hong Kong

As the state-of-the-art energy storage technology, lithium-ion batteries have been attracting lots of attention, but finite energy densities of mainstream Li-ion batteries cannot satisfy the overwhelming demand for large energy storage and commercial flammable liquid electrolytes are also plagued by safety concerns. Many efforts have focused on developing solvent-free single-ion conducting (SIC) polymer electrolytes to solve these issues by covalently immobilizing anionic groups onto a polymer backbone, which only allows Li^+ cations to be mobile through the polymer matrix, leading to minimal dendrite growth during charging/discharging process. While the SIC polymer electrolytes hold much promise for next-generation batteries possessing high safety and high energy density, this approach typically yields a significant drop of ionic conductivity at ambient temperature compared to liquid electrolytes. In this work, we engineered the networking of a series of solvent-free anionic network polymer electrolytes to improve ionic transport for Li-metal battery applications and investigated influencing factors of Li-ions transport. A series of branched polyethylene glycol linkers was connected with tetrakis(4−(chloromethyl)–2,3,5,6-tetrafluorophenyl)borate to form a family of anionic network polymers via nucleophilic substitution where the lithium cations are the dominant contributors to ionic transport as all borate anion nodes are physically anchored within the polymer framework, acting as the single-ion conducting polymers. The segmental mobility in anionic network polymers could be tuned by varying synthetic parameters such as the interanionic distance and the number of tethered branches. As the segmental mobility is predicted to increase with the interanionic distance whilst increasing the number of tethered branches causes the segmental mobility to decrease, we have chosen the trimer and tetramer polyethylene glycol linkers with different numbers of repeating units to engineer the segmental mobility. The increasing segmental mobility offered an elevated ionic conductivity (up to 3.02×10^{-7} S cm^{-1} at room temperature), revealing ionic transport was mostly controlled by engineering the segmental mobilities of polymers, especially at the given interanionic distance. With the increasing of segmental mobility by adding branches at the given interanionic distance, there is a significant increase (at least 4-fold) in ionic conductivity. Notably, there was a restricted ionic transport in fast segmental dynamics of the network polymers featuring free branches, implying that the branching would less contribute to ionic transport compared to the interanionic distance likely due to the frustration in changing the coordination site. Standout network polymer exhibited notable ion selectivity in Li+ cation transport (~0.979) and high oxidative stability (up to 4.2 V). The result partially reveals the ionic transport rule within the interpenetrated network polymer and gives insights on the design of a new class of

highly conducting electrolytes.
Reference: Chemical Engineering Journal (2022) 450, 138407; Chemical Science (2021) 12, 13248-13272

5:00 PM EN06.05.06
Bacterial-Cellulose-Derived Composite Membrane Electrolytes for Long-Shelf-Life Solid Zinc-Air Batteries Joo Young Park, Sung-Hae Kim, Sambhaji S. Shinde, Nayantara K. Wagh, Seol-Hee Han and Jung-Ho Lee; Hanyang University, Korea (the Republic of)

The global energy crisis demands a new rechargeable battery with high energy density, low cost, and earth-abundant elements that are significantly challenging for the next-generation energy storage system. Zinc-air batteries (ZABs) can meet these goals due to their high theoretical energy density and earth-abundant zinc reserves, but the liquid electrolytic cells employing aqueous solutions limit the commercial versatility because of difficulties in bipolar cell stacking for upscaling with lack of bendability. All-solid-state ZABs can resolve these issues, but they require a much more difficult technical challenge due to their unique half-open system requiring air circulation from the outside. This feature makes solid electrolytes vulnerable to water evaporation, CO_2 contamination, cathode redox reactions, electrochemical/mechanical instability, and poor cycle life, compared to aqueous liquid electrolytes.
In our work, we present almost non-drying bacterial celluloses and poly acrylic acid (BC/PAA) derived composite alkaline membrane electrolytes formed by reinforcing the polymerization of acrylic acid with the BC pellicles. The grown BC/PAA membrane has a three-dimensional (3D) nanofiber intertwined composite structure with high mechanical strength and hydrophilicity. Further, we optimized the characteristics of BC pellicles by varying nutrient sources in a culture media. BC/PAA membrane revealed excellent dimensional stability, high toughness, water retention capability, and a low swelling ratio. Furthermore, the fabricated solid ZABs with BC/PAA polymer electrolyte rendered excellent charge/discharge performance and superior long-shelf life for commercial availability.

5:00 PM EN06.05.07
Breakdown of Soft Anharmonic Phonons Heralds Fast Ionic Diffusion in Lithium Argyrodite Jingxuan Ding[1,2], Mayanak Gupta[1,3], Carolin Rosenbach[4], Naresh Osti[5], Douglas L. Abernathy[5], Wolfgang Zeier[4] and Olivier Delaire[1]; [1]Duke University, United States; [2]Harvard University, United States; [3]Bhabha Atomic Research Centre, India; [4]University of Münster, Germany; [5]Oak Ridge National Laboratory, United States

A fundamental understanding of the atomic structure and dynamics enabling fast ionic transport in solids is essential for the development of next-generation solid-state electrolytes (SSE). Focusing on the promising SSE candidate Li_6PS_5Cl with argyrodite structure, we resolve the coupling between fast diffusion of Li^+ and vibrational dynamics of the host framework through extensive inelastic and quasielastic neutron scattering measurements, combined with machine-learned molecular dynamics (MLMD) simulations based on first-principles data. Our results establish that host lattice vibrations enable an order-of-magnitude increase in Li^+ diffusivity at ambient temperature. Our experiments and simulations both show a clear overlap and interplay of hopping dynamics and vibrational frequencies in the terahertz regime, with a continuous spectral evolution from harmonic phonons to strongly anharmonic overdamped vibrations, and fast Li^+ diffusion. We identify the key degrees-of-freedom enabling fast Li diffusion as low-frequency dynamics of PS_4^{3-} polyanions, which are distinct from the commonly assumed "paddle-wheel" scenario. Bringing together neutron measurements and large-scale MLMD simulations, our results build a "beyond phonons" picture of complex atomic dynamics in SSEs in terms of overdamped spectral functions. These results offer microscopic insights into the mechanism of fast Li^+ diffusion in lithium argyrodites and provide guidance for the design of future SSE materials.

5:00 PM EN06.05.08
First-principles Study of Argyrodites Solid State Electrolyte for Battery Application Noah Fourby and Santosh KC; San Jose State University, United States

There is a growing research interest in identifying ideal solid electrolyte materials that is electrochemically stable and exhibit a very high ionic conductivity. Argyrodites are promising solid electrolytes as they demonstrate their high ionic conductivity at room temperature, low cost, and compatibility with Li electrodes. However, in order to realize its practical application, detailed ion conduction mechanism, defect chemistry, and interface properties need to be understood. Moreover, they are not stable as exposed to air and moisture, posing challenges during their manufacturing, and designing process. Thus, using Density Functional Theory (DFT), structural, electronic, and ionic properties are investigated. Thus, this study will provide significant insights into ion conduction mechanisms and strategies that can tune the ionic conductivity and stability of argyrodite-based electrolytes.
This project was supported in part by COE SJSU, DOE NERSC.

5:00 PM EN06.05.09
A Study on Correlation Between Ln Cation Size and Hydration Properties in Layered Perovskite Oxides Sihyuk Choi; Kumoh National Institute of Technology, Korea (the Republic of)

A discovery on novel triple ionic/electronic conductor (TIEC) oxide is vital to reduce the cathodic polarization resistance for high performance protonic ceramic fuel cells (PCFCs) due to its simultaneous triple (H^+/O2-/e-) conducting properties. Recently, layered perovskite $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+d}$ cathode with chemical formula of $AA'B_2O_{5+d}$ (A = lanthanide, A'= alkaline earth element, and B = transition metal) has been used as TIEC material. Generally, the layered perovskite structures are formed by size different between A-site and A'-site ions, consisting of sequential stacking layers …[A'O]–[BO_2]–[AO_d]–[BO_2]… along the c-axis. Thus, oxygen ion diffusivity is particularly fast from the formation of disorder-free channel in $A(Ln)O_d$ layer. However, most previous studies have only focused on the Ln cation effect on electrical properties and oxygen kinetics. Therefore, the aims of this study is to systematically investigate on the hydration properties with various Ln ions. Furthermore, we studied on the thermodynamic parameters based on hydration properties and electrochemical performance for PCFC devices.

5:00 PM EN06.05.10
Micro-Mechanical Testing of Highly Air-Sensitive Argyrodite and Argyrodite-Zirconia Composites by *In Situ* Nanoindentation and Micro-Cantilever Bending Johann Perera, Dominic Melvin, Ed Darnbrough, Peter Bruce and David Armstrong; University of Oxford, United Kingdom

All-solid-state-batteries (ASSBs) pave the way for safe use of lithium-metal electrodes due to their use of a solid electrolyte (SE). Short circuit failure caused by the penetration of lithium dendrites, resulting in the fracture of SEs, remains one of the largest challenges facing ASSBs; it is therefore essential to gain a better understanding of the mechanical properties of SEs. Due to the highly air-sensitive nature of SEs conventional mechanical testing techniques are not possible and as a result very little is known about their mechanical properties.

In this work, the mechanical properties of Argyrodite, an air-sensitive sulphide, was investigated using in-situ nanoindentation inside an enclosed Argon glovebox system. Both Berkovich and cube-corner nanoindentation testing procedures were used to measure elastic, plastic and fracture properties. A modulus of 20.4 GPa, hardness of 960 MPa and a fracture toughness of 0.76 MPa $m^{1/2}$ was measured. It has been shown that lithium dendrites are able to plate intergranularly through SEs, along the grain boundaries, leading to transgranular fracture of the grains. This led to the question as to what is the grain boundary strength of these SEs? Using an innovative technique, the grain boundary strength was measured to be 91.1 MPa. This was achieved by preparing a pentagonal microcantilever containing a single grain boundary at its fixed end and by bending the free end using cube-corner nanoindentation. This value demonstrates the pressure which the Li metal must exceed to be able to ingress into the SE along the grain boundary.

Our initial results show that to further advance the performance of SEs, their fracture properties must be improved. To facilitate this, Argyrodite-Zirconia composites were made to increase the fracture toughness. Using the same nanoindentation testing procedures, the mechanical properties of these composites were investigated. As the proportion of Zirconia was increased, so did the modulus and hardness values, as predicted by the Voigt and Reuss models. The modulus increased to 29.6 GPa and the hardness to 1.35 GPa; as further Zirconia was added, both modulus and hardness decreased. This trend was also observed for fracture toughness with an improvement to 0.96 MPa $m^{1/2}$ being achieved. These improvements in mechanical properties are also accompanied by improvements in our initial electrochemical test results, which show that increasing the proportion of Zirconia raises the current density needed to induce lithium dendrites.

5:00 PM EN06.05.11
Mechanistic Elucidation of Electrostatic Solvent Interactions within Composite Solid Electrolytes, with *In Situ* Safety Study Annie Y. Sun and Vilas G. Pol; Purdue University, United States

Lithium-ion batteries (LIBs) have spread throughout modern electronics rapidly since the technology’s advent in 1991. Since 2010, energy storage costs associated with LIBs have plummeted 88% from $1,100/kWh to $132/kWh today. Larger-scale electrochemical energy storage via LIBs is instrumental to the goal of decarbonization via electrification (especially in storing intermittently generated renewable energy) due to their higher energy density and efficiency than mechanical or chemical energy storage. The large quantity of energy storage required for stationary grid-scale applications also represents energy which may become dangerous if the components exothermically degrade over time. Commercially available LIBs hinge upon ion intercalation reactions through a liquid organic carbonate electrolyte. Liquid electrolytes are combustible, cannot inhibit lithium dendrites caused by lithium metal heterogeneously plating, and possess a limited electrochemical window of oxidative and reductive stability.

In addition to safety issues, these conventional LIBs may soon reach a point of diminishing returns in gains in energy density with current materials. A solid electrolyte in place of the liquid electrolyte and separator may fundamentally address these shortcomings. Solid electrolyte materials generally have superior thermal safety and facilitate the use of the lithium metal anode with exceptional theoretical capacity of 3860 mAh g-1 . High interfacial impedance, imperfect solid-electrolyte interphase (SEI) formation, and low room-temperature ionic conductivity (σ) present challenges to many current solid-state systems. However, composite solid electrolytes comprised of a polymer electrolyte, lithium salt, and solid inorganic electrolyte have shown great promise in creating a high-performance solid electrolyte.

Though current work in composite solid electrolyte systems acknowledge the presence of liquid solvent remnants within the system which are trapped by the interactions between the polar solvents and the dissolved ions, there exists a substantial knowledge gap into the detailed mechanism behind Li+ transport and how this mechanism is influenced by the residual solvent’s electrostatic interactions and coordination with the Li+ compared to the strength of a polar polymer chain’s association. This work designs novel electrolyte systems with composite quasi-solid-state electrolytes in which classes of compounds including phosphate esters and phosphoramides may function as a plasticizer and as a fire retardant within the composite polymer matrix. Characterizations and electrochemical tests fundamentally shed light upon the effect of electrostatic interactions when the dielectric constant of the solvent is well-matched with that of the polymer's crystalline phases.

We have established working principles for electrolyte design in which the composite strategy is seamlessly integrated into the greater quasi-solid-state system, and we have validated the performance and lifespan of the developed CQSSEs in with a variety of cathode chemistries. Finally, we have conducted thorough in-situ safety studies of functional cells in order to validate the thermal stability and fire suppressing properties of specified class of polar solvents. This framework for rationalizing the interplay of these electrolyte components may present a broad opportunities for boosting the viability of electrolytes in the solid state.

5:00 PM EN06.05.13
The Cluster of Competence for Solid-State Batteries (FestBatt) Felix Hartmann and Jürgen Janek; Justus Liebig University Giessen, Germany

We would like to introduce the German Competence Cluster for Solid State Batteries (FestBatt) to the participants and give an overview of the previous and current work and results in FestBatt. Our main goal is to drive the transfer of results between FestBatt and the academic world as well as industry. Due to the size of the cluster (>170 scientists), only selected highlights on solid electrolytes (based on thiophosphates, oxides and polymers), hybrid cell concepts as well as scalability and processing methods of these materials and cell design will be presented.The poster will be structured into i) current scientific challenges for solid electrolytes and solid-state batteries, ii) recent highlights from FestBatt, and iii) outlook/perspectives

FestBatt is a German research network funded by the German Federal Ministry of Education and Research (BMBF, German: Bundesministerium für Bildung und Forschung) under the umbrella concept "Research Factory Battery".

Website:
https://festbatt.net/en

5:00 PM EN06.05.14
High-Conduction Argyrodite Solid Electrolyte with Air-Stable Oxidized Shell for All-Solid-State Batteries Jong-Hyuk Bae[1,2], So-Ri Lee[1], Yoon-Cheol Ha[1] and You-Jin Lee[1]; [1]Korea Electrotechnology Research Institute (KERI), Korea (the Republic of); [2]Pusan National University, Korea (the Republic of)

All-solid-state batteries have been widely recognized as a promising next-generation battery because they can meet the growing demand for high energy density and safe energy storage systems. Sulfide-based solid electrolytes are one of the most effective types of solid electrolytes due to their superior Li-ion conductivity compared to other solid electrolytes. However, the low atmospheric and chemical stability of sulfides limits their large-scale applications. Previous studies have reported that the stability of sulfide-based solid electrolytes can be improved by replacing some of the sulfur with oxygen. However, it was difficult to simultaneously achieve high electrochemical stability and high ionic conductivity by introducing oxygen into the sulfide-based solid electrolytes.
In this study, we synthesized the halide-excess argyrodite, $Li_{6-x}PS_{5-x}X_{1+x}$, with high-conduction core and air-stable oxidized shell by oxidizing the surface of the argyrodite, and the atmospheric stability of the surface-oxidized solid electrolyte was compared to that of the oxygen-doped solid electrolyte. The surface oxidation of the argyrodites was investigated by depth profiling of X-ray photoelectron spectroscopy, confirming the formation of an oxidized shell

on the surface of the solid electrolyte.
The surface-oxidized electrolyte showed higher ionic conductivity (> 5 mS cm^{-1}) than the oxygen-doped one, and improved retention of ionic conductivity (> 80 %) after 24 h air exposure. Moreover, in terms of the electrochemical cell performance, they exhibited higher specific capacity and better cycle performance than oxygen-doped and pristine electrolytes.
Consequently, oxygen-substitution, especially surface-oxidation method is effective in improving air and electrochemical stability of sulfide solid electrolytes. The core-shell structure prevents the reduction of ion conductivity in air and maintains the argyrodite structure inside, resulting in improved cell performance in all-solid-state-batteries.

5:00 PM EN06.05.15
Lithium-Based Metal-Organic Frameworks as Quasi-Solid-State Electrolytes Pravalika Butreddy and Hemali Rathnayake; University of North Carolina at Greensboro, United States

Solid-state electrolytes (SSEs) are essential to developing high-voltage batteries for a crucial breakthrough in the development of electric vehicles. However, they have significant drawbacks, such as low ionic conductivities ($<10^{-5}$ S/cm) at room temperature, oxidation at high voltages, and large ionic transfer resistance. Recently, metal-organic frameworks (MOFs)-based SSEs have gained massive attention due to their ability to hold charged ionic species in their porous networks, which could facilitate faster ionic transport. Due to their unique features, such as porosity, high surface area, ordered channels, and modular designability, MOFs are used as unique host materials for designing SSEs. Incorporating lithium ions into MOF architectures was mainly performed by post-synthetic modification of the secondary building units or via the anion binding sites by creating open-metal sites. However, using pristine lithium-based MOFs as solid-state electrolytes has not been explored much. Herein, we have developed three isoreticular lithium-based MOFs using carboxylate linkers (Li-MOFs) through a solvothermal approach. The framework expansion approach was used to increase the porosity of Li-MOFs by keeping the same topology to obtain highly crystalline Li-MOFs with permanent porosity and a robust framework that facilitate lithium-ion conduction via the porous network. The structural, morphological characterization and ionic conduction of lithium ions in the presence of plasticizer solvents are studied to evaluate the potential applicability of these Li-MOFs as quasi-solid-state electrolytes for lithium-ion batteries.

5:00 PM EN06.05.16
High Performance of Ce-Doped $Li_7La_3Zr_2O_{12}$ Garnet Electrolyte for Solid-State Lithium Batteries Purna C. Rath[1], Yu-Syuan Jheng[2], Tai-Chou Lee[2] and Jeng-Kuei Chang[1,2]; [1]National Yang-Ming Chiao Tung University, Taiwan; [2]National Central University, Taiwan

Solid-state lithium batteries (SSLMBs), employing a composite solid electrolyte (CSE), with high energy density and enhanced safety are promising choices for next-generation energy storage devices. However, the high electrode/electrolyte interface resistance and poor Li^+ conductivity of the solid electrolyte are the major issues that severely hinder the SSLMB's performance. To reduce the interface resistance, a facile and cost-effective tape casting method was used to coat a 20 μm thick CSE directly onto a model $LiFePO_4$ (LFP) cathode. The tape-cast CSE can effectively percolate through the cathode layer, establishing Li^+ conduction pathways and enhancing the cathode/CSE interfacial contact. The effects of tape casting parameters, such as the polymer/Li salt ratio, oxide filler fraction, and casting thickness, on battery performance are examined. The advantages of a tape-cast CSE over a freestanding CSE in terms of reducing the interface resistance and increasing the specific capacity of LFP are clearly revealed. To increase Li^+ conductivity, we synthesize $Li_7La_3Zr_{2-x}Ce_xO_{12}$ (LLZCO), ($x = 0–0.15$) with various Ce concentrations and use the resulting CSEs for a full-cell study. LLZCO−0.10 is the optimal composition among the Ce-doped samples in terms of the charge transfer resistance, charge–discharge capacities, and rate capability of the cell. The Ce doping also improves cell cycling stability, suggesting that Ce^{4+} at the Zr^{4+} site can mitigate the Zr^{4+} reductive decomposition upon contact with the Li metal electrode. We believe that the proposed interface enhancement and Ce doping strategies are feasible and cost-effective for greatly increasing SSLMB performance.

5:00 PM EN06.05.17
Proton Ceramic Fuel Cells with Thin Film ZnO-$BaZr_{0.2}Ce_{0.6}Y_{0.1}Yb_{0.1}O_{3-d}$ Composite Electrolyte Heon Jun Jeong, Dong Hwan Kim, Keun Hee Kim and Joon Hyung Shim; Korea University, Korea (the Republic of)

Solid oxide fuel cells (SOFCs) have advantages such as fuel flexibility and high efficiency. Recently, study of proton ceramic fuel cells (PCFCs) where an electrolyte contains protons has been actively conducted. Compared with SOFCs, the PCFCs has the advantage with a relatively low activation energy (<0.5 eV) producing high power at low operating temperatures below 600°C. Currently, majority of PCFCs electrolyte materials is barium-based materials including Y:$BaZrO_3$ (BZY), Y:$Ba(Zr,Ce)O_3$ (BZCY), (Y,Yb):$Ba(Zr,Ce)O_3$ (BZCYYb). However, due to the relatively low grain-growth of those Ba-based materials, problems of poor bonding and mechanical instability frequently occur in many of previous reports. In particular, this can cause low OCVs and gas leakages in thin-film-based PCFCs. In this study, the performance of thin-film BZCYYb electrolyte-based PCFCs with ZnO sintering agent was evaluated. Based on the slurry of ZnO-added $BaZr_{0.2}Ce_{0.6}Y_{0.1}Yb_{0.1}O_{3-d}$ (BZCYYb2611), an electrolyte thin film of about 5 μm thickness was prepared by spin-coating technique. As a result, it was confirmed that the grain growth of the ZnO-added electrolyte was significantly improved and the density was also increased. The sintering temperature is 1300$^{\text{o}}$C, which is 50°C lower than the optimal sintering temperature of BZCYYb, 1350°C. OCV showed a result close to the theoretical value at 500°C to 1.1V or more. The fuel cell output was also measured to about 0.5W/cm^2 at 500°C, confirming improvement up to 50% compared to BZCYYb-based PCFCs in the same conditions except the electrolyte material. In this presentation, we will discuss more specific results of this improved PCFCs with the ZnO-BZCYYb thin film composite electrolytes.

5:00 PM EN06.05.18
Liquid Crystals for Increased Ionic Conductivity in Solid Polymer Electrolyte for Lithium Metal Batteries Isaac Alvarez Moises and Jean F. Gohy; Catholic University of Louvain, Belgium

The forefront of research for new electrolyte materials for tomorrow's electrochemical energy storage technologies is based on thoroughly designed molecular architectures. Nanostructured, uncharged liquid-crystalline molecules having schiff base and cyano moieties have been developed for application in lithium-metal batteries as solid electrolytes. In this line, we report herein the development of a new class of polymer electrolytes. We designed a poly(ethylene oxide) based matrix comprising liquid crystals, which give orientational properties, whereas the ethylene oxide chains are responsible for the ionic conductivity. Furthermore, the introduction of liquid crystals is anticipated to improved simultaneously the lithium-ion transference number and the dynamic stability of the interface between the solid polymer electrolyte and lithium anode. The approach is to enhance the ionic conductivity, which obeys Arrhenius-type, via ion hopping along the amorphous structure in an ordered morphology, resulting from the assembly of the orientated mesogens and the flexible ethylene oxide chains. The designed polymer matrix and liquid crystals are miscible with lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) salt up to 10:1:1 in molar ratio, and forms self-standing films with a conductivity of $1.8*10^{-4}$ $S*cm^{-1}$ at 60 °C. Focusing on the understanding of the structure-to-transport interplay and the demonstration of the proof-of-concept, we provide also strategies for their further development.

5:00 PM EN06.05.19
Effect of Oxygen Vacancies in Inorganic Fillers on the Performance of Composite Solid Electrolytes for All-Solid-State Li-Metal Batteries Heejun

Yun, Jinil Cho, Seonmi Pyo, Heebae Kim and Youn Sang Kim; Seoul National University, Korea (the Republic of)

All-solid-state Li-metal batteries (ASSLBS) are one of the most promising candidates for next-generation rechargeable batteries. Liquid electrolytes, which trigger the burning and explosion in conventional Li-ion batteries, are replaced with solid-state electrolytes in ASSLBs. These solid electrolytes make ASSLBs safer and more densely packable. Moreover, the solid electrolytes physically suppress the dendritic growth of Li-ion that penetrates the separator and finally causes cell failure. In detail, solid electrolytes are divided into three types: solid polymer electrolytes (SPEs), inorganic solid electrolytes, and composite solid electrolytes (CSEs). Among these three candidates, CSEs are the most fascinating components for ASSLBs. CSEs, which consist of SPEs and inorganic fillers, have all advantages (e.g., processability, chemical tunability, and cost-effectiveness) of solid polymer electrolytes in addition to the high ionic conductivity (10-10^2 folds than SPEs). However, the performance and stability improvement of the CSEs are stuck in a rut because of the complicated Li-ion conduction mechanism and properties in the CSEs.
Herein, we introduce that the oxygen vacancy (O_{vac}) in inorganic filler dominates the performance of the CSEs by creating a Li-ion-conduction percolation network. The highly ionic conductive (2.8×10^{-4} S cm^{-1} at 40 °C) and electrochemically stable CSEs are fabricated with poly(ethylene oxide) (PEO) and indium tin oxide nanoparticles (ITO NPs). In this CSE, the O_{vac}-rich ITO NPs immobilize the anion of the Li salt and make the Li ions conduct rapidly. Density functional theory (DFT) calculation of the binding energy between ITO NPs and anion of the Li salt verify the anion immobilization effect of the O_{vac} in ITO crystals. Furthermore, a series of electrochemical analysis and characterization tools (e.g., FT-IR, DSC, and solid-state magic angle spinning Li NMR) confirm the existence of a highly conductive PEO–ITO NP interface. Based on percolation theory, we demonstrate that the free Li ions, induced by ITO NPs, construct a Li-ion-conduction percolation network on PEO–ITO NP interface and enhance the electrochemical performance of the CSE. Also, the doubled Li transference number and long cycled Li symmetrical cell data (1204 cycles at 0.1mA cm^{-2}) verify that the introduction of O_{vac}-rich ITO NPs make a stable Li-ion flux in CSEs, even though ITO NPs cannot self-conduct Li ions (acting as passive filler). As a result, the LFP/CSE/Li cell exhibited unprecedented cycle stability and performance (154 mAh g^{-1} at 0.5C after 700 cycles). Furthermore, via UV-ozone oxygen-vacancy modification of the ITO NP surfaces, we directly confirmed that the O_{vac} of the inorganic filler governs the ionic conductivity of CSEs through the construction of Li-ion-conducting percolation networks. This fundamental finding of PEO–inorganic filler properties suggests a breakthrough that develops the advanced composite solid electrolyte and ASSLBs, which are practically usable.

5:00 PM EN06.05.21
Influence of Al/Ta Co-Doping by Molten Salt Synthesis Method on Li-Ion Conductivity of $Li_7La_3Zr_2O_{12}$ Solid Electrolyte Haeun Kang, Ji Hyeok Choi, Min wook Kim and Young Soo Yoon; Gachon University, Korea (the Republic of)

Oxide solid electrolytes with excellent lithium-ion conductivity and low interfacial resistance are essential for the development of lithium-ion battery as well as thermal battery and all solid state battery. In this study, we discuss molten salt synthesis (MSS) method for co-doped $Li_7La_3Zr_2O_{12}$ (LLZO) that can improve the Li ion conductivity of conventional oxide-based solid electrolytes. The synthesis method based on LiCl-KCl molten salt is easier to form the desired phase in a relatively short time and at a lower temperature than conventional solid-phase synthesis [1],[2]. MSS method has the disadvantage of forming an impurity phase during multi-component synthesis, but this can be overcome by Al/Ta co-doping. In addition, Al/Ta co-doping can theoretically induce more Li vacancies, and suppress 97h site substitutions that interfere with lithium ion conductivity during Al single doping. Particularly, the path of Li ions is expanded by inducing displacement to the Li 24d site. The production of pure cubic LLZO phases was carried out in the range of 900°C to 1000°C with a calcination process of less than 4 hr. The synthesized powder was pelletized and subjected to a heat treatment process for densification at 900°C for 6 hours. The morphology of the samples was revealed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and the phase structure was characterized by X-ray diffraction (XRD). Li^+ conductivity was measured using Electrochemical Impedance Spectroscopy (EIS) in the frequency range of 10 Hz to 1 MHz The LLZO fine powder co-doped with Al/Ta by the MSS method was found to be particles 0.5 to 3 μm smaller than the similarly developed Al-LLZO and Ta-LLZO. As a result, the ion conductivity was $1 \sim 3.0 \times 10^{-4}$ S cm^{-1}, and a small amount of Al/Ta co-doping was sufficient to impart stability to the garnet structure of LLZO. This study demonstrates the possibility of a co-doping effect to deepen the understanding of the solid electrolyte prepared by the MSS method and improve the lithium ion conductivity.

Reference
[1] Weller, J. Mark, Justin A. Whetten, and Candace K. Chan. "Synthesis of fine cubic $Li_7La_3Zr_2O_{12}$ powders in molten LiCl–KCl eutectic and facile densification by reversal of Li^+/H^+ exchange." *ACS Applied Energy Materials* 1.2 (2018): 552-560.
[2] Zhang, Yanhua, et al. "High-efficiency and low-cost preparation of solid electrolytes $Li_7La_3Zr_2O_{12}$ based on molten salt method." *Journal of Alloys and Compounds* 881 (2021): 160620.

SESSION EN06.06: Inorganic Solid Electrolyte III
Session Chairs: Valentina Lacivita and Yan Eric Wang
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2006

8:15 AM *EN06.06.01
***In Situ* and *Operando* XPS and Related Measurement Approaches for Interfacial Studies of Solid-Electrolyte Materials for Battery Applications**
Glenn Teeter; NREL, United States

In recent years there has been growing interest around *in situ* and *operando* approaches for studying interfacial phenomena, including charge- and mass-transfer processes relevant to solid-electrolyte systems and battery technologies in general. Laboratory-based X-ray photoelectron spectroscopy (XPS) and scanning Auger microscopy (SAM) are powerful techniques for analyzing surfaces and interfaces to reveal compositions and chemical states, including depth profiling and 2D mapping experiments. This presentation will discuss recent efforts by researchers at the National Renewable Energy Laboratory (NREL) to apply *in situ* and *operando* approaches to probe interfacial charge transfer and phase transformations relevant to the formation and evolution of the solid-electrolyte interphase (SEI) on novel solid-electrolyte materials. These experiments are enabled by the virtual electrode (VE) approach, in which electrochemical currents are driven during VE-XPS measurements on exposed interfaces via a combination of low-energy Li^+ ion and electron guns and ultraviolet-based photoemission.

8:45 AM EN06.06.02
A Two-parameter Space to Tune Solid Electrolytes for Lithium Dendrite Constriction Yichao Wang, Luhan Ye, Xi Chen and Xin Li; Harvard University, United States

Li dendrite penetration and associated microcrack propagation at high current densities is one main challenge to the stable cycling of solid-state batteries. The interfacial decomposition reaction between Li dendrite and solid electrolyte was used to suppress the Li dendrite penetration through a novel effect of "dynamic stability" recently. Here we use a two-parameter space to classify electrolytes and propose that the effect may require the electrolyte to occupy certain region in the space with a principle of delicately balancing two property metrics of both a sufficient decomposition energy with Li metal and a low critical mechanical modulus. Furthermore, we show that the position of electrolytes in such a space can be controlled by their chemical composition in our computational prediction by a combination of high-throughput computation and machine learning, with the compositions attainable by experimental synthesis through core-shell microstructures as well. The designed electrolytes following this principle further demonstrate a stable long cycling of 10,000 to 20,000 cycles at high current densities of 8.6 ~ 30 mA/cm^2 in solid state batteries, while in contrast the control electrolyte with nonideal position in the two-parameter space shows a faster capacity decay by at least an order of magnitude due to Li dendrite penetration.

Reference:
Wang, Y., Ye, L., Chen, X. and Li, X., 2022. A Two-Parameter Space to Tune Solid Electrolytes for Lithium Dendrite Constriction. *JACS Au*, *2*(4), pp.886-897.

9:00 AM EN06.06.03
Direct Measurements of Dendrite-Induced Stresses in Ceramic Electrolytes *via* Photoelasticity Christos E. Athanasiou[1], Cole D. Fincher[2], Craig Carter[2], Huajian Gao[3], Yet-Ming Chiang[2] and Brian Sheldon[4]; [1]Georgia Institute of Technology, United States; [2]MIT, United States; [3]Nanyang Technological University, Singapore; [4]Brown University, United States

The measurement of stress fields around lithium metal protrusions in solid electrolytes in operating conditions is critical for the design of next-generation, dendrite-resistant solid electrolytes. However, such stress measurements entail inherent experimental difficulties associated with acquiring accurate data at small scales in thin ceramic electrolytes.

By employing the principle of photoelasticity combined with electrochemical cycling in a plan- view cell the aforementioned challenges are bypassed, allowing not only to track the stress field as the dendrite events progress, but also to obtain full field stress information on a propagating dendrite in semi-transparent LLZTO electrolyte. This new experimental methodology allows for 1. quantification of the stress fields around the dendrite tip and 2. clear verification that the stress field observed at the experiments can be explained by linear elastic fracture mechanics.

9:15 AM EN06.06.04
Li$^+$ Conductivity Landscape in Lithium-Containing Argyrodites as a Function of Co-Doping on Lithium and Sulfur Sublattices Sokseiha Muy and Nicola Marzari; Ecole Polytechnique Federale de Lausanne, Switzerland

Lithium-containing Argyrodites with the parent phase Li_7PS_6 are among the most promising materials for solid-state ionic conductors in the next generation all-solid Li-ion battery. This material not only exhibits remarkable room-temperature ionic-conductivity (up to 24 mS/cm) but also great chemical flexibility, affording aliovalent substitutions on both anion and cation sublattices. In this talk, I will present detailed molecular dynamics simulations using the DeepMD neural network potentials trained on first-principle molecular dynamic data. The 'ionic conductivity landscape' of Li-containing argyrodites will be presented as a function of cation and anion doping on the Li- and S-sublattices with particular emphasis on the effect of the host lattice configurations on the computed ionic conductivity. The reliability of the trained neural network potentials with respect to the size and diversity of the training data will also be discussed. Finally, the extensive data from molecular dynamics trajectories will be analyzed along with the correlation analysis to shed new light on the mechanistic origins and the impact of various physical and chemical factors on the high mobility of Li-ion in this family of compounds.

9:30 AM BREAK

10:00 AM *EN06.06.05
The Mechanism by Which a Ag-Carbon Buffer Layers Improves Li Plating in Solid-State Batteries Gerbrand Ceder[1] and Howard Tu[2]; [1]Lawrence Berkeley National Laboratory, United States; [2]Rochester Institute of Technology, United States

Recently, it has been shown that the introduction of a carbon+Ag buffer layer between the solid-state electrolyte and a current collector leads to highly efficient and uniform Li plating [1-2]. The mechanism by which the buffer layer improves Li plating is not well understood, and the current hypothesis attributing this to the different adhesion energy of the buffer layer with the solid electrolyte and current collector is almost certainly not correct.
In this presentation we report on a combined continuum + ab-initio modeling effort to understand how Ag nanoparticles regulate the Li nucleation and growth. The understanding from this work also enables a rational selection of which other metals may or may not work.
Reference:
[1] Lee, Yong-Gun, et al. "High-energy long-cycling all-solid-state lithium metal batteries enabled by silver–carbon composite anodes." *Nature Energy* 5.4 (2020): 299-308.
[2] Suzuki, Naoki, et al. "Highly Cyclable All-Solid-State Battery with Deposition-Type Lithium Metal Anode Based on Thin Carbon Black Layer." *Advanced Energy and Sustainability Research* 2.11 (2021): 2100066.

10:30 AM EN06.06.06
Synthesis and Characterization of Halide Solid State Electrolytes and Their Integration in All-Solid State Batteries Julien Porcq[1,2,3], Virginie Viallet[1], Jérémie Auvergniot[3] and Claude Guéry[1]; [1]Laboratoire de Réactivité et Chimie des Solides (LRCS), France; [2]Centre National de la Recherche Scientifique (CNRS), France; [3]Umicore, Belgium

Ionic conduction in a solid was first observed by M. Faraday in 1833 on silver sulfide[1]. This discovery launched a series of studies on ionic conduction in this family of solids. In the 1920s, the conductivity of the lithium ion in one of the simplest halogenated solids, LiCl, was calculated using different equations[2]. After several years of research to master the concepts of conduction in solids and to develop different measurement methods, solid halogenated electrolytes such as $RbAg_4I_5$ or LiI made it possible to build the first all-solid batteries[3]. As all-solid lithium batteries were developed, halogenated electrolytes were abandoned in favor of sulfides, oxides and polymers which, among other advantages, have much higher ionic conductivity[4]. However, this family of electrolytes is experiencing renewed interest in 2018 with the research of Asano *et al.* who succeeded in synthesizing Li_3YCl_6 and Li_3YBr_6 compounds and integrating them into all-solid state batteries[5]. These compounds stand out from other halide electrolytes reported until now, by demonstrating an ionic conductivity of the order of magnitude of mS/cm. This discovery has led to other good solid halide ionic conductors such as Li_3InCl_6[6], Li_3ErCl_6[7], Li_3YbCl_6[8], ou Li_3ScCl_6[9].
In this work, several halide electrolytes have been successfully synthesized including Li_3InCl_6, Li_3YCl_6, Li_2ZrCl_6, $LiAlCl_4$. The method used was mainly ball milling, whose parameters were adjusted and refined for the compound Li_2ZrCl_6. The ionic conductivities of these compounds were measured, the best

result obtained was for Li_3InCl_6 with an ionic conductivity of the order of 1 mS/cm at room temperature. It was also shown that this electrolyte was unstable against lithium metal, forming a Li-In alloy, this phenomenon has also been reported in the literature[10]. A full NMC811 *vs* Li-In battery has also been assembled with this electrolyte.

References:
1. Faraday, M. Experimental Researches in Electricity. *Philos. Trans.* (1833).
2. Haven, Y. The ionic conductivity of Li-halide crystals. *Recl. des Trav. Chim. des Pays-Bas* **69**, 1471–1489 (1950).
3. Owens, B. B. *History of Solid-State Batteries*. (1987).
4. Manthiram, A., Yu, X. & Wang, S. Lithium battery chemistries enabled by solid-state electrolytes. *Nat. Rev. Mater.* **2**, 16103 (2017).
5. Asano, T. *et al.* Solid Halide Electrolytes with High Lithium-Ion Conductivity for Application in 4 V Class Bulk-Type All-Solid-State Batteries. *Adv. Mater.* **30**, 1803075 (2018).
6. Li, X. *et al.* Air-stable Li3InCl6 electrolyte with high voltage compatibility for all-solid-state batteries. *Energy Environ. Sci.* **12**, 2665–2671 (2019).
7. Schlem, R. *et al.* Mechanochemical Synthesis: A Tool to Tune Cation Site Disorder and Ionic Transport Properties of Li 3 MCl 6 (M = Y, Er) Superionic Conductors. *Adv. Energy Mater.* **10**, 1903719 (2020).
8. Park, J. *et al.* Heat Treatment Protocol for Modulating Ionic Conductivity via Structural Evolution of Li3-xYb1-xMxCl6 (M = Hf4+, Zr4+) New Halide Superionic Conductors for All-Solid-State Batteries. *Chem. Eng. J.* **425**, 130630 (2021).
9. Liang, J. *et al.* Site-Occupation-Tuned Superionic LixScCl3+ xHalide Solid Electrolytes for All-Solid-State Batteries. *J. Am. Chem. Soc.* **142**, 7012–7022 (2020).
10. Riegger, L. M., Schlem, R., Sann, J., Zeier, W. G. & Janek, J. Lithium-Metal Anode Instability of the Superionic Halide Solid Electrolytes and the Implications for Solid-State Batteries. *Angew. Chemie Int. Ed.* anie.202015238 (2021) doi:10.1002/anie.202015238.

10:45 AM EN06.06.07
Extending Electrochemical Window of Na^+ Halide Solid Electrolyte for All-Solid-State Na Ion Battery Juhyoun Park, Jun Pyo Son, Yeji Choi, Hiram Kwak and Yoon Seok Jung; Yonsei University, Korea (the Republic of)

All-solid-state Na ion batteries (ASNBs) using inorganic solid electrolytes (SEs) have attracted much interest owing to their combined potential advantages of improved safety and cost, compared to conventional lithium-ion batteries with flammable liquid electrolyte. Most studies on Na^+ SEs have focused on increasing ionic conductivity. Meanwhile, sulfide Na^+ SEs are highly attractive because they can be easily integrated into ASNB cells by simple cold-pressing-based fabrication. However, sulfide SEs are limited in operating low-voltage batteries due to their electrochemical instability over 2.5 V region (*vs.* Na/Na^+), which thus hinders achieving high energy density of ASNBs.
To alleviate this shortcoming, Na^+ halide SEs for 3 V class ASNB cells with $NaCrO_2$ have also been reported, but the number of the experimental reports is only a few: $NaAlCl_4$, Na_2ZrCl_6, $Na_{3-x}Er_{1-x}Zr_xCl_6$, and $Na_{3-x}Y_{1-x}Zr_xCl_6$.
In this presentation, our recent results on the development of new Na halide SE using interfacial Na^+ ion conduction with wide electrochemical window. Application to all-solid-state Na^+ ion batteries with operating voltage of 1.5-5.0 V (vs. Na/Na+) will be also presented.

[1] Hiram Kwak, et al., *Energy Storage Materials*, **37**, 47 (2021).
[2] Hiram Kwak, et al., *ACS Energy letters*, **7**, 1776 (2022).
[3] Juhyoun Park, et al. *ACS Energy Letters*, **7**, 3293 (2022)

11:00 AM EN06.06.08
Robust and Scalable Thin-Film Solid Electrolytes Processed in Open-Air Nicholas Rolston[1], Mohammed Sahal[1], Jie Molloy[2] and Xiaochuan Lu[2]; [1]Arizona State University, United States; [2]North Carolina A&T State University, United States

The ability to store electrical energy safely and inexpensively is a key component of future energy systems, long-range electric vehicles (EVs), and long-lasting electronics. Current Li-ion batteries employing liquid organic electrolytes have significant drawbacks in safety, reliability, capacity, and lifetime. Solid electrolytes (SEs) can replace flammable liquids, display improved (electro)chemical stability, and provide a physical barrier against short circuits caused by lithium dendrite propagation, leading to improved safety, prolonged battery life, and increased energy density. There has been increased focus by battery manufacturers and the automotive industry on the development of SEs and solid-state batteries (SSBs). However, a major obstacle to the commercialization of SEs and its implementation into SSBs is the inability to easily and scalably form thin films of this material with suitable ionic conductivity, mechanical, and interfacial properties to achieve SSBs with the desired cycling performance.
In this work, we process $Li_{0.3}La_{0.567}TiO_3$ (LLTO)as a thin film solid electrolyte due to improved air and moisture stability compared to other SEs. A scalable blade coating process is used with a rapid thermal sintering process at 1100 °C for 1 minute in ambient conditions to form dense and highly crystalline LLTO films. We perform cross-sectional backscattered electron imaging with microprobe analysis to detect the composition of the individual elements in the film. The film is fully dense with some noticeable segregation between lanthanum-rich and titanium-rich phases. A thin (~ 10 nm) surface layer that is carbonate rich is identified based on X-ray photoelectron spectroscopy. We introduce an open-air plasma system that has a reductive environment through the injection of forming gas to remove the carbonate layer and allow subsequent processing of a lithiated cathode with improved interfacial ion transport in anode-free all solid-state batteries. The resulting ionic conductivity of the SE as measured by impedance analysis is $1.1*10^{-4}$ S/cm, a value which is among the highest reported for undoped LLTO films. Furthermore, the LLTO film has a fracture toughness of ~20 J/m^2—a key metric for reliability—placing it among the most robust electrolytes and demonstrating promise for stable batteries.

SESSION EN06.07: Inorganic Solid Electrolyte IV
Session Chairs: Ali Coskun and Valentina Lacivita
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2006

1:30 PM *EN06.07.01
Accelerating Materials Discovery for Solid-State Batteries via High-Throughput Computation and Automated Laboratory Yan Eric Wang[1,2] and Valentina Lacivita[2]; [1]Samsung Advanced Institute of Technology-America, United States; [2]Samsung Semiconductor Inc., United States

Solid-state batteries have attracted tremendous academic and industrial attention as the likely successor to lithium-ion batteries. The key component of solid-state batteries is the solid-state electrolytes with high ionic conductivity and great interfacial stability against battery electrodes [1]. Traditional discovery of solid-state electrolyte materials for high ionic conductivity often proceeds based on trial-and-error without an understanding of underlying structure-composition-property relationships, and so far only a handful of lithium and sodium conductors have been discovered with desired conductivity.

Computational modeling based on density functional theory has become a cornerstone of materials design, by providing insights into fundamental processes that are not easily accessible in experiments, and enabling fast and efficient prediction even before material synthesis. Such predictive power has made computational modeling a critical tool to design new solid-state ionic conducting materials with desired properties and accelerate the development of next-generation batteries with solid-state electrolytes.

In this talk, I will present our recent findings in the physical and chemical design principles for solid-state materials with high ionic conductivity and stability. More specifically, I will discuss crystallographic features which would enable fast ionic transport in inorganic solids, such as body-centered-cubic in sulfides and corner-shared-polyhedron frameworks in oxides [2], and demonstrate how high-throughput calculations can be applied with such features in the design and discovery of ionic conductors [3]. I will also discuss our most recent efforts at Samsung Advanced Materials Lab, where we are developing tools for inorganic battery materials discovery by combining high-throughput computation and automated laboratory.

[1] Y. Xiao, Y. Wang, G. Ceder, et. al., “Understanding interface stability in solid-state batteries”, Nature Review Materials, 5, 105 (2020).
[2] K. Jun, Y. Wang, G. Ceder, et. al., “Lithium superionic conductors with corner-sharing frameworks”, Nature Materials 21, 924 (2022)
[3] R. Kim, Y. Wang et. al., “Computational Design and Experimental Synthesis of Air-Stable Solid-State Ionic Conductors with High Conductivity”, Chem. Mater. 33, 6909 (2021)

2:00 PM EN06.07.02

Identification of Potential Solid-State Li-Ion Conductors with Semi-Supervised Learning Daniel B. McHaffie, Forrest Laskowski and Kimberly See; California Institute of Technology, United States

All-solid-state batteries (ASSBs) are a promising technology to enable enhanced safety, energy density, and power density over conventional Li-ion batteries [1]. Crucial to the operation of ASSBs is a stable Li-ion solid-state electrolyte (SSE) with ionic conductivity comparable to that of conventional liquid electrolytes. Although an SSE with these required properties has yet to be discovered, thousands of known Li-containing materials remain unexplored. In this work, we utilize a semi-supervised learning approach to accelerate the identification of superionic conductors.

We construct a repository containing the experimental ionic conductivities of 1,346 compounds digitized from over 300 publications. Each of the ~26 000 Li-containing materials from the Inorganic Crystal Structure Database and Materials Project is represented using 180 unique descriptor-simplification combinations. Agglomerative clustering is performed, and experimental conductivity values are used as labels to evaluate the effectiveness of each descriptor. A particular spatial descriptor, Smooth Overlap of Atomic Positions, is found to minimize composite intracluster conductivity variance, indicating a strong correlation to ionic conductivity. By examining high-conductivity clusters, 212 previously unexplored candidate materials are identified. Through additional screening using bond-valence site energy and nudged-elastic band calculations, Li_3BS_3 is chosen as a promising compound for experimental validation. We demonstrate that with defects engineered through aliovalent substitution and high-energy ball milling, Li_3BS_3 exhibits a room-temperature conductivity greater than 1 mS cm^{-1}. The described semi-supervised learning method for assessing descriptor performance and identifying novel materials can be broadly applied for expediting materials discovery.

[1] Janek, J.; Zeier, W. G. A Solid Future for Battery Development. *Nat. Energy* 2016, *1* (9), 16141. https://doi.org/10.1038/nenergy.2016.141.

2:15 PM EN06.07.03

Thermodynamics of the Fast-Conducting Li_3PS_4 Polymorphs from First Principles Ronald Kam[1,2], KyuJung Jun[1,2], Luis Barroso-Luque[2], Julia Yang[3], Fengyu Xie[1,2] and Gerbrand Ceder[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Harvard University, United States

We present a first principles study of phase stability among the three Li_3PS_4 polymorphs (γ, β, α), among which the high temperature β and α phases have been demonstrated to be promising Li superionic conductors.[1] Despite experimental confirmation of phase transitions among these polymorphs, it is not yet understood why β can be stabilized at room temperature.[2] To model phase stability in this system, we treat configurational entropy contributions with density functional theory (DFT) calculations and the cluster expansion method, and vibrational contributions with harmonic phonon calculations. Analysis of DFT relaxations clarifies the nature of Li sublattices and ground state orderings. We predict $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ phase transition temperatures that are in good agreement with reported experimental values upon heating.[2] We find a strong competition between γ and β phases, rationalizing the direct $\alpha \rightarrow \gamma$ transition observed upon cooling, as well as the synthetic accessibility of β at room temperature. Configurational and vibrational sources of entropy are also separately examined and quantified. Our theoretical work provides clear thermodynamic understanding which can guide further experimental efforts in stabilizing the superionic conducting α and β Li_3PS_4.

References:
[1] Homma, K.; Yonemura, M.; Kobayashi, T.; Nagao, M.; Hirayama, M.; Kanno, R. Crystal Structure and Phase Transitions of the Lithium Ionic Conductor Li3PS4. *Solid State Ionics* **2011**, *182* (1), 53–58.

[2] Kaup, K.; Zhou, L.; Huq, A.; Nazar, L. F. Impact of the Li Substructure on the Diffusion Pathways in Alpha and Beta Li3PS4: An in Situ High Temperature Neutron Diffraction Study. *J Mater Chem A* **2020**, *8* (25), 12446–12456.

2:30 PM BREAK

3:30 PM *EN06.07.04

Dynamics Design of Solid Electrolytes for Solid State Batteries Xin Li; Harvard University, United States

Solid state battery is a mechanically more coupled device than the commercial liquid electrolyte Li-ion batteries. Mechanical constriction effect strongly modulates the electrochemical stability at all interfaces in a solid-state battery. This effect introduces some unique dynamical evolution of interface reactions upon battery cycling, understanding of which is challenging but also giving us an opportunity to design the battery performance beyond commercial Li-ion batteries. The talk discusses the design of "dynamic stability" at the electrolyte-electrode interfaces for a stable long cycling of Li metal anode solid state batteries, where Li dendrite penetration and cathode interface decomposition can be suppressed through this dynamic process. High-throughput ab initio computation, machine learning, and microstructure morphology control are used to design electrolyte compositions with enhanced dynamic stability. In the end, an anharmonic cation-anion coupling dynamics for enhanced Li-ion conductivity in sulfide solid electrolyte is also discussed.

4:00 PM EN06.07.05
Tuning Ionic Conductivity and Stability of Superionic Solid-State Electrolyte Tung Dang and Santosh KC; San Jose State University, United States

All-solid-state Li-ion batteries gained huge attention because they exhibit higher power density, wider electrochemical stability windows, and overall safety of solid-state electrolytes (SSE) compared to conventional liquid electrolyte-based batteries. Unfortunately, most of the SSE materials have not matched the ionic conductivity of their liquid counterpart. But, recent research and the synthesis of new materials have shown SSE can conduct ions at an equivalent or even higher rate. However, the electrochemical stability needs to be improved. There is a growing research effort in identifying a solid electrolyte that is both electrochemically stable and has a very high ionic conductivity. The $Li_{10}GeP_2S_{12}$ (LGPS) is one of the superionic conductors, is known for its high ionic conductivity that can be deployed as a solid electrolyte in batteries. However, LGPS is not stable as exposed to air and moisture, posing challenges during its manufacturing, and designing process. Thus, in an attempt to optimize the stability and ionic conductivity, the effect of antimony (Sb), tin (Sn), and oxygen (O) substitution on the conductivity and stability of LGPS is investigated using Density Functional Theory (DFT). The systematic study of compositional variation, phase stability, defects chemistry, and the impact on electronic properties and ionic conductivity is performed. Thus, this study will provide significant insights into ion conduction mechanisms and strategies that can tune the ionic conductivity and stability of LGPS-based electrolytes.

This project was supported in part by COE SJSU, DOE NERSC, and XSEDE.

4:15 PM EN06.07.06
Synthesis and Characterization of Sodium Anti-perovskite Ion Conductors for Solid State Batteries Adolfo Urrutia[1,2,3], Jérémie Auvergniot[3], Jean-Noël Chotard[1,4] and Raphaël Janot[1,2]; [1]Laboratoire de Réactivité et Chimie des Solides (LRCS), France; [2]Centre National de la Recherche Scientifique (CNRS), France; [3]Umicore, Belgium; [4]Université de Picardie Jules Verne, France

In 2020, 23 countries and states have announced bans on fossil fuel vehicles within the next couple of decades.[1] Current lithium-ion technologies present both gravimetric and volumetric energy density limitations.[2] These limitations can be overcome by the use of solid electrolytes and metallic anodes in all solid-state batteries.[2] Inorganic solid electrolytes can be classified into 4 main categories, oxide, sulfide, halide, and anti-perovskites, each with their own pros and cons.

The first anti-perovskites date back to 1915 and are the combination of alkali halides and their hydroxides.[3] Furthermore in the late 1900s, Jansen et al. reported the first ionic conductivities for Na-ion anti-perovskites on the order of 10^{-5} S/cm at 480 K.[4,5] Throughout the last decade, Na-ion anti-perovskites have been studied with reported conductivities between 10^{-2} to 10^{-9} S/cm at room temperature.[6] Through tailoring of the anti-perovskite crystal structure and composition, it is believed that the migration barrier for Na-ion hopping can be reduced, facilitating Na-ion motion through the structure.[7]

Because the perovskite and hence the anti-perovskite structure is so versatile, there are many different material compositions that can be studied. The anti-perovskites with most interest have been those with the simple X_3BA composition. Recently, interest has been drawn to anti-perovskites found in nature, ex: Kogarkoite $Na_3(SO_4)F$.[8]

In this work, we have studied various new and existing compositions of anti-perovskites and measured their ionic conductivities for use in solid state batteries. Some of the compositions studied include the new sulfate hydride Na_3SO4H[9], $Na_2(Ca/Mg)PO_4F$ isostructural to existing Na_2MPO_4F cathode materials, and $Na_3(S/SeO_4)(F/Cl)$. Recently, a new composition has been synthesized with conductivities around 10^{-3} S/cm at RT, a promising value for use as solid ionic conductors.

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4:30 PM EN06.07.07
Ionic Glass Electrolytes—The Role of Medium Range Order in Mechanics and Ion Conduction Andrew S. Westover[1], Sergiy Kalnaus[1], Nancy Dudney[1], Mordechai Kornbluth[2], Takeshi Egami[3,1] and Andrew Kercher[1]; [1]Oak Ridge National Laboratory, United States; [2]Robert Bosch LLC., United States; [3]The University of Tennessee, Knoxville, United States

One of the most intriguing classes of solid-state electrolytes is the family of ionic glasses. Ionic glasses are glasses that are primarily bound together with ionic bonds such as amorphous Li_3PO_4 and amorphous Li_4SiO_4 of which LiPON is the most well-known. Here we provide an in-depth structural characterization of the amorphous ionic glasses LiPON and LiSiPON with high Li content. Based on ab-initio molecular dynamics simulations, the structure of these materials is identified as an inverted glass structure with either isolated polyanion tetrahedra or polyanion dimers suspended in a Li^+ matrix. Based on neutron scattering data, this type of inverted structure leads to a significant amount of medium-range ordering as demonstrated by neutron total scattering. Further analysis highlights correlations between the degree of medium range order and the ionic conductivity and mechanical ductility. The combination of tunable ionic conductivity and ductility, has significant implications for solid electrolyte design that can enable next generation high-energy high-power solid state-batteries.

4:45 PM EN06.07.08
Functionalized and Surface Coated Fillers as Innovative Strategies for Realizing Li/Na Metal Solid-State Polymer Batteries Shanmukaraj Devaraj and Michel Armand; CIC Energigune, Spain

Solid-state batteries using alkali metal anodes are the future for next generation of automotive batteries. The development of Li and Na metal solid-state batteries requires efficient electrolytes to improve the performance of the cells in terms of ionic conductivity, electrochemical stability, interfacial compatibility and last but not the least, the mechanical stability for resilience towards dendrite formation that is a prime inhibiting factor for Li metal batteries.

To realize these targets two innovative approaches will be presented. Firstly, Solid Polymer Electrolytes (SPEs) with new functionalized ethyl cellulose

bearing a lithium/sodium fluorosulfonylimide group (Ethyl cellulose-LiFSI/NaFSI) is proposed as quasi single ion (Li^+/Na^+) conducting polymer electrolyte for all-solid-state lithium and sodium batteries. The functionalization enables a multifunctional strategy taking up the role of Li/Na salt, improving transference number as well as providing mechanical and electrochemical stability. The complex of Li(FSI-ethyl cellulose)/PEO exhibits a Li-ion transference number of $t_{Li}+ = 0.9$, and a Na ion transference number of $t_{Na}+ = 0.6$ for Na(FSI-ethyl cellulose),which are much higher than those reported for ambipolar LiFSI or NaFSI/PEO SPEs under the same measurement conditions. The generated SPEs showed a high electrochemical and mechanical stability as well as a practical ionic conductivity value of ~10^{-4} Scm^{-1} at 80 °C. All solid-state lithium, sodium and Li/Sulfur cells cycled with quasi single ion conducting hybrid SPE exhibit reversible cycling and good performance at 70 °C, making them promising, environmentally benign and cost-effective candidates for use in advanced energy storage systems.
In the second approach we have shown the surface modification of Ga-substituted $Li_7La_3Zr_2O_{12}$ (LLZO) with grafted polymers to be an essential strategy for the preparation of ceramic-rich electrolytes. Ceramic-rich polymer membranes with surface-modified LLZO show marked improvements in the quality of the membranes along with improvement of performance, in terms of electrolyte physical and electrochemical properties, as well as coulombic efficiency, interfacial compatibility, and cyclability of Li metal solid-state cells.

SESSION EN06.08: Virtual Session: Solid Electrolyte
Session Chairs: Haegyeom Kim and Jinhyuk Lee
Tuesday Morning, April 25, 2023
EN06-virtual

10:30 AM EN06.08.01
High-Performance Single-Ion Polymer Conductors for Solid-State Lithium Metal Batteries Kaihua Wen, Shundong Guan, Ce-Wen Nan and Liangliang Li; Tsinghua University, China

Solid-state lithium (Li) metal batteries (SSLMBs) have attracted much research interest due to safety and high energy density. It is necessary to develop solid electrolytes with large ionic conductivity, high Li-ion transference number, and good compatibility with electrodes for SSLMBs. One drawback of the traditional dual-ion polymer conductors is the low Li-ion transference number, which causes unwanted polarization in SSLMBs. In this work, we developed a single-ion polymer conductor (SIPC) with carbonyl and cyano groups. When the ion–dipole interactions between Li ions and carbonyl/cyano groups were precisely tuned, the SIPC possessed an excellent selectivity for Li-ion conduction (the Li-ion transference number was more than 0.9), a high room-temperature ionic conductivity of about 10^{-4} S cm^{-1}, a wide electrochemical stability window (>4.5 V, vs Li/Li^+), and a good electrochemical stability with Li metal during long-term cycling at 26 and 60 °C. With the optimized SIPC, $LiFePO_4$-based SSLMBs showed good rate and cycle performance in a wide temperature range from -20 to 90 °C. Using the same method, we also prepared sodium- and potassium-based SIPCs with high ionic conductivity and high cationic transference numbers. Thus, tuning the ion–dipole interactions in SIPCs is an effective way to enhance the electrochemical properties of solid polymer electrolytes.

10:45 AM EN06.08.02
Light-Induced Lattice Dynamics in Solid-State Electrolyte LLTO Jackson D. McClellan[1,2], Alfred Zong[2], Hanzhe Liu[3], Kim Pham[3], Scott K. Cushing[3] and Michael Zuerch[2]; [1]The Ohio State University, United States; [2]University of California, Berkeley, United States; [3]California Institute of Technology, United States

Conventional Li-ion batteries offer less safety and energy density compared to solid-state batteries. However, poor ionic conductivity in many solid-state batteries hinders its practical use in modern energy storage. Characterization of the origin of these effects, which come from the interaction of Li^+ ions with the atomic lattice, is important for the design and improvement of future solid-state batteries. One current electrolyte that is electrochemically stable and has demonstrated a sufficient ionic conductivity at high temperature is lithium lanthanum titanate (LLTO). Because it only demonstrates sufficient conductivity under heat, identifying the properties of this temperature-induced transition of the solid can reveal the direct affects lattice dynamics on conductivity, leading to improved understanding of which structural characteristics are important in solid-state electrolytes for future batteries. Here, we have performed time-resolved x-ray diffraction using the Advanced Photon Source at Argonne National Laboratory to examine the transient lattice change under photoexcitation and heating on LLTO grains in a powder pellet. Due to the high number of photons per pulse of the Advanced Photon Source, we can extract single-shot statistical variance of the change in lattice constant after excitation from 350 nm light and compare this with the averaged change in lattice constant over a series of pump-probe time-resolved scans. The relaxation time of the lattice constant and its relation to the relaxation time of the shot-to-shot variation reveals the lattice relaxation mechanism following the photoexcitation. The 350 nm photoexcitation mimics the extreme heating condition during the charging or discharging of solid-state batteries, and the resulting lattice deformation under these conditions is important to understand as the lattice collects/releases the Li-ions while under high thermal load.

11:00 AM EN06.08.03
Correlated Factors for Li-Ion Migration in Ionic Conductors with the fcc Anion Sublattice Runxin Ouyang[1], Hong Zhu[1] and Zhenming Xu[2]; [1]Shanghai Jiao Tong University, China; [2]Nanjing University of Aeronautics and Astronautics, China

The development of solid-state electrolytes (SSEs) with high lithium ionic conductivities is critical for the realization of all-solid-state Li-ion batteries. Crystal structure distortions, Li polyhedron volumes, and anion charges in SSEs are reported to affect the energy landscapes and it is paramount to investigate their correlations. In this study, we reveal that the distorted tetrahedrally occupied lithium is less energetic favorable than the distorted octahedrally occupied lithium, rationalized from the heatmap of anion charges, lattice volumes and sites distortion. Our works uncover the cooperative effect of lithium site distortions, anion charges and lattice volumes on Li ion migration energy barrier in superionic conductors of $LiMS_2$ (M =Sc, Ti, V, Cr, Mn, Fe, Co, Ni) and Li_2MO_3 (M =Sc, Ti, V, Cr, Mn, Fe, Co, Ni). Manipulating the distortion of tetrahedrally occupied lithium is more impelling than the adjustment of octahedrally occupied lithium distortion to lower Li ion migration barrier. The new descriptor, Li ion sites distortion, can provide new insights into the strategy for screening high conductivity solid-state electrolytes.

11:15 AM EN06.08.04
Effects of F and Cl Doping in Cubic $Li_7La_3Zr_2O_{12}$ Solid Electrolyte: A First Principles Investigation Yu Yang and Hong Zhu; Shanghai Jiao Tong University, China

Anion doping is recently attaining a lot of research interests for the solid-state electrolytes. In this study, we investigated the effects of F and Cl on the phase, electrochemical, and chemical stabilities, ionic conductivity, and diffusion mechanism in cubic $Li_7La_3Zr_2O_{12}$ (c-LLZO), based on density functional theory (DFT) calculations. It is found that a homogeneous diffusion network with low local structural distortion and the high Li jump numbers are beneficial for good ionic conductivity in c-LLZO. The introduction of a certain amount of Li vacancies can enhance both the Li jump numbers and the concerted migration percentage of c-LLZO. Our findings deepen the understanding of diffusion mechanism in c-LLZO and offer a valuable insight for the rational design of solid electrolytes.

11:30 AM EN06.08.05
Freeze Cast NASICON Solid Electrolytes: Towards High-Performance Sodium Batteries Eldho Edison[1], Elena Tervoort[1], Annapaola Parrilli[2] and Markus Niederberger[1]; [1]ETH Zürich, Switzerland; [2]Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Solid-state sodium batteries have received great interest recently as sustainable and viable electrochemical energy storage systems. To bolster the energy density as well as the safety of sodium batteries, it is crucial to develop solid-state electrolytes with high ionic conductivity and electrochemical stability. Among others, NASICON (Na^+ super ionic conductor) materials are promising candidates as solid electrolytes due to their high ionic conductivity and thermal and electrochemical stability. Herein, we employed a freeze-casting technique to develop porous NASICON solid electrolytes based on sodium aluminum titanium phosphate and sodium zirconium silicophosphate materials with high ionic conductivities. By controlling the slurry composition and sintering conditions, we optimized the porous solid electrolyte. We investigated the uniform distribution of parallel channels in the bulk of the freeze-cast solid electrolyte via X-ray tomography technique. Additionally, the effect of wetting agents including ionic liquid (sodium trifluoromethanesulfonimide in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide) and carbonate electrolytes (sodium perchlorate in propylene carbonate) on the electrochemical performance was explored. Furthermore, a prototype solid-state cell was assembled with the infiltration of sodium vanadium phosphate cathode material into the porous solid electrolyte. The resulting cell delivered a good capacity of nearly 100 mAh $g^{-1}_{cathode}$ and good cycle life with an energy density of nearly 330 Wh $kg^{-1}_{cathode.}$ The improved electrochemical performance could be attributed to the low tortuosity pathways which are uniformly distributed parallel to the thickness of the solid electrolyte, facilitating uniform and efficient sodium ion conduction. The study offers new insights into the optimization of ion conduction in solid electrolytes for sodium batteries.

11:45 AM EN06.08.06
Effect of Composition and Processing on the Multifunctional Properties of Single-Phase Structural Electrolytes Maghen Saltzman[1,2], Payton Parker[1] and Caiwei Shen[1]; [1]University of Massachusetts, Dartmouth, United States; [2]California Polytechnic State University, Pomona, United States

As the world becomes increasingly electrically dependent, energy storage is a factor which seriously limits progress. Unfortunately, popular methods of energy storage, such as lithium-ion batteries contribute significantly to unrecyclable waste once their short life cycles are over. Supercapacitors are an attractive alternative method of energy storage with significantly higher cyclability and power density than batteries. Moreover, multifunctional structural supercapacitors have been developed to further reduce the overall weight and size of products. Previous reports utilize bi-continuous phase materials as the electrolytes for structural supercapacitors, which show significant trade-off between the electrical and mechanical properties. Our research group has recently developed a single-phase solid polymer electrolyte that outperforms previous designs. The current work focuses on studying the effect of composition and processing on the multifunctional properties of such electrolytes. We analyze the thermal, electrochemical, and mechanical properties of the polymer electrolytes composed of polyethylene terphthalate (PET) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) at different compositions after various processing conditions to determine its suitability for use in the structural supercapacitors.

Different from the conventional solution casting method to prepare polymer electrolyte, our electrolytes were prepared by mixing and melting PET and LiTFSI together. The LiTFSI salt was fully dissolved in PET to form a single-phase solid solution. Samples with designed sizes were fabricated through injection molding. Some samples were exposed to a controlled humidity environment to improve their electrochemical performance. The thermal properties of samples with 0 to 50 wt% of LiTFSI were characterized by differential scanning calorimetry (DSC). The ionic conductivities of various dry and humidified samples were measured by using electrochemical impedance spectroscopy (EIS). The mechanical properties of similar samples were evaluated through 3-point bending tests.

It was determined that increasing the weight ratio of LiTFSI in our polymer electrolyte was related to a decrease in heat flow, decrease in melting point from 247 °C to 227 °C, slight increase in glass transition temperature, and decrease in crystallinity from 26% to approximately 0%. In fact, the polymer-electrolyte became essentially amorphous with more than 35 wt% LiTFSI. EIS tests showed that the ionic conductivity reached a peak value at a composition of 20 wt% LiTFSI for dry samples. The samples showed higher ionic conductivity when hydrated, and a peak ionic conductivity of about 34 μS/cm occurred at a 2 wt% absorption of water from the humid air. Finally, the 3-point bending tests demonstrated that increasing the water content of samples dramatically increased the ability to resist breaking from bending.

In conclusion, the results show that the phase and crystallinity of the single-phase structural electrolyte can be controlled through material composition and thermal processing. The mechanical toughness and ionic conductivity of the multifunctional electrolyte can be simultaneously improved through controlled hydration treatment. The optimization of material composition, thermal processing, and hydration treatment will lead to structural electrolytes with significantly improved overall multifunctionality.

SYMPOSIUM

April 10 - April 25, 2023

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SESSION EN07.01: Keynote Session
Session Chairs: Min-Ha Lee and Hua Zhou
Monday Afternoon, April 10, 2023
Moscone West, Level 2, Room 2007

1:30 PM *EN07.01.01
Developing Materials for Energy Technologies with Decreased Critical Materials Ryan T. Ott; Ames National Laboratory (USDOE), United States

The transition to clean energy technologies creates increasing demand for materials with enhanced performance in harsh environments. These materials often rely on critical materials such as rare earth elements (REE), which enable increased functionality. To address the supply and demand imbalances of these critical materials, we are working to accelerate the development of new materials with decreased critical material content. Specifically, we use high-throughput synthesis and characterization techniques to develop permanent magnet alloys with more abundant materials like Ce and La substituted for critical REE (e.g., Nd, Pr, Dy). This work includes integrating rapid synthesis and testing of alloy libraries over large composition ranges with bulk synthesis of down-selected compositions to accelerate the development of new alloys. We are also addressing critical materials challenges by developing new Al alloys that create market demand for overly produced REE (e.g., Ce), while eliminating the need for critical Li and Sc alloying additions. Using combinatorial additive manufacturing (AM) techniques, we have developed new Al-Ce alloys for advanced manufacturing techniques (e.g., AM and extrusion) that show enhanced performance in harsh conditions. The alloys exhibit excellent processing flexibility, enhanced corrosion resistance and thermal stability. The alloys can both reduce critical material usage in key energy technologies and help address supply-demand imbalances in REE.

2:00 PM *EN07.01.02
Strategy of Critical Materials on the Li-Ion Battery Industry of Korea Min-Ha Lee; Korea Institute of Industrial Technology, Korea (the Republic of)

Demand for Li-ion secondary battery (LiB) drastically increases by the explosion of Electric vehicle (EV) market. The major supplier of LiB is limited in China, South Korea and Japan account 91.8% for over the world in 2022. Supply chain of LiB to EV manufacturer tackled by physical limitation of producing capacity, supply instability of core minerals and geopolitical control of trade.
In these reasons, securing a superior position in the global market with high technology and mass production capacity is critical point of industry.
We introduce how Korean government and companies set up strategy to resolve critical issues in energy industry for securing critical materials (CRMs), especially LiB.
Recently announced ‘Secondary Battery Industry Innovation Strategy’ by Korean government will explain and emphasize example of securing supply chain of CRMs in LiB by (1) formation of Korea team to secure core minerals domestic resource and (2) develop new recycling technology from company in South Korea. Because importance of establishment a sustainable battery circulation system (closed-loop) for recycling waste lithium ion batteries is urgently need to guarantee alternative resources supplying CRMs in Lib industry.
In the last part, we define and discuss the concept of materials flow/business flow applied to CRMs in LiB energy industries. Different aspects of supply risk beyond scarcity will be brought into the discussion through examples of regulation and of geopolitical risk.
We conclude with careful speculation about the roles of resilience and adaptation in future risks analysis, drawing on the perspective global market trends.

2:30 PM *EN07.01.05
Defects-Engineered Bismuth Telluride Alloys Towards Waste Heat Recovery Kyung Tae Kim; Korea Institute for Materials Science, Korea (the Republic of)

Among various types of thermoelectric materials, bismuth telluride (Bi_2Te_3) based alloys have been considered as a key material for waste heat recovery as well as active control in temperature. Recently, Intensive effort to engineer the microstructures of bismuth telluride have been made to overcome the current limitation on its thermoelectric energy conversion performance levels (ZT) in viewpoint of defects. In this presentation, we report two plausible powder metallurgy routes to achieve microstructures which exhibit defect-engineered interfaces in p-and n-type bismuth telluride alloys, respectively. For designing favorable defects of p- and n-BiSbTe alloys, the defect formation energy has thermodynamically been calcaulated by First-principle calcuation based on density functional theory under a certain sintering condition. First, considering the wavelengths of carriers and phonons, we introduce geometrical point defect assembly structures in a nano-scale of about 5-10nm are created and dispersed in the p-type BiSbTe crystalline grain. This nanostructure contributes to a reduction in the lattice thermal conductivity and increase in carrier density. Second, novel synthetic process of n-type BiSbTe alloys with antisite defect such as Te@Sb or Te@Bi rather than BiTeSe has been developed by at the same time utilizing the concept of creating dislocation network arrays. As results of these, the fabricated bismuth telluride alloys show peak ZT values of 1.3 for p-type and 1.2 for n-type, respectively which are 1.6 times higher than those of both pristine BiSbTe alloys fabricated by the same method without defect engineering. And characteristically, the defect-engineered bismuth tellurides show simultaneous control which lowers thermal conductivity despite significantly increased electrical conductivity. We think this defect engineering-based fabrication process using conventional powder metallurgy provide a new avenue for improving and modulating the efficiency of thermal-to-electrical conversion in bismuth telluride. Thus, the newly developed materials can be utilized for waste heat recovery of shipbuilding but also can be applied for thermal energy harvester in ICT field.

3:00 PM BREAK

SESSION EN07.02: PGE Nanomaterials I
Session Chairs: Tanya Prozorov and Peter Sushko
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2007

10:30 AM *EN07.02.01
Electrocatalysis by Single-Atoms—A Modeling Perspective Gianfranco Pacchioni; Univ Milano-Bicocca, Italy

One of the objectives of electronic structure theory is to predict chemical and catalytic activities. This is a challenging target due to the large number of variables that determine the performance of a heterogeneous catalyst. The complexity of the problem has reduced considerably with the advent of single atom catalysts (SAC), new systems consisting of a single transition metal stabilized on a solid matrix. SACs offer great potential advantages compared to more conventional supported metal nanoparticles in terms of selectivity and of material needs in order to prepare the catalysts. A lot of attention has been given in particular to graphene-based SACs for electrocatalytic reactions such as the oxygen reduction (ORR), the oxygen evolution (OER) and the hydrogen evolution (HER) reactions. In this context we assist to a rapidly growing number of theoretical studies based on density functional theory (DFT) and of proposals of universal descriptors that should provide a guide to the experimentalist for the synthesis of new catalysts. In this talk we critically analyze some of the current problems connected with the prediction of the activity of SACs based on DFT: accuracy of the calculations, neglect of important contributions in the models used, physical meaning of the proposed descriptors, inaccurate data sets used to train machine learning algorithms, not to mention some severe problems of reproducibility. It follows that the "rational design" of a catalyst based on some of the proposed universal descriptors or of the DFT screening of large number of structures should be considered with great caution [1-3].

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[2] G. Di Liberto, Luis A. Cipriano, G. Pacchioni, "Universal principles for the rational design of single atom electrocatalysts? Handle with care", ACS Catalysis, 12, 5846-5856 (2022).
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11:00 AM EN07.02.02
Wet-chemical Synthesis of Tin Oxide and Titania Supported Iridium Oxide Nanoparticles with Ultralow Iridium Density as Novel Catalysts for PEM Electrolysis Melisande Kost[1], Peter Zehetmaier[2], Markus Doeblinger[1], Dina Fattakhova-Rohlfing[2,3] and Thomas Bein[1]; [1]LMU Munich, Germany; [2]Forschungszentrum Jülich GmbH, Germany; [3]Universität Duisburg-Essen, Germany

The proton exchange membrane (PEM) is a promising and intensively researched technology for large-scale production of hydrogen from sustainable sources. However, the economic viability of the PEM process remains limited by the high capital cost of the individual components, particularly the rare and valuable iridium used as a catalyst for the oxygen evolution reaction (OER). An established approach to reduce Ir loading in PEM is to disperse the catalytically active material on corrosion-stable supports with formation of a catalyst with low volumetric Ir density, which increases the noble metal mass-based activity. The material and morphology of the support, as well as the coating process, have a strong influence on catalyst performance and are investigated here to optimize catalyst performance and further reduce iridium content
Here, a novel and scalable catalyst synthesis is presented in which corrosion-resistant crystalline SnO_2 and TiO_2 nanoparticles are coated with an ultrathin layer of amorphous iridium hydroxide using a simple low-temperature wet chemical synthesis. In a further step, the amorphous $IrO(OH)_x$ layer is oxidized in a molten salt-assisted process. This process enables controllable phase transformation and crystallization to form a layer of interconnected, partially crystalline IrO_x nanoparticles with a size of ≈1.5 - 2 nm on the surface of the supporting nanoparticles, which form a percolation pathway. To elucidate the impact of different core-shell designs, transmission electron microscopy (TEM) imaging with a strong focus on iridium coating and crystallinity was performed. The final compounds contain highly active iridium oxide with overall very low Ir weight fractions of only 16% compared to a modern reference catalyst with 75 wt% Ir. Measurements on a rotating disk electrode (RDE) showed that SnO_2-supported IrO_x exhibits higher electrochemical activity and stability than TiO_2-supported IrO_2 at low loading. Further investigation of the membrane electrode assembly (MEA) in a single-cell electrolyzer indicates the possibility of future large-scale application in PEM at industrially relevant current densities.

11:15 AM EN07.02.03
Component & Size-Tunable Metal Nanoparticle via Ultrafast Non-Equilibrium Synthesis—Design of Electrocatalysts for High-Performance Energy Conversion Systems Ji-Yoon Song and Hee-Tae Jung; Korea Advanced Institute of Science & Technology, Korea (the Republic of)

Metal nanoparticles (MNPs) are one of the most attractive materials in diverse applications due to their high electronic and catalytic activity. It has been reported that MNP engineering such as alloying, controlling particle size and formation density can derive unexpected effects leading to high catalytic performance. Unfortunately, in previous methods, alloying is possible only with thermodynamically miscible combinations of metals, and phase separation occurs as the number of the metals is increased due to the increased instability. Furthermore, the unavoidable aggregation of MNPs from particle migration and coalescence and Ostwald ripening during synthesis process result in ununiform NP size and density on the supports which cause low performance and reproducibility. Thus, the development of a universal and effective method for MNP engineering is highly demanded.
In this presentation, we demonstrate a general strategy to overcome the abovementioned obstacles by adopting the carbothermal shock (CTS) method for electrocatalytic energy conversion systems. Immiscible metal alloying and multi-metallic NPs (>4 elements) can be fabricated with high uniformity within 1 second through ultrafast heating/cooling process. Based on the CTS method, the modulation of support materials is simultaneously conducted to develop a full electrode system for high energy conversion efficiency. As the result, we present diverse electrocatalyst designs (i.e. Ru-Cu alloy on 3D carbon foam, Pd on boron nitride nanotube and Cu on cellulose) for electrocatalytic energy conversion systems to move up Net-Zero-World ecosystem; such as carbon dioxide (CO_2) reduction to ethylene (C_2H_4) and nitrogen (N_2) reduction to ammonia (NH_3).

11:30 AM EN07.02.04
Nanoporous PtIr Nanosheets as Bifunctional Electrocatalysts for Regenerative Proton Exchange Membrane (PEM) Fuel cells Ramchandra Gawas[1], Swarnendu Chatterjee[1], Xiong Peng[2] and Joshua Snyder[1]; [1]Drexel University, United States; [2]Lawrence Berkeley National Laboratory, United States

The hydrogen economy is critical for deep decarbonization of the energy sector owing to high energy density of H_2 as a fuel, clean operation, and flexible implementation in terms of scale (W to GWs), source and end-use. To this date, proton exchange membrane water electrolyzers (PEMWEs) and fuel cells (PEMFCs) remain as emergent technologies for H_2 production and utilization due to the development in polymer electrolyte membranes, high current density operations, etc. These devices however operate in highly acidic conditions requiring significant amounts of platinum group metals (PGM)-based materials. Thus, widespread adoption of PEM devices depends on advancements in material development as well as device integration to lower total

system costs and improve efficiencies.
Our group has developed a novel approach to make nanoporous nanosheets of Ir (np-Ir NS). These np-Ir NS show superior catalytic activity and durability as anodic oxygen evolution reaction (OER) electrocatalysts in comparison to commercial IrO_2 nanoparticle catalysts. The unique morphology of nanoporous nanosheets allows support-free integration into catalyst layers and a form factor that results in significantly lower ohmic losses at high current density.[1]
In this work, we implement the previously developed, top-down approach to synthesize nanoporous nanosheets of PtIr (np-IrPt NS). These alloyed np-IrPt NS show excellent electrocatalytic properties for hydrogen oxidation reaction (HOR) and oxygen evolution reaction (OER), comparable with state-of-the-art PGM catalysts. Bifunctional catalytic properties make np-IrPt NS ideal candidates for regenerative fuel cell applications. We will also discuss the integration of np-IrPt NS into regenerative proton exchange membrane fuel cell (R-PEMFC) devices.
References:
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11:45 AM EN07.02.05
Synthesis of Palladium–Based Nanoparticles with Tuneable Sizes for Catalytic Applications Anastasia Kappelou[1,2], Laura Torrente Murciano[1], Nicoleta Muresan[2] and David Thompsett[2]; [1]University of Cambridge, United Kingdom; [2]Johnson Matthey, United Kingdom

This work demonstrates the continuous synthesis of palladium-based nanoparticles with controllable sizes and a narrow size distribution using continuous flow microreactors for catalytic applications. This new method enables for the first time, the elucidation of size-activity relationships, decoupling size and supports effects. In addition, the easy scale-up of the method can lead to a new way of designing and manufacturing catalysts.

Metallic palladium and palladium-based nanoparticles have been extensively studied in a wide range of catalytic applications, including their use in air pollution remediation catalysts in the automotive industry.[1,2] However, the relationships between their catalytic activity and size and composition remains unknown due to the dynamic structure of the nanoparticles under catalytic conditions. In this study, the 3D configuration of microreactors enables continuous colloidal synthesis of palladium-based nanoparticles using hydrolysis and reduction methods. The combination of laminar flow in the microreactors (characterised by low Reynolds numbers) and the promotion of transitional flows (i.e. Langragian turbulence) through 3D configurations leads to a narrow residence time which is translated into narrow size distributions even in the absence of steric capping ligands.[3]

This study investigates the effect of different palladium precursors on the rate of reaction and stability during the synthesis. Palladium oxide (PdO) nanoparticles with sizes below 5 nm are formed through hydrolysis under basic conditions and supported on ceria supports via electrostatic interactions. Metallic palladium nanoparticles are synthesised either by consecutive reduction of the PdO or the direct reduction of the metal precursors using strong a reducing agent. The results reveal the higher instability of the Pd nanoparticles with respect to PdO counterparts in the absence of capping ligands, being greatly affected by the initial speciation of the precursors. Mechanistic understanding as well as the size-activity relationship for the model CO oxidation reaction will also be presented.

[1] L. Liu and A. Corma, Chemical Reviews, 2018, 118, 4981–5079.
[2] S. Specchia, E. Finocchio, G. Busca, P. Palmisano and V. Specchia, Journal of Catalysis, 2009, 263, 134–145.
[3] K. J. Wu, G. M. de Varine Bohan and L. Torrente-Murciano, Reaction Chemistry and Engineering, 2017, 2, 116–128.

SESSION EN07.03: Rare Earth and Lithium Session I
Session Chairs: Yoshiko Fujita and Chong Liu
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2007

1:30 PM *EN07.03.01
Peptide Surfactants at Air-Aqueous Interfaces for Lanthanide Recovery Kathleen Stebe; University of Pennsylvania, United States

We envision a new, green, froth flotation method to separate Rare Earth Elements (REEs) using peptide surfactants to complex selectively to REE cations and drive their adsorption to rising air bubbles sparged through the solution. The REEs are then collected in the enriched foam formed from these bubbles at the top of the solution. The unique feature of this envisioned separation are the surface active peptides designed to bind selectively with particular REEs. We are working to develop these molecules and to understand the molecular details of their complexation with REEs and their adsorption in the complex environment of a fluid interface. This research is performed by a team of researchers at the University of Pennsylvania, City College of New York, the University of Illinois at Chicago, and Northwestern University under the support of the grant DOE BES DE-SC0022240.
Our peptide surfactants are based on lanthanide binding tags (LBTs), peptide sequences with hydrophilic residues arranged as a binding loop that forms a coordinating sphere of ligands around the REE cation. The peptide sequences in LBTs are derived from calcium binding loops in natural calcium binding proteins and have been optimized to bind particular REEs. In the literature, LBTs have been optimized by screening methods to coordinate with high affinity to particular lanthanides (e.g. terbium and europium), which strongly luminesce when coordinated in the loop. LBTs are widely exploited as probes; LBTs grafted into proteins serve as fluorescence reporters of protein structure. We append hydrophobic peptide sequences to the LBTs to make them amphiphilic. We have demonstrated that the LBT-derived peptide surfactants complex REEs in the bulk aqueous phase, are surface active, and adsorb to an air/water interface in un-complexed and complexed forms. We have quantified the binding affinity and aggregation in water, and peptide surfactants' ability to adsorb and complex with REE cations at the interface using technologies at NSF's ChemMatCARS facility at the Advanced Photon Source of Argonne National Laboratory. These studies are supported by molecular modeling of the peptide surfactants in the region of the air-water interface. Current efforts focus on exploring how changes in the amino acid sequence of the peptide loops alter their selectivity and interaction in the bulk and the interface.

2:00 PM *EN07.03.02
Separating f-Elements and Harnessing Their Unique Properties When Globalization Breeds Conformity Joshua Woods[1], Sabari Ghosh[1], Jia-Ahn Pan[1], Emory Chan[1], Michael Connolly[1] and Rebecca Abergel[2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley/Lawrence Berkeley National Laboratory, United States

With a large number of lanthanides deemed critical materials, f-elements play a major role in many human-driven activities, such as in nuclear energy, clean energy technologies and catalysis. Separation of f-elements from each other can be arduous due to their similar physical and chemical properties, and significant efforts are currently being pursued to develop more efficient partitioning processes. These processes are not only important in the context of the nuclear fuel cycle but also to ensure adequate supply of those metals that are among the most critical materials for clean energy technologies, and for which future supply disruptions can be avoided with new strategies for recovery and recycling. As a result of these needs, novel approaches to detect, separate and recover f-block elements are direly needed. Harnessing the unique capabilities of f-block metal cations so that one may selective tune the resulting properties involves exercising control over the first coordination sphere of the metal ions. Using high-affinity, chelating ligands is one pathway for controlling Ln local coordination geometry, and currently the highest affinity *f*-block binding is achieved by organic, bio-inspired ligands. We will discuss some innovative ligand synthetic pathways linking specific metal binding units to polyamine, macrocyclic, and polymeric peptoid and protein scaffolds, which, combined with advanced structural characterization techniques are used to achieve unprecedented f-element separation under a wide range of conditions. In a time that favors harmonization, creative scientific solutions to global challenges often necessitate input from a wide variety of backgrounds. The results presented here stem from a team that boasts diversity in scientific discipline, cultural background, and seniority level. Applying our diversity and taking advantage of each f-element's uniqueness, we seek to facilitate new technologies that can be accessed by all.

2:30 PM EN07.03.03
Theoretical Studies on the Solvation Structure of Lanthanide Cations in Hydrated Layered Birnessite Woo Cheol Jeon[1], Siqi Zou[2], Chong Liu[2] and George C. Schatz[1]; [1]Northwestern University, United States; [2]The University of Chicago, United States

Rare earth elements (REs) refer to 17 elements including lanthanides, yttrium and scandium, and among the REs, lanthanides have been of particular interest. They can be used in the industrial applications such as fine chemistry, atomic clocks, phosphors, optical fibers, and high-performance alloys. Each of them has its own unique and diverse electronic properties, which means that having effective ways to separate mixture is important. Two distinctive characteristics and available for separations: ionic radius and Lewis acidity, with the former decreasing and the latter increasing as atomic number increases. These characteristics can induce significant differences in coordination and binding affinities when they are ionized and bind to solvent molecules. Furthermore, their coordination can be altered when they are solvated and confined to solid ionic channels. However, experimental characterization methods still have limitations in characterizing the coordination environment of lanthanide cations. Here, we theoretically investigate the structures and energetics of lanthanide cations confined in hydrated layered birnessite. Density functional theory calculations are implemented with a combination of explicit and implicit solvation. Each system with different types and concentrations of lanthanide cations is modeled and optimized to investigate the changes in coordination in different hydration environments. And the structures are characterized by the coordination number of each atom pair and X-ray diffraction which can be compared to experimental data. In addition, the configurations of hydrated structures and hydration energies of cations in the ionic channel are compared with those in bulk water solution to explain the feasibility of cation transportation into the ionic channel. Based on these results, we propose that cation coordination is mainly influenced by the altered oxidation state of the host material and the presence of water molecules.

2:45 PM EN07.03.04
Bio-Inspired Polymeric Ion Capture for Critical Materials Harvesting Erik D. Spoerke[1], George D. Bachand[1,2], Susan Rempe[1,2], Stephen Percival[1], Leo J. Small[1], Amanda Peretti[1], Pengyu Ren[3] and Elizabeth Wait[3]; [1]Sandia National Laboratories, United States; [2]Center for Integrated Nanotechnologies, United States; [3]The University of Texas at Austin, United States

There is a clear and growing need to develop new, environmentally friendly, cost-effective methods for harvesting of critical materials for energy applications including rare earth metals (REMs; lanthanides plus yttrium and scandium) and other metals vital to rapidly growing technologies, such as batteries. These critical materials, however, are often found in dilute concentrations or in complex mixtures, making them difficult and expensive to harvest and separate. We are exploring a bio-inspired approach to capturing critical metals, following examples set by biological entities, such as methyltrophic bacteria, which are capable of highly efficient and effective capture and concentration of REMs. Here, we describe our combined computational and experimental efforts to understand the key interactions between solvated ions, water, and functional ligands that are responsible for biology's remarkable ion harvesting capacity. We then use this understanding to inform the design of synthetic systems aimed at effective harvesting of energy-critical materials. We describe the efficacy (and limitations) of engineered peptide, polymer, and nanomaterial systems capable of efficient, reversible capture of target mineral elements. Following inspiration from biology promises to reveal key insights needed to unlock new routes to cost-effective harvesting of materials critical to emerging energy applications.
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3:00 PM BREAK

3:30 PM *EN07.03.05
Adsorption And Intercalation of Rare Earth Elements In Micas: What Can We Learn About Separation of Rare Earth Elements Sardar B. Alam[1], Dapeng Jing[2], Eshita Samajpati[3], Alberto Perez-Huerta[3], Paul p. Spry[2], Shawn M. Kathmann[4] and Tanya Prozorov[1]; [1]US DOE Ames National Laboratory, United States; [2]Iowa State University of Science and Technology, United States; [3]The University of Alabama, United States; [4]Pacific Northwest National Laboratory, United States

Rare earth elements (REEs) are essential to the economic growth and national security of the United States. Increasingly, the supply chain of these critical minerals becomes vulnerable to disruptions. To exploit secondary sources of REEs effectively, there is an urgent need to learn about the localized environment of REEs in these sources, thereby enabling enhanced recovery and separation approaches optimized across a broad variety of REE and sources, with greater efficiency and selectivity. Regolith-hosted ionic-adsorption clay minerals preferentially adsorb heavy REEs (HREEs) released through the weathering and dissolution of granites and igneous rocks by rainwater. This REE-containing water then flows through the clays, resulting in a natural separation process. The most soluble and lightest elements (LREEs) pass through clays, while the least soluble and heaviest remain adsorbed, resulting in the formation of heavy REE-enriched minerals with minable concentrations from 50 to 1500 ppm.

In contrast, in micas, the REE observed retention trend is reversed, with the light REEs adsorbed at larger amounts and intercalating deeper into the mineral structure, compared to HREEs. By determining the speciation, spatio-chemical environment and quantum mechanical interactions and polarity of rare earths in micas, we are working to obtain the information on key issues affecting REE adsorption, including structural, electrostatic and hydration effects, coordination and oxidation state of the RE ions in these natural layered minerals.

4:00 PM EN07.03.06
Mechanically Strengthened High Magnetic-Performance Sm-Co Sintered Magnets Through Microstructure Engineering Baozhi Cui, Xubo Liu, Ikenna C. Nlebedim and Jun Cui; Ames Lab, United States

As a critical functional material, Sm-Co sintered magnets have been used for energy, information, defense, manufacturing, and health technologies.

However, the utilization of these magnets is restricted by their brittleness.
Sm-Co sintered magnets with improved mechanical properties and well-maintained magnetic properties have been designed and fabricated *via* additive-modified microstructure engineering. A small amount of Sm_2O_3 fine particulates (e.g., 0-3 wt%) has been incorporated into the $Sm_2(CoFeCuZr)_{17}$ sintered magnet to refine the grain size by up to approximately 50% and narrow the grain size distribution. Doping 3 wt% Sm_2O_3 increases the flexural strength by 62% while maintaining magnetic performance.
Both grain-refined unimodal microstructure and heterogeneous laminated coarse/fine grain microstructure were strategically designed and formed. Numerical micromechanics simulation indicates that the fracture is dominated by intragranular mode. The mechanical strength is mainly enhanced by additive-induced grain refinement.
These mechanically strengthened high magnetic-performance magnets will be more cost-effective, efficient, and robust for various functional applications.

4:15 PM EN07.03.07
Development of Layered Oxides for Electrochemically Driven Li Extraction from Dilute Li Sources Grant Hill and Chong Liu; University of Chicago, United States

Due to the rising demand of Li-ion battery powered vehicles, the lithium supply chain is projected to experience strain in the coming decades. This strain can be mitigated by developing new Li extraction methods that can access unconventional Li sources such as seawater. Electrochemical Li extraction has demonstrated high selectivity and recovery rates from dilute Li sources; the insertion host material selection plays a key role in the overall performance. However, few materials have been explored nor have materials been tailored for Li extraction from these multi-cation solutions. With this in mind, we developed a core-shell structured $(NaLi)_{1-x}CoO_2$ by non-Faradaic ion-exchange using parent $LiCoO_2$ with Na ions. Using electrochemical intercalation, this material successfully extracted Li from 1:20,000 Li: Na aqueous solution to 7.6:1 Li: Na, which is a Li selectivity of 1.5 x 10^5 over Na. Based on the same principles, we expanded the capacity and lifetime for layered cobalt oxides using electrochemically assisted ion-exchange. Parent $Na_{1-x}CoO_2$ was used to extract dilute Li and maintain high selectivity for multiple Li extraction sequences. After significant structural changes from the first Li extraction, high Li recovery performance can be maintained over multiple extraction sequences. Additionally, we also report C-rate dependence during the deintercalation recovery step, indicating the importance of method development for optimizing material performance. This work highlights the need for further understanding of layered oxides for Li extraction and the potential of system design for improved Li recovery capacity and lifetime.

4:30 PM EN07.03.08
The Role of Solid Solutions in Iron Phosphate-based Electrodes for Selective Electrochemical Lithium Extraction Gangbin Yan and Chong Liu; University of Chicago, United States

The lithium supply issue mainly lies in the inability of current mining methods to access lithium sources with dilute concentrations and complex chemistry. Electrochemical intercalation can enable lithium extraction from dilute water sources. However, the co-intercalation of lithium and the main competitor, sodium ions, occurs during extraction. The response of host materials to this process is not fully understood. This aspect limits the rational material design for improving lithium extraction.

In this talk, using one-dimensional (1D) olivine iron phosphate ($FePO_4$) as a model host, I will introduce the co-intercalation behavior of lithium and sodium ions and the control of lithium selectivity through intercalation kinetic manipulations. By combining computational and experimental investigations, we noticed that lithium- and sodium-rich phases tend to separate in the host. Exploiting this mechanism, I will discuss how the sodium-ion intercalation energy barrier can be increased by using partially filled 1D lithium channels generated via non-equilibrium solid-solution lithium seeding or remnant lithium in the solid solution phases. Furthermore, the lithium selectivity enhancement during co-intercalation shows a strong correlation with the fractions of solid-solution phases with high lithium content (i.e., Li_xFePO_4 with $0.5 \leq x < 1$). Finally, I will describe how the host material's particle morphology, size, and defect content could affect the solid-solution formation pathway, which further influences Li selectivity.

SESSION EN07.04: Rare Earth and Lithium Session II
Session Chairs: Long Luo and Kelsey Stoerzinger
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2007

8:15 AM *EN07.04.01
Molecular-Level Understanding of Mineral-Water Interfaces for Improved Beneficiation of Rare Earth Ores Vyacheslav Bryantsev; ORNL, United States

The criticality of rare-earth element (REE) resources requires responsible and efficient extraction of these elements from mined ores. These elements are often present in mineral deposits at levels well below those economically exploitable, occurring as complex mixtures of rare earth intermixed with commercially valueless, or gangue, minerals. As such, they must undergo extensive processing to ultimately isolate the rare earth in elementally pure forms for use in their respective applications. However, physical processes such as gravity separation and chemical approaches such as froth flotation by which REEs are extracted from their minerals have remained relatively unchanged over the last century, highlighting the need for more efficient strategies for extracting REEs from mined ores. Inspired by natural biomineralization, we seek to discover fundamental principles of molecular recognition at mineral-water interfaces and apply them for selective separation of rare earth from complex mixtures. In this talk, I will give several examples of how we develop an in-depth understanding of key underlying molecular interactions at the surface of REE-bearing bastnaesite, xenotime, and monazite minerals. Such advances are possible by employing a multimodal approach combining density functional theory calculations, calorimetry measurements, and multiple surface-sensitive spectroscopic techniques, including vibrational sum frequency generation, attenuated total reflectance Fourier transform infrared, Raman, and X-ray photoelectron spectroscopies. We anticipate that our extensive, molecular-level understanding of water and collector molecules adsorption on the REE mineral surfaces will provide insights into the design of more efficacious collector ligands for rare-earth separation from complex mixtures and lean sources.

8:45 AM *EN07.04.02
Modelling the Uptake, Transport and Separation of Multiply Charged Ions Through MoS_2 Membranes George C. Schatz; Northwestern University, United States

This talk will present recent studies of the Schatz group in collaboration with the Chong Liu and her group concerning the uptake and transport of multiply charged ions (Cu^{2+}, Pb^{2+}, lanthanides) through membranes that consist of stacked MoS_2 layers. Two levels of theory have been considered: electronic structure calculations using VASP, and molecular dynamics using empirical potentials. The electronic structure calculations involve studies of ion hydration both in the bulk and inside the membrane with models that contain 10-60 explicit water molecules, along with implicit water. These calculations are able to capture important features of the experiments concerning ion-solvent coordination number, membrane interlayer separation, relative binding energy of ions in the membrane, and how hydration varies with location of the ion and whether the MoS_2 is or isn't functionalized with acetate. This leads to a realistic picture of the uptake experiments. Our MD studies of ion transport and separation are able to provide qualitative understanding of the dependence of ion dehydration that takes place as the ion enters the membrane, and dependence of diffusion on strength of interaction of the ion with the membrane, but the empirical potentials are apparently not accurate enough to capture subtle effects that reflect chemical interactions of the ions with the membrane, especially concerning variation of the interlayer separation while the ion diffuses, and the transport of mixtures of different ions.

9:15 AM EN07.04.03
Surface X-Ray Studies of Rare Earth Group Ion Transport Pathway on Functionalized Monolayer MoS_2 Maoyu Wang and Hua Zhou; Argonne National Laboratory, United States

Rare earth elements (REs) have been identified as critical elements with short-term supply risks. They are essential in modern technologies and devices such as permanent magnets, optical fiber, and medical imaging agents. [1,2] REs exhibit very similar chemical properties but varied electronic properties, and their application requires high purity of every single element. Therefore, achieving effective and efficient separation among REs from one another has been the challenge since their discovery and this task is especially critical now to enable recycling to secure the REs supply. Currently, the solvent extraction used in industrial productions induces a negative impact on the environment due to the drawbacks of energy and chemical intensiveness. [3-5] Based on the two important properties of REs: ionic radius (decreasing with an atomic number) and Lewis acidity (increasing with atomic number), [2] we proposed to create two-dimensional (2D) solid ionic channels with stacked 2D materials (such as MoS2) that are able to modulate the dehydration, transport, and hydration of REs. To achieve selective transport of REs by rational design, a better understanding of the binding and conduction of REs ions through the 2D channels is required. Hence, we established an understanding of binding thermodynamics on the single monolayer MoS2 with the functionalized surface as a model system to determine how lanthanide RE ions contact and interact with pristine and surface functionalized monolayer 2D materials. We combined surface X-ray diffraction (crystal truncation rod) and gracing incidence X-ray absorption spectra to provide a precise local coordination configuration. This allows us to create an accurate molecular-level structural model for the electronic structure computation and modeling, which would be better to reconstruct the ion transport pathway and realize the selectivity control among REs. The outcomes will have immediate impact to enabling new energy efficient separation methods, especially transport-based separation technologies (membrane separation), to be applied to REs extraction, separation, and recycling.

9:30 AM EN07.04.04
Computational Optimization of Nickel Metal Recovery from Li-ion Cathodes for a Circular Economy in Energy Storage Julia Yang[1,1], Amanda Ooi[2], Kyle Bystrom[1], Ah-Hyung Alissa Park[2,2,2] and Boris Kozinsky[1,3,1]; [1]Harvard University, United States; [2]Columbia University, United States; [3]Robert Bosch LLC Research and Technology Center, United States

In order to achieve the clean energy transition for our sustainable future, energy-relevant materials including critical minerals are required in unprecedented quantities. Thus, it is urgently needed to develop metal recovery methods for unconventional resources such as increasingly Nickel (Ni)-rich Lithium (Li)-ion battery (LiB) spent cathodes (i.e., NMC (containing Ni, Manganese (Mn), and Cobalt (Co)) or NCA (containing Ni, Mn, and Aluminum). Ethaline, a green, tunable, and non-toxic deep eutectic solvent (DES) with a 2:1 molar ratio of ethylene glycol and choline chloride, has been shown to recover critical metals such as Ni from black mass, albeit at the expense of its thermal decomposition and generation of toxic byproducts.

In this work, we use first-principles calculations and electrodeposition to demonstrate that ethaline can in fact be used as a stable solvent to recover Ni from NMC111. We quantify the extent of Ni recovery using ICP-OES/MS and characterize the purity and composition of electrodeposited Ni with SEM/EDX, FTIR, and XPS. To understand the apparent sluggish transport of divalent Ni in ethaline, we use on-the-fly active learning (using FLARE: Fast Learning of Atomistic Rare Events [1]) and machine learning methods to approximate the potential energy surface and recommend ways to tune ethaline to optimize divalent Ni transport and subsequently, more efficient Ni recovery.

[1] Vandermause, J., Torrisi, S.B., Batzner, S. et al. On-the-fly active learning of interpretable Bayesian force fields for atomistic rare events. npj Comput Mater 6, 20 (2020)

9:45 AM BREAK

10:15 AM *EN07.04.05
Rare Earth Ions at Aqueous Soft Interfaces Amanda J. Carr, Seung Eun Lee, Srikanth Nayak, Raju R. Kumal and Ahmet Uysal; Argonne National Laboratory, United States

The increasing demand in electronic display, battery, catalysis, and magnet technologies requires better refinery and recycling processes for rare earths and other critical materials. Some of the common separation technologies include liquid liquid extraction (LLE), membranes, sorbents, and capacitive deionization. In all of these separation processes, rare earth ions adsorb on or transfer through an interface. Therefore, understanding the molecular-scale details of trivalent ion adsorption at these interfaces is crucial to developing high capacity, high throughput, and highly efficient separation technologies. LLE is one of the go-to methods in heavy element separations. In LLE, metal ions are transferred from an aqueous phase into an organic phase with the help of amphiphilic extractant molecules. The aqueous phase speciation, interfacial interactions, and the organic phase structures create a complex free-energy landscape that require a detailed investigation. We pay special attention to interfaces. We combine multiple surface sensitive techniques to investigate extractant-metal interactions and interfacial water structures. I will emphasize the connections and correlations between the interfacial structures and the rare earth extraction trends.
Graphene based membrane and sorbent materials have been extensively studied in recent years, due to their mechanical stability, unique structural and functional properties, tunability, and high surface area. Graphene based materials, alone or as additives, can be very useful under harsh conditions of heavy element separations, where the stability of polymer based materials fail. In spite of their popularity, molecular scale details of ion adsorption at graphene and graphene oxide interfaces are poorly understood. Especially, understanding the interplay between the ion hydration and adsorption is very challenging at these interfaces. We utilize *in situ* synchrotron X-ray scattering and vibrational sum frequency generation (VSFG) spectroscopy techniques to study trivalent ion adsorption at graphene and graphene oxide surfaces. Our initial studies focus on the two end points of the broad graphene based materials spectrum. High quality pristine graphene and graphene oxide.

10:45 AM *EN07.04.06
Recycling of Critical Materials to Meet Clean Energy Goals Yoshiko Fujita; Critical Materials Institute, Idaho National Laboratory, United States

The goal of the U.S. Department of Energy's Critical Materials Institute (CMI) is to increase the resilience of supply chains for critical materials essential to the clean energy transition and decarbonization. These materials (e.g., rare earth elements, lithium, cobalt, nickel, graphite) are contained in components and devices indispensable to electric vehicles and renewable energy adoption, such as magnets and motors, hard disk drives, and batteries. In addition to developing technologies to enhance primary production and developing substitute materials and processes less reliant on critical materials, expanding and improving the recycling and recovery of materials from end-of-life products will be necessary. Current recycling methods such as pyrometallurgy can recover most of the metal value in end-of-life products, but rare earth element (REE) and lithium recovery are challenging. Moreover, pyrometallurgy and other conventional end-of-life recovery approaches often have significant energy and environmental costs. CMI has focused on developing more environmentally sustainable approaches for critical material recycling, often coupled with co-recovery of high value materials such as copper and gold that can improve economic returns. These lower impact processes may include unconventional methods such as microbiology and electrochemistry in the recovery strategy, as well as novel chemistries. Researchers must consider upstream and downstream operations, and in some cases develop complete flowsheets to maximize recovery value. Iterative economic and environmental assessments during development mitigate the risk of funding approaches with limited commercial utility. This presentation will cover a selection of critical material recycling approaches developed within CMI, an Energy Innovation Hub funded by the Advanced Manufacturing Office of the U.S. Department of Energy.

11:15 AM EN07.04.07
Ultrafast Lithium Recovery by Microwave Assisted Lithium-Ion Battery Cathode Recycling Using Deep Eutectic Solvents Sohini Bhattacharyya, Salma H. Alhashim and Pulickel Ajayan; Rice University, United States

Lithium-ion batteries (LiBs) are crucial in the move towards a net-zero carbon economy. With the spurt in the electrical vehicles sales, LiB sales are touted to triple from 250 million units in 1999 to 700 million 2030. This in-turn has culminated in the double-edged problem of LiB waste management on one hand and supply of critical materials (e.g., cobalt, nickel, graphite, lithium, and manganese) on the other. These essential materials have limited reserves, many of which lie in conflicted regions and war zones. Considering the current trends in mobile and stationary LiBs usage, the demand for graphite, lithium, and cobalt is expected to increase by almost 500% by 2050, whereas a shortage of nickel is estimated to arise within the next 5-6 years. Thus, the recycling of LiB systems is essential to reduce environmental hazards while establishing a circular green economy, diminishing the need for extensive mining. Among the prevalent methods for recycling LiB cathodes, hydrometallurgy, involving the use of a lixiviant to dissolve the precious elements from the cathodes, is simple, requires less energy and shows high efficiencies. However, conventional methods of hydrometallurgy use concentrated acids and harsh solvents, e.g., peroxides which that end up adversely affecting the environment. Although green solvents like organic acids or deep eutectic solvents (DESs) have been explored as lixiviants for hydrometallurgical LiB cathode recycling, they require much higher temperatures and longer times as compared to concentrated inorganic acids, making them economically unsustainable.[1] DESs, comprising a hydrogen bond donor and acceptor, are environmentally benign, biodegradable and low cost. They have exceptional metal dissolution properties that has been used in metal electrodeposition, extraction, and recovery, and are also promising lixiviants for the hydrometallurgical leaching of LiB cathodes[2] and do not need any additional reducing agents. In this work, we report the ultrafast recovery of Li from LiB cathodes in a Choline chloride (ChCl):Ethylene glycol (EG) based DES. We observe Li leaching efficiencies as high as ~80% within 5 mins and ~95% in 15 mins from commonly used cathode materials, e.g., NMC ($LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$) and NCA ($LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$). The leaching efficiency remains almost unaffected by lowering the temperature significantly or by increasing the solid-to-liquid ratio. A combination of experimental results and DFT calculations have been used to investigate the leaching mechanism, where EG acts as a hydrogen bond donor, while Cl^- from ChCl assists in solvation of the cations. While Co and Ni form terachlorometalate complexes, Li remains in close contact with Cl^- ions in a van der Waals type interaction, which is energetically and kinetically more favorable, leading to its faster leaching. The increased concentration of ChCl in the DES improves the leaching efficiency due to the higher availability of Cl^- ions. The Li thus leached is recovered by precipitation in the form of Li_2CO_3. This work delineates an economically viable and environmentally benign pathway for LiB cathode recycling, while also providing insights into its leaching mechanism, which will be instrumental in the future design of such lixiviants.

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(2) Tran, M. K.; Rodrigues, M.-T. F.; Kato, K.; Babu, G.; Ajayan, P. M. Deep Eutectic Solvents for Cathode Recycling of Li-Ion Batteries. *Nat Energy* **2019**, *4* (4), 339–345. https://doi.org/10.1038/s41560-019-0368-4.

11:30 AM EN07.04.08
Stimuli-Responsive Ligand Systems for Rare Earth Element Separation Ilja Popovs; Oak Ridge National Laboratory, United States

Rare earth element separation is one of the most challenging demixing problems of the modern age. The difficulty of separating lanthanides into groups stems from their chemical similarity in the most prevalent +3 oxidation state and only marginal change in ionic radii of the cations across the series. Even more challenging is the adjacent lanthanide separation, which in conventional solvent extraction process requires hundreds of stages to isolate individual REE in high purity. Additionally, overall process consumes large volumes of chemicals and produces waste. We have designed an electrochemically-driven separation of REEs using smart ligand. Depending on the redox state of the ligand, it can be soluble in either organic or aqueous phase, thus imparting the solution with selectivity towards heavy lanthanides. By applying electrical current or through addition of reducing or oxidizing reagent, we can control partitioning of both the ligand and the lanthanide of interest in the phase of choice. Dual ligand system allows efficient separation of near adjacent lanthanides with high efficiency. Mechanistic considerations, ligand design strategy and REE separation performance of this novel system will be presented.

11:45 AM EN07.04.09
Investigating Molecular Systems Based on Rare-Earth Metals via SX-STM Sarah Wieghold[1], Nozomi Shirato[1], Kyaw Zin Latt[1], Volker Rose[1], Eric Masson[2] and Saw Wai Hla[1,2]; [1]Argonne National Laboratory, United States; [2]Ohio University, United States

Rare-earth metals exhibit promising optical, magnetic, and catalytic properties and are used in a wide variety of energy conversion applications and emerging quantum technologies. Recently, molecular systems such as coordination complexes and supramolecular networks have attracted attention due to their potential to precisely control the location and local environment of the rare-earth atoms by incorporating them into a molecular scaffold. These molecular approaches provide an engineering control in which the metal ion, bond length, angle and functionality of the organic linker can be varied depending on the application.

In this contribution, we present a synchrotron x-ray scanning tunneling microscopy (SX-STM) approach to investigate molecular systems based on various rare-earth atoms and organic linker moieties at the nanoscale. We use STM to study the inter- and intramolecular interactions of supported molecular systems at the nanoscale. Further, we use x-ray absorption near edge spectroscopy (XANES) via SX-STM to probe the local oxidation state and change in the total electron yield (TEY) depending on the rare-earth concentration. This work provides fundamental understanding of local chemical environment of rare-earth ions caged inside the molecular scaffolds and will be useful for designing novel rare-earth molecular systems for potential applications.

SESSION EN07.05: PGE Nanomaterials II
Session Chairs: Dongsheng Li and Ahmet Uysal
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2007

1:30 PM *EN07.05.01
Grain Boundary Rich Noble Metal Nanoparticle Assemblies—Synthesis, Characterization and Reactivity Long Luo; Wayne State University, United States

Grain boundaries (GBs) have been previously used extensively to control mechanical strength, plasticity, and conductivity, and recently, the interest in GBs has extended to their catalytic properties. Here, we present a comprehensive study on the synthesis, characterization, and reactivity of grain-boundary (GB)-rich noble metal nanoparticle (NP) assemblies. A facile and scalable synthesis of Pt, Pd, Au, Ag, and Rh NP assemblies is developed, in which NPs are predominantly connected via Σ3 (111) twin GBs, forming a network. Driven by water electrolysis, the random collisions and oriented attachment of colloidal NPs in solution lead to the formation of Σ3 (111) twin boundaries and some highly mismatched GBs. This synthetic method also provides convenient control over the GB density without altering the crystallite size or GB type by varying the NP collision frequency. The structural characterization reveals the presence of localized tensile strain at the GB sites. The ultrahigh activity of GB-rich Pt NP assembly toward catalytic hydrogen oxidation in air is demonstrated, enabling room-temperature catalytic hydrogen sensing for the first time. Finally, density functional theory calculations reveal that the strained Σ3(111) twin boundary facilitates oxygen dissociation, drastically enhancing the hydrogen oxidation rate via the dissociative pathway. This reported large-scale synthesis of the Σ3 (111) twin GB-rich structures enables the development of a broad range of high-performance GB-rich catalysts.

2:00 PM EN07.05.02
Relationships Between Structural Inhomogeneities at Atomic-Scale and Functional Properties Hyoju Park, Micah Prange, Peter V. Sushko and Dongsheng Li; Pacific Northwest National Laboratory, United States

Catalytic activity is highly influenced by the bonding of reactants to solid surfaces to modulate the energetic barriers that must be overcome. The strengths of these bonds can be modified by the choice of material composition and control of the atomic arrangements. For example, researchers have found that deformation in the crystal lattice (strain) significantly affects catalytic activity. In turn, the strain distribution can be tailored by defects, grain boundaries, and the interaction of the catalyst with underlying support.
In this work, we employ high-resolution transmission electron microscopy (TEM) to investigate the atomic structures of heterogeneous catalysts (e.g., Pt supported on TiO_2 nanoparticles), focusing on the detailed characterization of their structure, including bonding states, strain distribution, defects, and grain boundaries, especially at the contact areas of nanoparticle assemblies and the interfaces of catalyst with underlying support. In addition, using in-situ TEM, we explore kinetics and dynamics of catalytic reactions upon exposure to various conditions at the surfaces of catalysts and the interfaces of catalyst and support materials by observing the evolution of the surface structures of nanoparticles and the active epitaxial sites at the interfaces. The experimental results based on the structural analysis and catalytic activity tests corroborated with *ab initio* simulations based on the density functional theory to explore the structure-function relationships and establish factors responsible for the enhanced catalytic activity. This provides an insight that allows utilizing the structural inhomogeneities and designing surface structures and compositions for tailored functionality of catalytic materials.

2:15 PM EN07.05.03
Effect of Contacts in Assemblies of Nanoparticles on Hydrogen Adsorption and Kinetics Nanjun Chen[1], Hyoju Park[1], Xin Geng[2], Micah Prange[1], Long Luo[2], Dongsheng Li[1] and Peter V. Sushko[1]; [1]Pacific Northwest National Laboratory, United States; [2]Wayne State University, United States

Numerous studies have demonstrated a strong coupling between the lattice strain and catalytic activity of platinum group elements. Understanding the strain–activity relationships require creating new types of strained nanoscale materials. Here, we investigate strain distribution in assemblies formed by attachment of metastable Pt and Pd nanoparticles. Through the formation of coherent and incoherent interfaces at the particle-particle contacts, these systems give rise to unusual coordination environments and strain states that may affect their catalytic activity. Transmission electron microscopy observations suggests that octahedral nanoparticles form preferentially face-to-face, corner-to-corner, and corner-to-face contacts. We use classical molecular dynamics to simulate the nanoparticles attachment process leading to the formation of particle-particle contacts and to create plausible atomistic models of these contacts depending on the relative orientation of the nanoparticle. Characteristics of the atomic sites in the vicinity of the contacts regions, including coordination number and local interatomic distances, allow us to relate the structure of the particle-particle contacts and the corresponding strain distributions to their ability to bind and accumulate hydrogen species. These predictions are then validated against *ab initio* simulations and further linked to the local electronic properties of the interfacial atoms. This study deepens our mechanistic understanding of the role of nanoparticle contacts in hydrogen adsorption and provides suggestion on a viable path towards rational design of hierarchical structures with a high affinity to hydrogen.

2:30 PM EN07.05.04
Artificial Intelligence Multiscale Modeling for Highly Ordered Pt@PtCo Core-Shell Catalysts as Durable Electro-Catalysts in the PEM Fuel Cell Jong Min Lee[1], Song Jin[2,3], Mun Seon Kang[1], Minseon Park[4], Sung Mook Choi[1] and Min Ho Seo[5]; [1]Korea Institute of Energy Research, Korea (the Republic of); [2]Korea Institute of Materials Science (KIMS), Korea (the Republic of); [3]Gwangju Institute of Science and Technology (GIST), Korea (the Republic of); [4]Pohang University of Science and Technology (POSTECH), Korea (the Republic of); [5]Pukyong National University, Korea (the Republic of)

Development of highly active electrocatalysts that are cost competitive takes the center stage in research fields for next-generation electrochemical energy conversion and storage systems like fuel cell and metal-air battery. Regarding the systems for commercialization, there are various challengeable issues, which should overcome sluggish kinetics and stability on the electrocatalyst for the aimed reactions such as oxygen reduction reaction (ORR) occurred in the high over-potential and harsh conditions. Although there was huge technological advancement as minimizing the usage of a noble metal or developing non-precious owing to many attempts to reach the purpose in the past decade, it still needs further improvement in order to gain acceptance in the market. To find new material or optimize it, the efficient way would be initialized from the knowledge of the underlying physical and chemical mechanisms in a material system. For this reason, therefore, fundamental studies using quantum mechanics (QM) along with experimental confirmation have been commonly conducted to explain the activity and stability of oxygen reactions. These approaches are very successful and provide fundamental insight to scientists and researchers. Nevertheless, calculative simulations are still the restrictions to obtaining trustable data and predicting correct consequences, especially on large-scale modeling. This talk will present recent efforts for accurate modeling with experimental data. We predicted and validated the ORR activity and stability for PtCo alloy and Pt@Co core-shell structure in density functional theory (DFT). The force field, which is an efficient way of describing the dynamics with large-scale simulations, was developed to simulate large-scale models via machine-learning Force Fields. This synergetic approach using both computational models and experiments with physicochemical analyses would accelerate to find new materials and optimize catalyst performance. This work was supported by the NRF of Korea Grant and by the Technology Innovation Program of MOTIE [NRF- 2022R1A2C2093090 & 20019175]

2:45 PM BREAK

3:15 PM *EN07.05.05

Understanding Competitive Electrochemical Reactions on Strained Surfaces Kelsey A. Stoerzinger[1,2]; [1]Oregon State University, United States; [2]Pacific Northwest National Laboratory, United States

In heterogeneous electrocatalysis, reactants adsorb on a materials surface, and subsequently transfer electrons to or from the solid in conjunction with ionic motion, forming and breaking chemical bonds. This complex interface—between a solid surface and a reactive gas and/or liquid—can change dramatically with the electrochemical potential that drives such reactions. For example, materials can change oxidation state (where changes in the surface oxidation state are associated with adsorbates, and bulk changes require diffusion of oxygen through the material itself) or change their structure/phase. Such changes in a catalyst are intimately linked to their functionality and activity for desired electrochemical reactions.

We have been investigating how metal electrocatalysts react with species from aqueous solution by electrochemical approaches with complementary spectroscopy. We are particularly motivated by complex reaction environments where multiple species – such as reducible reactants and protons – compete for sites on the surface, influencing the activity for reduction reactions. This competition and resultant activity depends on the applied voltage, but also characteristics of the electrocatalyst itself, such as strain and the presence of defects. We will share how such changes in a material's bulk influence competitive processes on the surface and the formation of hydride phases under electrochemical conditions.

3:45 PM EN07.05.06

Catalytic Performance Promotion of Pd Cluster Towards H_2O_2 Production by Potential-Driven Coordination Adjustment Zhiping Deng and Xiaolei Wang; University of Alberta, Canada

Electrochemical synthesis of hydrogen peroxide has been emerging as an appealing process for the onsite production of this chemically valuable oxidant, while its commercial application is still hindered by the development of efficient electrocatalyst. Herein, we design an efficient electrocatalyst for the electrochemical synthesis of H_2O_2 consisting of Pd cluster loading on hollow mesoporous carbon spheres (HMCS). Pd coordination environment is well designed with S in the first coordination sphere and O in the second coordination sphere. The as-prepared material exhibits superior performance with high H_2O_2 selectivity (maximum value: 99%) over a wide potential range of 0 to 0.6 V. Moreover, a high kinetics mass activity (4.059 A mg^{-1} at 0.45V) of Pd_x/HMCS is achieved, which is almost three times larger than the state-of-the-art Pd-Hg alloy catalyst. What's more, in neutral electrolyte, Pd_x/HMCS also a positive onset potential of 0.647 V and high H_2O_2 selectivity of 84-93% within a wide potential range. The excellent performance can be attributed to the unique Pd cluster structure and optimized Pd coordination environment, especially the oxygen modification on HMCS support. In-situ Raman results reveal that under potentials, oxygen atoms transfer from the second coordination sphere (oxygen containing functional groups on HMCS) to the first coordination sphere (Pd-O bond). Density functional theory (DFT) calculations confirm that such oxygen coverage helps optimize the *OOH binding energy on Pd surface, resulting in significantly enhanced catalytic performance towards H_2O_2 production. This work reveals the structure difference between in-situ and ex-situ situations, proposes a new mechanism for the improved performance, and provides new insights into the future catalyst design.

4:00 PM EN07.05.07

The Study of Surface Stability of Pt_3Co Alloys Under Oxygen Pressure Using AP-XPS and AP-STM Jeongjin Kim[1], Jeong Young Park[2], Hiroshi Kondoh[3], Toyoshima Ryo[3] and Bongjin S. Mun[4]; [1]Brookhaven National Laboratory, United States; [2]KAIST, Korea (the Republic of); [3]Keio University, Japan; [4]Gwngju Institute of Science and Technology, Korea (the Republic of)

The Pt_3Co alloys has been the choice of catalyst for the proton-exchange membrane fuel cell due to significantly higher oxygen reduction rate (ORR) than pure Pt catalyst. While the Pt_3Co catalyst received much attentions for its excellent performance and extensive lifetime in fuel cell applications, the basic questions such as the role of Co in ORR and the chemical active states of Co elements, have not been clearly answered. To address the basic knowledges on these aspects, the study on a model system is highly necessary.

In this presentation, utilizing both ambient pressure X-ray photoelectron spectroscopy and scanning tunneling microscopy, our investigation on the surface chemical states and surface morphology of Pt_3Co (111) single crystal will be presented. Under the elevated oxygen pressure and temperature, the presence of surface segregation of transition metals is clearly observed. However, the surface morphology and chemial states in Pt_3Co are slightly different from those of Pt_3Ni alloy. To identify the chemically active site on surface, the reactivity of the nanostructured oxides and Pt is tested under CO oxidation condition, revealing important information on the role of interfacial oxygen on the nanostructured metal oxides.

4:15 PM EN07.05.08

Synthesis and Characterization of Pt and Pd Nano-Shells to Optimize the Performance and Reduce the Cost of Expensive Catalysts Alexandre Foucher and Frances Ross; Massachusetts Institute of Technology, United States

The transition to sustainable and efficient industrial processes requires the development of novel nano-catalysts to enhance the production of chemicals and energy. Unfortunately, many catalysts used for important processes are composed of the most expensive transition metals. For instance, Pt is an ideal catalyst for the production of H_2 or for fuel cells, while Pd is an essential catalyst for CO oxidation in catalytic converters or for the hydrogenation of alkynes. To reduce the use of these two metals and ultimately achieve sustainable and cost-efficient catalysis, we synthesized monodisperse core-shell Cu-Pt and Cu-Pd particles with a solvothermal method. The Cu core was then removed through thermal oxidation, which caused the migration of Cu oxide through the Kirkendall effect, and left empty shells of Pt and Pd. The thickness and size of the shells could be controlled. *In situ* transmission electron microscopy at high temperatures and under a gaseous atmosphere demonstrated the stability of the samples. The core-shell configuration allows an increased surface area of exposed Pt and Pd to catalyze gases or liquids. Oxygen reduction reaction (ORR) measurements on the Pt nano-shells and CO oxidation analysis on Pd nano-shells showed enhanced activity and stability. Thus, the design of these nano-shells with enhanced functionality can help to achieve sustainable supply of expensive materials for the chemical industry.

4:30 PM EN07.05.10

Superior Performance and Stability of Anion Exchange Membrane Water Electrolysis—Non-Precious Electrocatalysts for the Oxygen Evolution

Reaction Ju-chan Yang[1], Jaehoon Jeong[1], Ji-hoon Lee[1] and Sung Mook Choi[1,2]; [1]Korea Institute of Materials Science, Korea (the Republic of); [2]University of Science & Technology, Korea (the Republic of)

The application of electrocatalysts with high activity to a practical water electrolysis cell is a crucial challenge for the production of pure hydrogen and commercialization of the water electrolyzer. Herein, the Cu–Co oxide electrocatalysts were synthesized for the OER through pH-controlled co-precipitation to apply as the anode electrode of AEMWE. We developed nano-sized $Cu_{0.5}Co_{2.5}O_4$ with abundant oxygen vacancies very easily and creatively by using the difference in precipitation rate with the pH of Cu and Co. It was confirmed that $Cu_{0.5}Co_{2.5}O_4$, which has been optimized by pH control, has many oxygen vacancies and a large amount of Co3+, which is an active site for the OER. Because of this, it exhibits superior catalytic activity and long-term stability in the half-cell tests. Recent reports on electrocatalysts for water electrolysis have only focused on catalytic activity in half-cell tests. An important point for the commercialization of water electrolysis is that they should show excellent performance even when the catalyst is applied to an electrolyzer. This study not only compared the catalytic activity of the synthesized $Cu_{0.5}Co_{2.5}O_4$ catalyst but it also directly applied a full cell for the AEMWE system to confirm the performance of practical hydrogen production. The performance of the AEMWE cell was higher than that of any AEMWE cells reported in the literature, even compared to the AEMWE using IrO_2 as an anode.

SESSION EN07.06: Poster Session I: Critical Materials for Energy
Session Chairs: Chong Liu and Hua Zhou
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN07.06.01
Fabrication of ZnV2O4 Nanoparticles Embedded in Carbon Nanofibers as a Cathode Material for High-Performance Aqueous Zn-Ion Batteries
Jiwon Jung, Jeong-Ho Park, Na-Yeong Kim, Ilgyu Kim and Min Kyeong Gi; University of Ulsan, Korea (the Republic of)

Recently, lithium-ion batteries have led the related market. However, the price of Li is expected to increase continuously, leading to unbalance of demand and supply for LIBs used for electric vehicles (EVs) and energy storage systems (ESS). For replacing LIBs, electrically rechargeable aqueous zinc-ion batteries (ZIBs) have been spotlighted due to Zn's attractive properties, such as being environmentally friendly, low price, and high stability. Nevertheless, the low capacity of ZIBs is attributed to low-capacity cathode material, restricting their practical utilization. To increase the capacity of ZIBs, ZnV_2O_4 containing the Zn element has recently been considered. However, the ZnV_2O_4 cathode developed so far shows various problems of low electronic conductivity and low surface area limiting reaction sites. Here, we suggest ZnV_2O_4 nanoparticles embedded in carbon nanofibers (ZVO@CNFs) as a promising cathode material for ZIBs. The ZVO@CNFs were synthesized using the electrospinning process and heat treatments, including stabilization and carbonization. The fabricated ZVO@CNFs were investigated by SEM, TEM, XRD and XPS to confirm how can the ZVO nanoparticles form inside. In addition, Raman analysis was conducted to know the composition of ZVO@CNFs and crystal lattice information. The ZIB cell with the ZVO@CNFs was evaluated for its feasibility. Charge and discharge tests and rate tests were conducted for the ZIB cell with ZVO@CNFs, which delivered a specific capacity of approximately 300 mAh/g at a current density of 500 mA/g, and excellent stability for 250 cycles. CV(Cyclic Voltammetry) was conducted to determine the voltage window, reversibility, and impurities in the system where the redox reaction occurs.

5:00 PM EN07.06.15
Hydrothermally Synthesized Cobalt-Iron-Based Nanocomposite Doped Sulfur and Phosphorous for Energy Storage Application Shiva Bhardwaj[1,2], Rishabh Srivastava[1,2], Teddy Mageto[1,2] and Ram Gupta[1,2]; [1]Pittsburg State University, United States; [2]National Institute for Material Advancement, United States

The continuous use of fossil fuels for energy production leads to their depletion at a faster rate. The amount of energy produced using fossil fuels generates carbon dioxide(CO_2), leading to global warming. However, using these fossil fuels to create devices that store energy might decrease our dependency on fossil fuels and produces less CO_2. Various devices can store energy, like batteries, supercapacitors (SC), and fuel cells. Among these devices, SC outperforms others with several advantages, including high-power density, fast charge discharge, and low-cost production. This work introduces cobalt-iron-based nanocomposites prepared using a hydrothermal synthesis route followed by sulfurization and phosphorization. The crystallinity of nanocomposites has been confirmed using X-ray diffraction, where crystalline nature improves from as-prepared to sulfurized to phosphorized. The as-synthesized CoFe-nanocomposite exhibits a specific capacitance (C_{sp}) of 120 F/g at 1 A/g, along with a power density of 3752 W/kg and a maximum energy density of 4.3 Wh/kg. The results improved after sulfurization showing 183 F/g at 1 A/g with 3892 W/kg, 7.9 Wh/kg of power, and energy density. Furthermore, the phosphorized nanocomposite shows the best performance by exhibiting 252 F/g at 1 A/g and the highest power and energy density of 4183 W/kg, 10.1 Wh/kg. This shows that the results get improved more than twice. The electrochemical impedance spectroscopy study shows the lowest charge transfer resistance for the phosphorized nanocomposite. The 95% capacitance retention after 5000 cycles shows cyclic stability of phosphorized CoFe. Our research thus offers cost-effective and highly efficient energy storage devices.

5:00 PM EN07.06.02
Enhancing Selectivity Towards CO over Co/CeO_2 Catalyst for CO_2 Hydrogenation by Calcination Rena Oh[1], Xiaoyang Huang[2], Yanping Zheng[2], Ki Tae Nam[1], Gyeong-Su park[1] and Seong Keun Kim[1]; [1]Seoul National University, Korea (the Republic of); [2]Xiamen University, China

Seeking energy sources to supplant fossil fuel is a confronted task to mitigate atmospheric CO_2 concentration and suppress global warming problem. Electricity-based fuel (E-fuel), synthesized from green H_2 and CO_2, is one of solutions. Due to a thermodynamic unfavourability of C-C bond formation through direct CO_2 hydrogenation, synthetic fuels are usually generated by CO hydrogenation, i.e., Fischer Tropsch synthesis, which requires selective CO production by electro-catalytic CO_2 reduction or thermos-catalytic CO_2 hydrogenation. Here, we demonstrated a simple preparation method of Co/CeO_2 catalyst to increase the selectivity towards CO during CO_2 hydrogenation. Generally, Co-based catalysts of metallic Co nanoparticles with metal oxide support material are well-known for its selective production towards CH_4. However, we found that by using CeO_2 support calcined at an unusually high temperature, the CO selectivity significantly increased over Co/CeO_2 catalyst under atmospheric pressure at a wide range of reaction temperature. We investigated the microstructure of catalysts and identified the formation of reduced CeO_{2-x} surface layer in the CO-selective catalyst, corroborated by *in-situ* X-ray photoelectron spectroscopy and high-resolution transmission electron microscopy with electron energy loss spectroscopy. Based on the catalyst structure, we suggested that CO-production is correlated to an enhanced reduction of CeO_2 support and the reduced CeO_{2-x} may be preserved during CO_2 hydrogenation without sacrificial oxidation instead of metallic Co due to a weak metal-support interaction. In addition, the CO-selectivity further enhanced upon the additional pretreatment over the reduced catalyst, which is attributed to the formation of carbon structures encapsulating the Co surface.

5:00 PM EN07.06.03
Mechanism Investigation of Enhanced Electrochemical H_2O_2 Production Performance on Oxygen-rich Hollow Porous Carbon Spheres Zhiping Deng and Xiaolei Wang; University of Alberta, Canada

Electrochemical oxygen reduction is a promising approach for the sustainable decentralized production of H_2O_2, but its viable commercialization is hindered by the insufficient development of efficient electrocatalysts. Here, we demonstrate a promising carbon-based catalyst, consisting of oxygen-rich hollow mesoporous carbon spheres (HMCS), for selective oxygen reduction to H_2O_2. The as-prepared HMCS exhibits high onset potential (0.82 V) and half-wave potential (0.76 V), delivering a significant positive shift compared with its oxygen-scarce counterparts and commercial Vulcan carbon. Moreover, excellent H_2O_2 selectivity (above 95%) and electrochemical stability (7% attenuation after 10 hours operation) make this material a state-of-the-art catalyst for electrochemical H_2O_2 production. The outstanding performance arises from a combination of several aspects, such as porous structure-facilitation of mass transport, large surface area, and proper distribution of oxygen-containing functional groups modification on the surface. Furthermore, the proposed ORR mechanism on HMCS surface reveals that -OH functional groups help promote the first electron transfer process while other oxygen modification facilitates the second electron transfer. Furthermore, we investigate the porosity engineering effect on catalytic performance inconsistency through a material platform consisting of a series of HMCS samples. The performance comparison of HMCS samples in RRDE and Zn-air battery together with the simulation of diffusion behavior reveals that in low current density conditions large surface area is preferred but the mass transport governs the performance in high current density region. On account of the favorable porous structure, HMCS-8 nm delivers the most excellent practical performance (166 mW cm^{-2}) and performs well in the bifunctional Zn-air battery for the wastewater purification (70% RhB degraded after 2 min and 99% after 32 min).

5:00 PM EN07.06.04
***In Situ* Formed Nickel Silicide as a Recombination Layer for Perovskite/TOPCon Tandem Solar Cells** Dowon Pyun, Jiryang Kim, Dongjin Choi, Seok-Hyun Jeong, Changhyun Lee, Jiyeon Hyun, Ha Eun Lee, Sang-Won Lee, Hoyoung Song, Solhee Lee, Yoonmook Kang, Donghwan Kim and Hae-Seok Lee; Korea University, Korea (the Republic of)

Up to date, perovskite/silicon 2-terminal tandem solar cells have shown continuous improvement of efficiency. The majority of highly efficient tandem solar cells are employing transparent conductive oxide (TCO) as an interlayer to connect top and bottom subcells. However, TCO requires additional deposition process, such as sputtering, which can negatively affect the performance of bottom subcell especially in open circuit voltage. Furthermore, high cost and scarcity of indium in TCO could hinder commercialization of tandem solar cells in near future. In this work, nickel silicide was proposed as a new concept of in-situ recombination layer which can replace TCO. NiO_X was directly deposited on n^+ poly-Si and anealed at high temperature. During annealing, Ni atoms in NiO_X diffused into n^+ poly-Si, which results in formation of nickel silicide. Contact properties of NiO_X/n^+ poly-Si with 2 different interlayers (NiSi, ITO) were measured and compared with energy band diagram. Ohmic contact was confirmed with nickel silicide, while schottky contact with ITO. Furthermore, diffusion of Ni leads NiO_X film to be Ni-deficient, which can improve carrier extraction and also FF. These results imply the potential of nickel silicide as a recombination layer for perovskite/TOPCon tandem solar cells.

5:00 PM EN07.06.05
A Study on PID-p(polarization) Phenomenon in Bifacial p-PERC Solar Module Solhee Lee, HongJun Jang, Yoonmook Kang, Donghwan Kim and Hae-Seok Lee; Korea University, Korea (the Republic of)

Bifacial solar cells have high efficiency by receiving light from both sides, and are in the spotlight as a solar cell that ultimately lowers the levelized cost of electricity (LCOE). Looking at the status of the global solar market, bifacial solar modules accounted for nearly 30% in 2021, and is expected to occupy more than 60% in 2032. Among them, bifacial p-PERC solar cells started to be commercialized in 2017, and mass production lines already exist. However, when a solar module is actually installed outside to generate an output of 600 V or higher, as time goes by as it is exposed to a high temperature and high humidity environment, PID (potential-induced degradation) degradation occurs in some cells within the module. This is a problem already known to occur in crystalline silicon solar cells, and solutions are being actively studied. In the bifacial p-PERC solar cell, it is known that the degradation at the back side is greater than that at the front side. In previous studies, it is known that PID-s (shunting) at the front and PID-p (polarization) degradation occurs at the rear, and the mechanism of rear polarization has not been clarified. In this study, a bifacial p-PERC solar module was fabricated and PID and recovery experiments were conducted, and characteristics were analyzed through light J-V, dark I-V, external quantum efficiency (EQE), and electroluminescence (EL) image measurements.

5:00 PM EN07.06.06
Highly Active and Stable Ir, Ru Metal Catalysts on t-ZrO_{2-x} Supports with Uniform Structure Derived from Metal-Organic Frameworks for Hydrogen Evolution Reaction Jonghwan Park[1,2], Mansu Kim[2], Sohui Kim[1,2], Joseph T. Hupp[2] and Dongmok Whang[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Northwestern University, United States

Electrocatalysts play a key role in green hydrogen production, essential for establishing sustainable society. Platinum group metals(PGM) are well-known for its high catalytic efficiency and stability for electrochemical hydrogen evolution reactions(HER). However, high cost of PGM hinders practical application of electrocatalysts. Supported metal catalysts are regarded as one of the potential solution by reducing the amount of metal content while maintaining the activity of catalysts. Nitrogen doped carbon and oxides are used as supports for catalyst metals to enhance stability of the catalyst metals in strong acid or basic conditions, even improving the intrinsic activities of catalysts by tuning the electronic structure of metals. Especially oxygen deficient oxides like t-ZrO_{2-x} are well known for their strong interaction with metals. Due to the abundant oxygen vacancies on the surface of t-ZrO_{2-x} particles, metals can be strongly bonded to t-ZrO_{2-x} particles. Furthermore, various ions and molecules can be absorbed on the surface of t-ZrO_{2-x} particles in aqueous solution where HER is conducted out. Those surface properties of t-ZrO_{2-x} particles can promote HER reactions on metal catalysts. In this study, we made the supported metal catalysts with the structure where M(M= Ir, Ru)-ZrO_{2-x} particles are well dispersed on the porous carbon using metal-organic frameworks(MOF) as a precursor. Uniform structure of M-ZrO_{2-x}/C was derived from chemically homogeneous nature of MOF. During the pyrolysis process of MOF in inert condition, ZrO_2 nods form t-ZrO_{2-x} nanoparticles on the conductive carbon matrix. Porous carbon matrix derived from MOF with high surface area facilitates the mass transport in HER. M-ZrO_{2-x}/C catalyst showed enhanced activity and greatly improved stability compared to commercial catalysts despite of low content of metals. Moreover, we found that surface property of t-ZrO_{2-x} nanoparticles can promote HER on the metal as a cocatalyst depending on the surrounding conditions.

5:00 PM EN07.06.07
A $NiCo_2O_4$ Electrocatalyst with a Thin Graphitic Coating for the Anion Exchange Membrane Water Electrolysis of Wastewater Jae-Yeop Jeong, Jaehoon Jeong and Ju-chan Yang; Korea Institute of Materials Science, Korea (the Republic of)

Water electrolysis has been suggested as one of hydrogen production system, following steam reforming, photoproduction, fossil fuel and gas extraction. Among these methods for production of hydrogen, the most attractive merit of water electrolysis is their high efficiency and the generation of high purity hydrogen without environmental pollution. Anion exchange membrane water electrolysis (AEMWE) is a technology that has recently attracted attention

because it combines the advantages of existing polymer exchange membrane water electrolysis (PEMWE) and alkaline water electrolysis (AWE). Similar to PEMWE, AEMWE can be manufactured in a stack with a solid membrane, so it has high purity of hydrogen with high pressure. And, it is possible to reduce cost by using a non-noble based electrode by operating in an alkaline atmosphere. However, since the performance is lower than other precious electrocatalyst, it is urgent to develop a high efficiency non-precious metal catalyst to overcome this problem.
We demonstrate the simple preparation of a non-precious metal catalyst based on $NiCo_2O_4$ (NCO). Further, we used high-energy ball milling with graphite to modify the NCO catalyst to prepare a material with small particle size, high surface area and high conductivity, which enhanced the electrocatalytic performance of the materials in electrochemical tests and when applied to an anion exchange membrane water electrolyzer. Crucially, comparison of the performance of the pristine NCO catalyst and that modified with graphite (NCO@C) revealed that the latter showed better activity and durability for the hydrogen and oxygen evolution reactions under alkaline conditions. Further, we applied the possibility of using this electrocatalyst in alkaline wastewater and observed similar performance and durability to that in pure electrolyte.

5:00 PM EN07.06.08
Thermal Selenization of Transition Metal-Based Nanomaterials Renata Palowska[1,2], Mikolaj Kozak[1,2], Marta Zych[1,2], Agnieszka Brzozka[1], Lifeng Liu[2] and Grzegorz D. Sulka[1]; [1]Jagiellonian University, Poland; [2]International Iberian Nanotechnology Laboratory, Portugal

Transition metal selenides (TMSs) belong to the group of materials interesting to water electrolysis research, due to their favourable electrocatalytic activity towards either hydrogen (HER) or oxygen (OER) evolution reactions, good conductivity and stability [1]. Additionally, some TMSs have been reported to show catalytic activity towards both HER and OER [2], and might be used in both acidic and alkaline environments [3]. The most commonly used TMS synthesis paths include electrodeposition, hydro/solvothermal methods and chemical vapour deposition (also called thermal selenization) [3]. Among them, thermal selenization seems to be quite useful, as it can be combined with a variety of transition metal precursor preparation methods, allowing for various morphologies and stoichiometries.
In this contribution we show how thermal selenization can be used in tandem with electrodeposition to prepare Co, Ni or Mn-based materials. Transition metal nanostructures were prepared via electrodeposition from either aqueous or ethaline-based solutions. Then, thermal selenization was performed in a tube furnace in temperatures ranging from 400°C to 600°C, under an inert atmosphere, for up to 2 h. Scanning electron microscopy, X-ray powder diffraction and energy-dispersive X-ray spectroscopy measurements were carried out to determine the morphology and phase content of obtained TMS nanomaterials.

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Acknowledgements
This research was supported partially by the National Science Centre Poland (grant no. 2017/26/M/ST5/00715), and partially by a Talent Management minigrant under the “Exellence initiative – research university” programme of the Polish Ministry of Education and Science.

5:00 PM EN07.06.09
Molten Metal Catalyst with Ceramic for CO_2-free Hydrogen Production Young Jae Lee, Waqas Muhammad and Hyungtak Seo; Ajou University, Korea (the Republic of)

Hydrogen energy is sustainable and clean energy, but the process of hydrogen production is not clean. The major hydrogen production route is based on steam methane reforming. This method generates a lot of CO_2 when hydrogen is produced (i.e., 9-15 ton of CO_2 per 1 ton of H_2). As hydrogen is claimed as environmentally benign energy resources or carriers, steam methane reforming is not suitable. Therefore, a new strategy for clean hydrogen production is highly on demand.
Methane pyrolysis can achieve CO_2-free hydrogen production using thermal catalysts. Solid metal catalysts have beneficial advantages for methane pyrolysis at lower operating temperatures. However, the solid metal catalysts in methane pyrolysis have a fatal limitation which suffered from deactivation. When the solid metal catalysts react with methane on active sites, solid carbon as reaction products deposit on it.
Molten catalysts were used to overcome the drawback of the solid metal catalyst. After the reaction, the products (most of the carbon) escaped to the surface by density difference instead of being deposited on active sites. In this work, reported molten Nickel bismuth (NiBi) catalyst with addition of cerium (IV) oxide (CeO_2) aiming promotion effect of conversion rate was prepared as a methane cracking catalyst.
The methane conversion rate was measured by gas chromatography (GC) at various temperatures and methane gas flows. After conversion rate evaluation, the catalyst stability test upto 100 hours was performed. The catalyst activation was maintained for 70 hours. Compared to molten NiBi catalyst, the performance of molten CeO_2-NiBi catalyst showed enhanced methane conversion rate and increased reactivity as time goes on. It means CeO_2 also helps the pyrolysis reaction as the catalyst. These results showed not only molten metal but also other various materials like ceramics can be composed for methane pyrolysis strategies.

5:00 PM EN07.06.10
Transition Metal-Doped Complex Metal Oxide as Highly Efficient Electrocatalyst for Oxygen Evolution Reaction in Alkaline Media Minsol Kwon, Taehyun Kwon and Dongju Lee; Chungbuk National University, Korea (the Republic of)

As the global energy crisis grows, hydrogen is attracting attention as a sustainable and clean energy to replace fossil fuel. Electrochemical water splitting by renewable energy, such as sunlight and wind, is a pollution-free way to produce large amounts of hydrogen and oxygen. The development of non-noble electrocatalysts with low cost, excellent performance and durability for overall water splitting is very important. Complex transition metal oxide, such as nickel iron oxide, nickel cobalt oxide, and cobalt iron oxide, exhibits relatively good performance in the oxygen evolution reaction. Recently, many studies have been conducted on improving the performance of oxygen evolution reaction due to the fast and brisk transfer of electrons through doping.
In this work, we investigated the effects of transition metal doping on electrocatalytic performance of nickel iron oxide prepared by hydrothermal method. The transition metal-doped nickel iron oxide electrocatalyst showed better performance and stability in the oxygen evolution reaction for overall water splitting due to efficient charge transfer.

Acknowledgement
This work was supported by the National Research Foundation of Korean (NRF) grant funded by the Korea government (Ministry of Science and ICT) (2021R1F1A1058854) and the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government (MOTIE, 20217510100020, Development of platform process using common core and materialization technology for rare metal recovery from industrial low-grade waste liquid).

5:00 PM EN07.06.11

Thiometallate Precursors for the Synthesis of Supported Pt and PtNi Nanoparticle Electrocatalysts— Size-Focusing by S Capping Woo Yong Choi; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Thiometallate precursor enabled the monodisperse synthesis of supported Pt nanoparticles and the in situ formation of S, which were caught directly in a collection system by the nanoparticle synthetic processes consisting of impregnation and thermal processes. S is proven to act as a capping agent in generating highly stable nanoparticles with the size ranging from 2 nm to 3 nm and further favors the formation of monodispersed particles by solid-state digestive ripening. The proposed synthetic methodology can be applied to high-quality PtNi alloy nanoparticle systems. The prepared carbon-supported Pt and PtNi nanoparticles were characterized as electrocatalysts for the oxygen reduction reaction and exhibited superior performance and durability to commercial Pt/C.

5:00 PM EN07.06.12

Fluorine-Decorated Graphene Nanoribbons with Tailoring Chemical Exfoliation State for an Anticorrosive Polymer Electrolyte Membrane Fuel Cell Song Jin[1,2], Jong Min Lee[3], Minseon Park[4], Jeemin Hwang[3], Sung Mook Choi[2] and Min Ho Seo[5]; [1]Gwangju Institute of Science and Technology, Korea (the Republic of); [2]Korea Institute of Materials Science, Korea (the Republic of); [3]Korea Institute of Energy Research, Korea (the Republic of); [4]Pohang University of Science and Technology, Korea (the Republic of); [5]Pukyong National University, Korea (the Republic of)

Pt-supported carbon material-based electrocatalysts are formidably suffering from carbon corrosion when H_2O and O_2 molecules are present at high voltages in polymer electrolyte membrane fuel cells (PEMFCs). In this study, we discovered that the edge site of a fluorine-doped graphene nanoribbon (F-GNR) was slightly adsorbed with H_2O and was unfavorable with O atoms after defining the thermodynamically stable structure of the F-GNR via the DFT calculations. Based on the computational predictions, the physico-electrochemical properties of F-GNRs with tailoring fully or partially exfoliated state were investigated as support materials for electrocatalysts and the additives in the cathode of a PEMFC. In electrochemical evaluations, the Pt/F-GNR with controlled exfoliation states (fully or partially) showed much lower degradation rate in the carbon corrosion condition and were effective in the cathode as additives compared to commercial Pt/C, resulting from the improved carbon corrosion durability owing to the improved structural stability and water management. Notably, the F-GNR with highly stable carbon corrosion contributed to achieving a more durable PEMFC for long-term operation.

5:00 PM EN07.06.13

Doped Transition Metal Based Electrocatalyst for Water Splitting Seunghun Lee[1], Yangdo Kim[1], SeoHyun Park[2] and Yoo Sei Park[2]; [1]Pusan University, Korea (the Republic of); [2]Chungbuk University, Korea (the Republic of)

Electrochemical water splitting is attracting attention as a next-generation renewable energy technology that uses renewable electricity from solar or wind energy to produce hydrogen. So, developing cost-effective and highly active electrocatalysts for enhancing the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is a significant challenge for overall water splitting. Currently, benchmark catalysts for oxygen evolution rely on noble metal oxides such as iridium oxide (IrO2) and ruthenium oxide (RuO2), and the most effective catalyst for hydrogen evolution is a platinum (Pt)-based noble metal catalyst. However, these precious metal materials are not widely applied due to their high price and scarcity. The development of highly active, highly functional electrocatalysts for electrochemical water splitting offers several advantages in simplifying device manufacturing and reducing costs. Various transition metal-based electrocatalysts (i.e., oxides, phosphides, sulfides and hydroxides..) were developed to overcome the disadvantages of precious metal-based catalysts, showing high catalytic activity against total water electrolysis. In particular, transition metal-based hydroxides are considered promising electrocatalysts due to their high catalytic activity and excellent durability. This study manufactured a transition metal-based catalyst improved through doping as a catalyst for total water electrolysis and analyzed its characteristics as a water electrolyte electrode catalyst through surface, composition, and electrochemical analysis.

5:00 PM EN07.06.16

Metal Organic Framework Catalyst of Mesoporous K-doped $NiCo_2O_4$ for Improved Oxygen Evolution Nam-Woon Kim[1], Jihun Oh[2] and Hyunung Yu[3]; [1]Samsung Electro-Mechanics, Korea (the Republic of); [2]Korea Advanced Institute of Science and Technology (KAIST), Korea (the Republic of); [3]KRISS, Korea (the Republic of)

The water splitting reaction is a key process for the conversion and storage of clean and renewable energy, but requires a highly efficient non-precious metal electrocatalyst to reduce wide overpotentials for oxygen evolution reaction (OER) or hydrogen evolution reaction (HER). In particular, many efforts have been applied to explore high-efficiency OER catalyst because the OER has a higher kinetic barrier than the HER. Here, we have developed a novel K-doped $NiCo_2O_4$ (NCO) catalyst derived from the metal organic framework structure of Prussian Blue analogue (PBA) to demonstrate a high-performance OER electrode. The material is prepared with a simple hydrothermal synthesis method using the potassium (K) precursor present in the PBA. The K-doping in the NCO catalyst shows a high conductivity not only to increase the number of active oxygen vacancies but also change their intrinsic properties such as binding energy. The cyclic voltammetry (CV) scan of the K-doped NCO catalyst showed a low overpotential value of 0.292 V at a current density of 10 mA cm^{-2} and a Tafel value of 49.9 mV dec^{-1}, outperforming a commercial OER catalyst (Iridium). The synthesized K-doped NCO can be utilized as high performance electrode materials for metal-oxide batteries and supercapacitors.

5:00 PM EN07.06.18

Suitability of Tungsten Nitride (WN) as a Sustainable Hard Coating Material for Nuclear Applications Sri Bharani Ghantasala and Sumitra Sharma; National Institute of Technology Silchar, India

The recent technological advancements led to the development of fourth generation nuclear reactors with an improved thermal efficiency. This ensures an effective and efficient power generation through the nuclear power plants operating at higher temperatures. Consequently, the components of the nuclear reactors generally made up of nickel (Ni) based super-alloys are exposed to extreme temperatures, severe wear and corrosion resulting in increased maintenance and replacement costs. Moreover, Ni is considered to be critical raw material (CRM) as per the 2010 and 2014, EU reports [1]. In this regard, the nuclear industry traditionally uses chromium (Cr) film synthesized using electro-deposition that provides decent corrosion and wear resistance. However, the recent regulation norms on the Cr restricted the usage due to its harmful nature and adverse health effects [2]. So, it is highly important to explore new materials in order to protect the nuclear components from extreme wear and corrosion at high temperatures. The viability of transition metal nitrides (TMNs) as protective hard coating materials has thrown much attention in the current research to address the increasing industrial demand. The reason for this could be their significant structural, morphological, thermal and mechanical properties. Out of various TMNs, tungsten nitride (WN) possesses a peculiar property of solid lubricity that makes it highly wear and scratch-resistant. Furthermore, this material can withstand upto very high temperature and it is chemically inert. On account of this, WN is known to be one of the best refractory and corrosion resistant material [3]. However, tungsten (W) is also considered to be a CRM as per the 2010, 2014 and 2017, EU reports. In this context, it is required to fabricate highly durable and reliable WN films to ensure the sustainable utilization of the W metal in nuclear applications. To achieve this, the current study adopts magnetron sputtering, a physical vapor deposition (PVD) technique, to deposit high-quality uniform WN films with excellent morphological and substantial adhesive properties. The WN films were produced at argon (Ar) flow rate of 30 sccm and a varying nitrogen (N_2) flow percentages of 5 %, 15 % and 25 % of total gaseous mixture (i.e. Ar + N_2) at a deposition power of 30 W and 300 ^{o}C substrate temperature (for initial 15 min of the deposition) using magnetron sputtering. The X-ray diffraction (XRD) technique confirmed the presence of the FCC β-W_2N phase of WN at a N_2 flow of 5 %. It was also confirmed by the formation of W $4f_{7/2}$ and W $4f_{5/2}$ doublet peaks at the binding energies of 30.6 and 32.8 eV, respectively, depicted through W 4f core level spectra of X-ray photoelectron spectroscopy (XPS). On increasing the N_2 flow percentage, the β-W_2N is converted to mixed phases of β-W_2N and δ-WN (hexagonal) and further increment leads to the formation of amorphous phases of WN. In addition to this, field emission - scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) portrayed the formation of dense microstructures with a root mean square (RMS) surface roughness of 1.15 nm at a N_2 flow of 5 %. The mechanical properties of the WN films such as hardness and elastic modulus are found to be 32.66 GPa and 163.64 GPa, respectively characterized via nano-indentation test. Furthermore, the nano scratch test performed on the WN film resulted in a considerable wear rate and a friction coefficient of 0.33. These experimental outcomes would be sufficient enough to propose WN as a suitable material for sustainable protective hard coatings in nuclear reactors.

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SESSION EN07.07: Hybrid Nanomaterials for Catalysis
Session Chairs: Swetlana Schauermann and Chengjun Sun
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2007

8:15 AM *EN07.07.01
Critical Materials: Atomic Level Investigations and Manipulation of Individual Rare Earth Complexes on Materials Surfaces Saw W. Hla; Argonne National Laboratory/Ohio University, United States

Complexes containing rare-earth ions [1] attract great attention for their technological applications ranging from spintronic devices to quantum information science. While charged rare-earth coordination complexes are ubiquitous in solution, they are challenging to form on materials surfaces that would allow investigations for potential solid-state applications. In this talk, we will present formation and atomically precise manipulation of rare-earth complexes on a gold surface [2]. Atomic scale characterizations of individual rare-earth complexes are performed with the most advanced instrumentation including low temperature scanning tunneling microscope manipulation, and synchrotron X-ray scanning tunneling microscopy. Although they are composed of multiple units held together by electrostatic interactions, the entire complex can be rotated as a single unit on a one-complex-at-a-time basis when electrical energy is supplied from a scanning tunneling microscope tip. Here, 100% control of their rotational directions is achieved using a negative electric field. Moreover, we form rare-earth ionic clusters composed of a precise number of 2, 4 and 6 units on a gold crystal surface. Unlike other non-ionic molecular clusters, the observed rare-earth clusters are very stable. Furthermore, they are conformationally chiral and their high mobility on the surface suggests that they are in a two-dimensional liquid state. Taken in concert, these experiments provide unparalleled atomic level information of the rare-earth ion environment within the complexes and will enable to develop rational blueprints for the design and synthesis of new structures with improved functions for potential applications in rare-earth separation, tribology, nanotechnology, and quantum information science.
This work is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Science and Engineering Division. Work performed at the Center for Nanoscale Materials, and Advanced Photon Source, both U.S. Department of Energy Office of Science User Facility, was supported by the U.S. DOE, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.
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8:45 AM *EN07.07.02
Heterogeneous Catalysis for Sustainable Chemical and Energy Technologies: an Atomistic View Swetlana Schauermann; Kiel University, Germany

The molecular transformation of carbon dioxide to value-added chemicals and synthetic fuels is one of the most promising approaches towards sustainable chemical and energy technologies starting from economical and renewable feedstock. Heterogeneous catalysis is of the most effective technologies capable of activation and chemical transformation of CO_2 to a broad class of compounds such as alcohols, different types of oxygenates, alkenes. An atomistic-level understanding of heterogeneously catalysed processes of CO_2 activation and chemical transformations is an important prerequisite for the rational design of new effective catalysts. Towards this goal, we follow a rigorous surface science approach to obtained a detailed understanding of the reaction mechanisms, kinetics and thermodynamics of processes involved in chemical conversion of carbon dioxide on well-defined model oxide-based surfaces. We employ a unique combination of the state-of-the-art experimental tools including multi-molecular beam techniques, infrared and polarization-modulation infrared reflection-absorption spectroscopy, scanning tunnelling microscopy, single crystal adsorption calorimetry to address these major issues and derive precise structure-reactivity relationships.

In my talk, I will focus on the interaction of CO_2 and H_2O with different types of well-defined oxides – CoO, Co_3O_4 and Fe_3O_4 – prepared by epitaxial growth on metal single crystals under ultra-high vacuum conditions. Specifically, it will be shown that CO_2 can be effectively activated on these oxide surfaces and react with H originating from the co-adsorbed hydroxyl groups formed upon adsorption and dissociation of water. The mechanistic picture of the latter process will be discussed in more detail for water interaction with model Fe_3O_4(111)/Pt(111) oxide.[1] Combining single crystal adsorption calorimetry, infrared spectroscopy on the isotopically labelled iron oxide and theoretical studies, we show that water dissociates readily on iron oxide surfaces forming a dimer-like hydroxyl-water complex and prove that the generally accepted model of water dissociation to two individual OH groups is incorrect.

In the second part, I will introduce a concept of ligand-directed heterogeneous catalysis and provide an example on how purposeful functionalization of a catalytic surface with co-adsorbed organic molecules can dramatically enhance chemoselectivity in hydrogenation of multi-unsaturated hydrocarbons. Specifically, I will present a mechanistic study on formation and dynamic changes of a ligand-based heterogeneous Pd catalyst for chemoselective hydrogenation of α,β-unsaturated aldehyde acrolein.[2] Deposition of allyl cyanide as a precursor of a ligand layer renders Pd highly active and nearly 100 % selective toward propenol formation by promoting acrolein adsorption in a desired configuration via the C=O end. Employing a combination of real space microscopic (STM) and *in operando* spectroscopic (IRAS) surface sensitive techniques, we show that an ordered active ligand layer is formed under operational conditions, consisting of stable butylimin species, which turns the surface highly selective toward the desired product. Obtained atomistic-level insights into the formation and dynamic evolution of the active ligand layer under operational conditions provide important input required for controlling chemoselectivity by purposeful surface functionalization.

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9:15 AM EN07.07.03
Facets Control Photoelectrochemical Water Oxidation in Strontium Titanate Single Crystals Samutr Assavachin, Anna C. Kundmann, Chengcan Xiao and Frank E. Osterloh; University of California, Davis, United States

Photocatalytic water splitting requires successful electron-hole separation toward its specific redox sites to perform H^+ reduction and H_2O oxidation simultaneously. Exposed facets of a catalyst can act as either a reduction or oxidation site controlling charge separation and photocatalytic activity of the material. This is the basis for the near unity water splitting quantum efficiency of the CoO(OH)/SrTiO3/Rh/Cr2O3/ photocatalyst reported by the Domen group (Takata, T., et al. Nature, 2020, 581, 7809, 411-414). In this work, we demonstrate photoelectrochemistry dependence on exposed facets of hydrogen reduced strontium titanate single crystals ($SrTiO_3$, $E_g = 3.2$ eV) with three different exposed facets [100, or 110, or 111] showing drastic differences for water oxidation photocurrent (0.01, 0.66, 1.53 mA cm^{-2}) at 0.72 V versus RHE applied bias in 0.5M Na_2SO_4 electrolyte at pH = 6.06 under UV illumination (60 mW cm^{-2}). Photocurrent onsets are observed at 0.42, -0.35, -0.38 V versus RHE for the [110], [100], and [111] crystals. Reduced $SrTiO_3$ single crystals were annealed at 1,100^{o}C in forming gas atmosphere (10% H_2 in argon) leading to a broad optical absorption from 400 nm into the IR region from the presence of Ti^{3+} states. Based on the optical absorption at 1,000 nm, the [110], [100], and [111] facets have electron donor concentrations of 4.1x10^{18}, 6.01x10^{18}, and 5.85x10^{18} # cm^{-3} respectively, after the H_2 treatment, much higher than as received crystals which are all approximately ~ 4x10^{17} # cm^{-3}. Controlled photoelectrochemical scans with 20% (v:v) added methanol yield photocurrents of 0.31, 1.31, and 2.90 mA cm^{-2} for the [110], [100], and [111] crystals respectively. Photocurrent onsets are -0.45, -0.38, -0.38 V versus RHE. Compare to OER photocurrent onsets, [111] remained unchanged, [110] was slightly shifted, and [100] experienced the strongest shift towards a reducing potential. This is the same current density trend observed for water oxidation, suggesting that differences in band bending control the photocurrent in these systems rather than the water oxidation kinetics. These findings will be discussed together with surface photovoltage, X-ray photoelectron spectroscopy, and Mott Schottky data for these systems.

9:30 AM EN07.07.04
Atomically Dispersed Ir Catalysts on Si Photoanode for Efficient Photoelectrochemical Water Splitting Sang Eon Jun and Ho Won Jang; Seoul National University, Korea (the Republic of)

Hydrogen is expected to become sustainable future energy due to zero-emission, non-toxicity, and large energy density. However, it usually exists in covalent compounds tightly bonded with other elements such as oxygen, nitrogen, and organic materials. One of the promising electrochemical methods to obtain pure hydrogen from these compounds is a solar water splitting. As a photoelectrode, Si has been widely investigated owing to its excellent charge carrier mobility, long carrier diffusion length, earth abundance, and wide-range solar spectrum absorption. Nevertheless, the poor catalytic activity, chemical corrosion in aqueous electrolyte, and negative valence band position limit its practical application. Hence, it is necessary to apply the photoelectrochemical catalysts having large amounts of active sites with complete coverage of photoelectrodes.
Single atom catalysts (SACs) have been recently investigated in electrochemical (EC) reaction to not only maximize the atomic efficiency of platinum group element (PGE) catalysts but also introduce unconventional geometric and electronic structures. The modification of the chemical state of single atoms induced by electronic interactions with the support matrix plays an essential role in improving catalytic activity and stability. However, stabilizing atomically dispersed PGE single atoms on Si photoanodes for photoelectrochemical-oxygen evolution reaction is still challenging due to the scarcity of anchoring sites.
Here, we demonstrate the decoration of Ir SAs on Si photoanodes and reveal the role of SAs on the separation and transfer of photogenerated charge carriers. NiO/Ni thin film, an active and highly stable catalyst, enables to embed the Ir SAs in its lattices by locally modifying the electronic structure. The existence of atomically dispersed atoms, electronic structure, and environmental coordination were identified by high-resolution transmission electron microscope (TEM), X-ray absorption near edge structure (XANES), and X-ray absorption fine structure (EXAFS) analysis. In addition, the roles of the isolated Ir SAs, enabling effective photogenerated charge transport by suppressing the charge recombination and lowering the thermodynamic energy barrier in the rate-determining step, were revealed by intensity-modulated photocurrent spectroscopy (IMPS) and DFT calculations. As a result, the Ir SAs/NiO/Ni/ZrO2/n-Si photoanode shows a benchmarking photoelectrochemical performance with a high photocurrent density of 27.7 mA cm-2 at 1.23 VRHE and 130 h stability. This study proposes the rational design of SAs on Si photoelectrodes and reveals the potential of the PGE SAs to boost photogenerated charge carrier kinetics.

9:45 AM EN07.07.05
Investigating the Electrocatalytic Activity and Stability of Cobalt-based Materials during the Oxygen Reduction Reaction in Acidic Media Ashton Aleman, Gaurav A. Kamat, Aniket Sandip Mule, Melissa E. Kreider, Michaela Burkes Stevens and Thomas Jaramillo; Stanford University, United States

Thermodynamically, cobalt has a large potential window of instability in acidic media that impacts its usage in devices for energy storage. In particular, leaching of cobalt from the Pt-Co/C catalyst cathode in commercial proton-exchange membrane fuel cells (PEMFCs) can limit the fuel cell's overall performance and lifetime. Enabling longer device lifetimes would involve strategies to stabilize cobalt-based materials while maximizing their utility. This presents an opportunity to develop an understanding of cobalt's stability in acidic media under reaction conditions. In this work, we study the material stability and catalytic performance of Co foil during the oxygen reduction reaction (ORR) in 0.1 M $HClO_4$ by performing *in-situ* elemental analysis (with an inductively coupled plasma mass spectrometer, ICP-MS) and additional *ex-situ* characterization. By coupling ICP-MS with electrochemical testing (on-line ICP-MS), we simultaneously monitor Co dissolution and electrochemical ORR activity as functions of electrochemical protocol and electrolyte gas saturation, and then use Atomic Force Microscopy (AFM) to compare the surface morphology and roughness of Co before and after electrochemical testing. In this study, we investigate the impact of catalysis, starting potential, potential range, and time on the material stability and catalytic activity of Co. In the flow cell, ORR onset (-0.2 mA cm^{-2}) occurs nominally at -0.55 V relative to the reversible hydrogen electrode (RHE). To evaluate the role of catalysis, we compare Co dissolution in O_2 vs N_2 saturated electrolyte in which we observe a ~9 fold increase in dissolved Co under O_2 saturation relative to N_2 saturation at 0 V vs RHE despite negligible faradaic current. After ORR onset, Co stabilizes and there is < 25 ng s^{-1} dissolution at -0.8 V vs RHE for both gases, despite the difference in current density between the two gases being -0.5 mA cm^{-2} . These results indicate that the presence of O_2 destabilizes the surface despite the absence of catalysis. Furthermore, when evaluating the role of starting potential, potential range, and time, we observe changes in the catalytic activity, material stability, and surface morphology. These findings showcase the importance of considering different experimental parameters when designing protocols for activation and operation of commercial catalysts. Altogether, this work provides important insights to reduce the dissolution of cobalt metal in acidic media. Such understanding will motivate future studies to improve the stability of cobalt-based materials for a variety of applications, including fuel cells, lithium-ion batteries, and electrolyzers.

10:00 AM BREAK

10:30 AM *EN07.07.06
Effects of Crystal Lattice Deformation on Catalytic Activities Miao Song, Peng Ren, Zexi Lu, Hyoju Park, Micah Prange, Peter V. Sushko and Dongsheng Li; Pacific Northwest National Laboratory, United States

Deformations of hierarchical structures at the atomic scale, especially long-range ones, can significantly enhance their functional behavior, such as catalytic activity. Metastable states or grain boundaries during the synthesis and processing of nanomaterials can introduce and control deformations (strains) in crystal lattices. We will design the deformations in the crystal lattice to enhance the catalytic functionality of catalysts, such as TiO_2 and platinum-group-based metals, by controlling their synthesis processes of phase transformation and particle aggregation. For example, TiO_2 polymorphs have distinct properties that have been widely employed in various applications. It is well known that these polymorphs can transform into more stable phases, such as from anatase to rutile and from TiO_2-B to anatase. Here, based on results from semi-in-situ transmission electron microscopy, density functional theory, and X-ray photoemission experiments, we discover a physical picture of transitional structures, in which continuous variations in atomic positions form along these two phase-transformation pathways. These gradient structures give rise to continuous band bending, which promotes electron-hole separation and inhibits their recombination across the bulk of the particles, leading to a large functionally active volume fraction and resulting in high photoactivity. We also seek to control deformations in supporting materials and their effect on catalytic materials to uniquely tailor functionalities. These findings suggest that extended gradient structures (lattice deformations) can be designed to advance new functions not achievable using abrupt interfaces.

11:00 AM EN07.07.07
Electronic Structure and Charge Trapping at the Interface of Pt and Strained Anatase Micah Prange[1], Quinn Carvalho[2], Sri K. Padavala[2], Kelsey A. Stoerzinger[2,1], Hyoju Park[1], Dongsheng Li[1] and Peter V. Sushko[1]; [1]PNNL, United States; [2]Oregon State University, United States

Since the rate of photooxidation reactions at the (001) surface of anatase TiO_2 depends strongly on charge separation efficiency, much effort has been expended elucidating factors that are believed to contribute to the electron-hole separation, including effects of surface structure, reconstruction, and undercoordination, while the effect of underlying bulk anatase has been relatively ignored. Inspired by recent observations of strained regions of anatase-like TiO_2 in heat-treated samples, we explore whether the coupling between lattice strain and electronic properties in these regions can facilitate efficient separation of photoexcited electron-hole pairs, thus increasing their catalytic activity. To this end, using density functional theory, including hybrid exchange-correlation functionals, we quantify the dependence of the near-surface band structure and charge transfer properties on the degree of local deformation near strained anatase (001) surfaces and their interfaces with Pt. We show that hole, electron, and triplet exciton biding energies in the surface and subsurface layers of anatase depend on the degree of strain in the anatase lattice. We calculate the energetic positions of the Pt d band centers and edges relative to the surface states, and we evaluate the possibility of spontaneous hole and electron transfer to Pt particles supported by anatase in experimentally observed strain states. Our results are consistent with experimentally observed enhancement of water splitting at the surface of thermally treated anatase, which points to a significant effect of the heat-induced deformations on post excitation charge carrier dynamics and photoredox catalysis.

11:15 AM EN07.07.08
Toward Elucidating the Role of Noble Metal Co-catalysts in Photocatalytic Oxidation of Methane to Methanol Gang Wan, Chenlu Xie, Eddie Sun and Arun Majumdar; Stanford University, United States

The availability of methane as the principal component in the natural gas resources and a potent greenhouse gas calls for the development of efficient mitigation strategies for its conversion to value-added chemicals and fuels, such as methanol. Methanol is a key vector to fuel a future. And a direct methane-to-methanol conversion holds the promise as a drop-in replacement for the methane reforming, which is highly energy-intensive process. Activation of C-H bond in methane is the key step in the direct methane-to-methanol conversion, which has been demonstrated to benefit from the use of free radicals. Photochemical methane activation offers intriguing and vital opportunities by generating free radicals directly from water and oxygen and thus is promising for large scale fuel production. Such photocatalytic process involves the use of inorganic semiconductor catalysts and noble metals nanoparticles co-catalysts. Despite intensive studies, the photocatalytic methane oxidation faces the challenge of a limited selectivity toward methanol, and the catalytic functions of different noble metal co-catalysts remain largely unexplored.

In this talk, on the basis of catalysts design, in-situ X-ray absorption spectroscopy, electron paramagnetic resonance and kinetic studies, we will discuss the relationship between the role of co-catalysts, the controlled generation and diffusion of free radicals, and the selectivity toward various liquid products. Such molecular-level insights are expected to facilitate the selective functionalization of light alkanes and offer informative design principles for photocatalysts.

11:30 AM EN07.07.09
Nanocrystalline Non-stoichiometric CeO_x on Pt Heterogeneous Catalysts for Selective Oxidation of Methanol to Methyl Formate Gyu Rac Lee, Kyoungjae Song, Jeong Young Park and Yeon Sik Jung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Due to the increasing energy and environmental crisis, the utilization of C1 chemistry has gained much attention as a reliable pathway for “green chemistry” over several decades. Among various intermediates in C1 chemistry, methyl formate is one of the key components to produce more than 50 chemical products in the field of industry. In general, most methyl formate is produced by the carbonylation and dehydrogenation reaction of methanol. Since these reactions proceed at elevated temperatures, the selectivity for methyl formate generation is inevitably low, producing unintended by-products such as carbon dioxide. In this regard, the catalytic methanol oxidation reaction (MOR) capable of forming methyl formate even at room temperature can be considered an efficient alternative route. However, because MOR can generate both carbon dioxide and methyl formate via full oxidation and partial oxidation respectively, it is essential to maximize the partial oxidation selectivity of MOR for achieving the desired component.

Recently, the formation of heterogeneous catalysts with platinum group metals (PGMs) and reducible metal oxides has been attempted because they provide enhanced reaction rate and partial oxidation selectivity in MOR, which is derived from the strong metal-support interactions (SMSI). The charge transfer between PGM and metal oxide occurs by forming the interfaces and this electronic interaction at the interface is the origin of the SMSI. Especially, several studies already revealed that the metal-oxide interface plays an important role to accelerate MOR performance and partial oxidation selectivity is correlated with the concentration of the interface. However, it is still unclear how the oxidation state or chemical composition of constituent materials in heterogeneous catalysts correlates with partial oxidation selectivity and methyl formate generation.

Here, to explore the effect of the oxidation states of support oxides on partial oxidation selectivity in MOR, we fabricate heterogeneous catalysts composed of nanocrystalline non-stoichiometric CeO_x nanowires and Pt film (CeO_x/Pt). The oxidation state of CeO_x nanowires was controlled with varying annealing atmospheres (vacuum, Ar, Air, O_2). Although there was no noticeable difference in the crystallinity of CeO_x nanowires depending on the annealing conditions, it was confirmed that the ratio of O/Ce and the amount of Ce (III) changed after the annealing process depending on the processing conditions. To evaluate the turnover frequency (TOF) and the selectivity to methyl formate generation toward MOR, a batch reactor experiment was carried out. We verified that all the CeO_x/Pt regardless of annealing conditions exhibit higher TOF and methyl formate selectivity compared to a Pt film used as a reference. Interestingly, although there is no TOF difference among the samples, CeO_x/Pt with vacuum treatment achieved almost 70% of significantly enhanced selectivity to methyl formate compared to the others. Further analysis revealed that a high fraction of the Ce (III) in CeO_x/Pt obtained with vacuum treatment boosted the catalytic selectivity. Our findings provide a new pathway to design heterogeneous catalysts with exceptional selectivity for achieving desired product by engineering the chemical composition in the metal oxide.

11:45 AM EN07.07.10
Cu Single-atom Catalyst on Metal Oxide Support for Efficient and Selective Photocatalytic Nitrate–Ammonia Conversion Hyun Sik Moon and Kijung Yong; POSTECH, Korea (the Republic of)

Photocatalytic nitrate (NO_3^-) reduction to ammonia (PcNRA) is considered a promising NH_3 production route to alternate N_2 reduction from an energy point of view. NO_3^- is highly soluble in water, which precludes the limitation of reactant solubility, and the N=O bond can be dissociated at a relatively low energy of 204 kJ mol^{-1} compared to the N≡N bond. There are two possible pathways for photocatalytic NO_3^- reaction: N_2 formation via five-electron reduction (0.74 V vs. NHE) and NH_3 formation via eight-electron reduction (0.69 V vs. NHE). The former reaction is both kinetically and thermodynamically favored, and therefore most previous studies on photocatalytic NO_3^- reduction have primarily produced N_2 in a water treatment manner. Thanks to the intensive effort, PcNRA has recently achieved excellent selectivity towards NH_3 synthesis, but its catalytic activity falls short of practical standards. In this work, we present a single-atom Cu-doped TiO_2 nanosheet (Cu-TNS) photocatalyst for selective as well as highly efficient PcNRA. The incorporation of single-atom Cu into the TiO_2 matrix preferentially occurs at Ti vacancies and this site-specific Cu introduction induces spontaneous defect formation such as oxygen vacancy and lattice distortion. The single Cu site accumulates photogenerated electrons, significantly suppressing charge carrier recombination and allowing more electrons to participate in NO_3^- reduction, while the unique properties of the Cu species ensure the high selectivity for NH_3 formation. Moreover, the spontaneous defect formation accelerates NO_3^- adsorption, effectively eliminating the reactant activation barrier. Consequently, the simultaneous presence of Cu single atom, oxygen vacancy, and lattice strain in Cu-TNS synergistically stimulates PcNRA, leading to 62-fold enhancement in ammonia production compared to the pristine sample, and an apparent quantum yield of 11.7% at 330 nm under optimised conditions.

SESSION EN07.08: Energy Storage, Hydrogen Technologies and CO2 Capture I
Session Chairs: Leora Dresselhaus-Marais and Hua Zhou
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2007

1:45 PM EN07.08.01
Expanding the Materials Search Space for Multivalent Cathodes Ann C. Rutt[1] and Kristin A. Persson[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Multivalent batteries are an energy storage technology with the potential to surpass lithium-ion batteries, however their performance has been limited by the low voltages and poor solid-state ionic mobility of available cathodes. Developing high-performance multivalent batteries also provides an opportunity to consider sustainability factors to avoid the growing concerns over resource constraints from projected increases in Li-ion battery production. A computational screening approach to identify high-performance multivalent intercalation cathodes among materials that do not contain the working ion of interest has been developed which greatly expands the search space that can be considered for materials discovery. This approach has been applied to magnesium cathodes as a proof of concept and lessons learned from the resulting data are discussed in further detail.

2:00 PM EN07.08.02
NaF-Rich Solid Electrolyte Interphase for Dendrite-Free Sodium Metal Batteries Mengyang Xu, Yang Li, Muhammad Ihsan-Ul-Haq, Nauman Mubarak, Zhenjing Liu, Junxiong Wu, Jang-Kyo Kim and Zhengtang Luo; Hong Kong University of Science and Technology, Hong Kong

Efficient energy storage systems are essential to the widespread application of renewable energy, as well as fulfilling the rapidly growing demand of mobile devices and electric vehicles. Sodium metal batteries (SMBs) have attracted much attention as a sustainable technology owing to the high theoretical energy density and abundance of Na. However, the practical realization is hindered by several critical challenges arising from high reactivity of metallic Na with organic electrolyte and its uneven deposition. A NaF-rich SEI layer on Na metal surface has been explored to demonstrate its beneficial effect on electrochemical performance of SMBs. Unlike previous strategies based on expensive and unstable fluorinated electrolytes to form NaF-rich SEI layers, this work employs PTFE micro powders that react with molten Na, whose process is much simpler at a lower cost. The spontaneous reaction with Na metal converts C-F to NaF which suppresses the formation of dendrites as proven by combined depth-profiling X-ray photoelectron spectroscopy (XPS) and time-of flight secondary ion mass spectrometry (ToF-SIMS) and theoretical DFT calculations. The full battery prepared with a $Na_3V_2(PO_4)_3$ cathode delivers 99% retention of Coulombic efficiency after 400 and 600 cycles at 1C in ether- and carbonate-based electrolytes, respectively. The SEI layer design strategy presented here can shed new insights into the development of high-performance dendrite-free Na metal and solid-state batteries.
The authors acknowledge the supports by the Research Grant Council of Hong Kong SAR (Project numbers 16208718, 16304518), NSFC-RGC Joint Research Scheme (N_HKUST607/17), and the IER foundation (HT-JD-CXY-201907), "International science and technology cooperation projects" of Science and Technological Bureau of Guangzhou Huangpu District (2019GH06), Guangdong Science and Technology Department (2020A0505090003), Research Fund of Guangdong-Hong Kong-Macao Joint Laboratory for Intelligent Micro-Nano Optoelectronic Technology (2020B1212030010). Technical assistance from the Advanced Engineering Materials Facilities and the Materials Characterization and Preparation Facilities at HKUST is greatly appreciated.

2:15 PM DISCUSSION TIME

2:30 PM BREAK

3:30 PM EN07.08.04
Ultrasonic Spray Deposition and its Uses in Manufacturing New Bespoke Graded Electrodes for Energy Storage Devices Matthew Tudball, Thomas S. Miller and Paul Shearing; University College London (UCL), United Kingdom

Li-ion batteries are become an increasing necessity in daily life, however with lithium and cobalt prices ever increasing, new types of batteries that utilise more abundant materials are becoming more essential.

Lithium sulphur batteries boast a much higher theoretical specific capacity than traditional Li-ion batteries (1672 mAh/g)[1] while removing the need for expensive and difficult to source materials such as cobalt and nickel. The current major issues of LiS batteries include, their short cycle life, due to sulphur loss through the polysulfide shuttle and subsequent parasitic reactions, as well as their poor rate capability, due to the low conductivity of sulphur and Li_2S as well as the pore blocking (surface deposition) of these species at high charge and discharge rates. It is thought that tuning the carbon support of the cathode can create electrodes with higher conductivity and a suitable pore network can allow for higher rate capable LiS batteries which increases their functionality and versatility.[2]
The ultrasonic spray technique allows for layer by layer deposition of material and can therefore be used to form through-thickness gradient structures. This has benefits over traditional film deposition methods such as doctor blading where the full film is deposited at once. By altering the ink composition throughout the spray the structure of the film can be changed, this is particularly important with electrochemical devices where movement of a species into the film is necessary.

This work involves the spray deposition of graded films for use in Li-ion and LiS batteries. LiS cathodes are fabricated with a conductive additive gradient, employing higher conductivity carbon near the current collector and a more porous carbon at the surface of the film. This is particularly useful for improving the rate capability of the cells, which is often hampered by the pore blocking effect of non-conductive sulphur species. By creating through-thickness pore channels, electrolyte wetting can be improved which can lead to improved homogeneity of solid S_8 and Li_2S deposition. This gradient structure has been tested previously with lithium iron phosphate cathodes and was shown to improve capacity at high C-rates.[3]

Recent literature has shown that the addition of metal nanoparticles in the sulphur cathode can help to catalyse the electrodeposition of solid S_8 and Li_2S. Applying this metal in a gradient can help to prevent build-up of solid non-conductive material at the surface of the electrode, which helps improve rate capability, lengthen lifetime of the cell and improve sulphur utilisation.[4]

This gradient spray technology is not specific to LiS batteries and has potential uses in a wide range of thin film manufacture, from other battery types to super-capacitors and fuel cells, allowing for manufacture of bespoke designed films for a range of applications.

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4. V. Marangon, D. Di Lecce, D. J. L. Brett, P. R. Shearing and J. Hassoun, *Characteristics of a gold-doped electrode for application in high-performance lithium-sulfur battery*, **Journal of Energy Chemistry**, 2022, **64**, 116-128.

3:45 PM EN07.08.05
Manipulating the Diffusion Energy Barrier at the Lithium Metal Electrolyte Interface for Dendrite-free Long-life Batteries Zhongjiu Yang[1,2], Jyotshna Pokharel[2] and Yue Zhou[1,2]; [1]University of Texas at Dallas, United States; [2]South Dakota State University, United States

The high theoretical capacity and low reduction potential make lithium metal one of the promising candidates for anode materials. However, there are some challenges such as the growth of the lithium dendrites and associated electrolyte decomposition which lead to limited cycling performance and safety concerns. One of the effective strategies to counter these challenges is to construct a protective artificial solid electrolyte interphase. A straightforward method with scale potentials to manufacture lithium nitrate-rich SEI to minimize the diffusion energy barrier of lithium-ion across it is discussed. Different from polycrystalline lithium nitrate SEI manufactured from conventional experiments, our lithium-rich SEI is phase-pure/single crystalline interphase which has high mechanical strength and low lithium-ion diffusion barrier. The combination of integrating phase field simulations with experiments is applied to elucidate the correlation among lithium-ion transference number, diffusion behavior, concentration gradient, and the stability of the lithium metal electrode. By applying this unique lithium nitrate-rich SEI into both symmetric cells and full lithium-metal batteries, excellent charge/discharge cycling performance is achieved. We realize long stable plating/stripping cycling up to 3500 hours at 0.5mA cm^{-2} for the symmetric cell and cycling up to 500 cycles at 160 mAg^{-1} (1C rate) for the full cell. These studies develop a new understanding of the designing and engineering of an ideal artificial SEI for stable and high-performance lithium metal batteries.

4:00 PM EN07.08.06
Applying Life Cycle Analysis (LCA) for Materials Selection in Li-O_2 Batteries Melodie Chen-Glasser, Amy E. Landis and Steven C. DeCaluwe; Colorado School of Mines, United States

Li-O_2 batteries are often discussed as solution to overcome the limited range of electrified vehicles. Their theoretical high energy density is promising; however, the technical challenges of parasitic reactions and high charging voltage have led to exploration of a wide range of catalysts, solvents, and cathode structures. The wide variety of materials and different reporting metrics used in Li-O_2 battery research makes it difficult estimate their environmental impact. As the ultimate goal of battery development is to reduce environmental impacts by eliminating fossil fuel consumption, their experimental design should be guided by LCA. This paper will examine a range of commonly used materials for Li-O_2 batteries and determines the variation in their environmental impacts, allowing researchers to pre-select their materials by their sustainability. In addition, five new LCA are performed on experimental Li-O_2 batteries, demonstrating how LCA can be used as a metric to drive experimental research.

4:15 PM EN07.08.08
Reducing Voltage Hysteresis in Li-rich Sulfide Cathodes by Tuning the Metal-ligand Covalency Xiaotong Li, Eshaan Patheria and Kimberly See; California Institute of Technology, United States

Multielectron redox can be achieved by leveraging the redox activity of lattice anions (anion redox) in addition to the transition metal, to significantly increase the capacity of cathode materials. Li-rich sulfides are promising cathode candidates for anion redox since they operate at voltages within the electrolyte stability window and sustain high capacity. A promising system for the study of anion redox is based on Li_2TiS_3 (d^0 Ti^{4+} is redox inactive), whose redox activity can be “activated” by substituting redox-active transition metals. There have been systematic studies on the capacities with different substitution ratios. Besides the capacity, another essential challenge of anion redox is the large voltage hysteresis between the charge and discharge processes. In this work, we seek to explore the influence of metal-ligand bond covalency (overlap between the metal *d* and sulfur *p* states) on the voltage hysteresis during anion redox. By substituting redox-active transition metals (e.g. Fe^{2+}, Mn^{2+}, Co^{2+}) in Li_2TiS_3, we aim to systematically adjust the position of transition metal *d*-states relative to the S *p*-states. The electrochemical activities were characterized for Mn^{2+} and Co^{2+}-substituted Li_2TiS_3 ($Li_{1.33-2y/3}Ti_{0.67-y/3}M_yS_2$, M = Mn and Co, $y = 0 - 0.5$). After Mn substitution, the redox process is “activated” and the capacity increases until $y = 0.3$. More interestingly, the voltage hysteresis is reduced from 500 meV in Li_2TiS_3 to 150 meV in $y = 0.3$ sample for the first cycle. Overall, this system offers fundamental insights to deepen our understanding of structure-property relationships that govern reversible anion redox.

SESSION EN07.09: Poster Session II: Critical Materials for Energy
Session Chairs: Peter Sushko and Hua Zhou
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN07.09.01
Synergistic Effects of LSPR and Z scheme Heterojunction on $W_{18}O_{49}$/Au/g-C_3N_4 for Efficient Photocatalytic Hydrogen Production Covering UV-Vis-NIR Inju Hong and Kijung Yong; POSTECH, Korea (the Republic of)

Recently, Z-scheme heterojunction that enables high spatial charge separation, wide-spectrum solar light harvesting, and simultaneously enhances powerful redox capacity, has attracted considerable attention for photocatalytic hydrogen (H2) production. However, it remains challenging to design strategies to accelerate charge transfer in heterojunctions. Solid-state electron mediators can be a solution to this problem. Inserting solid-state electron mediators at the Z scheme heterojunction interfaces not only facilitate charge transfer in the Z-scheme system, but also prevent undesired backward reactions. Among the various solid-state electron mediators studied so far, Au, in particular, is efficient in promoting charge transfer dynamics, and its localized surface resonance (LSPR) effect is advantageous for light harvesting in the visible light region. In addition to metal Au, defects in non-metallic and nonstoichiometric semiconductors have the same properties because they are likely to generate high-density free carriers, leading to induce the occurrence of LSPR. For this reason, $W_{18}O_{49}$ (WO_{3-x}) has an LSPR effect due to its abundant oxygen vacancies, which can result in absorption into near-infrared regions (NIR) containing more than half of the solar energy emitted to the earth.
Here, we introduced Au nanoparticle mediators at the interface of the Z-scheme $W_{18}O_{49}$/g-C_3N_4 heterostructures, in which Au nanoparticles not only served as a charge mediator for Z-scheme but also brought about the LSPR effects. In addition, the light absorption region over a wide spectrum was extended using NIR reactive $W_{18}O_{49}$. The photocatalytic hydrogen production rate of $W_{18}O_{49}$/Au/g-C_3N_4 was 3465 μmol/g*h, which is 1.9 times higher than that of $W_{18}O_{49}$/g-C_3N_4 (1785 μmol/g*h) and 2.8 times higher than that of single g-C_3N_4 (1242 μmol/g*h) under 1 sun irradiation. The improved photocatalytic H_2 production activity of $W_{18}O_{49}$/Au/g-C_3N_4 is attributable to synergistic effect of LSPR and Z scheme heterojunction.
First, Z-scheme charge transfer is incorporated by the Au NP mediator, which enhances charge separation and increases redox potentials. Second, the plasmonic Au NPs can sensitize $W_{18}O_{49}$/Au/g-C_3N_4 to visible light using hot electron injection arising from LSPR-related effects, e. g. resonant photo-induced coherent oscillation of free charges. Third, the abundant oxygen vacancies of the nonstoichiometric semiconductor $W_{18}O_{49}$ (WO_{3-x}) generated a high density of free carriers, providing a high possibility to induce the occurrence of LSPR. In addition, the LSPR of $W_{18}O_{49}$ extends the photoreaction region of $W_{18}O_{49}$/Au/g-C_3N_4 to NIR irradiation, leading to remarkable solar H_2 production. After consecutive solar hydrogen production experiments, both photocatalytic activity and catalytic structure remained unchanged, emphasizing the superior stability and reusability of this photocatalyst.
For these reasons, $W_{18}O_{49}$/Au/g-C_3N_4 is a good photocatalyst showing the high photoactivity of H_2 production extended to the visible and NIR region, and we propose the importance of integration of Z-scheme heterostructures and mediators based on LSPR effects.

5:00 PM EN07.09.02
Direct Growth of Ni(Fe,Mo)P Nanowires for Enhanced Alkaline Water Splitting with Facile Method Hyogyun Roh and Kijung Yong; Pohang University of Science and Technology, Korea (the Republic of)

Hydrogen as a renewable energy becomes more attention to solve the CO_2 emission. However, electrochemical H_2 production with zero CO_2 emission is still too expensive owing to high price of noble metal based electrocatalysts. Although cheap transition metal based electrocatalysts have impressively improved in recent researches, their low conductivity and poor activity on electrolysis limit the replacing noble metal. The self-supporting synthesis of various nanostructured electrode is a novel approach for developing cheap transition metal electrocatalyst with improved surface reaction area and long-term stability. In this research, NiFeP, NiMoP, NiCoP, and NiVP nanowires are fabricated by earth abundant transition metal through a two steps process: cation exchange from Zn oxide to metal oxide and surface phosphorization. The prepared samples are electrochemically tested as hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) catalysts in alkaline (1 M KOH) solution. The OER activities of all NiMP (M = Fe, Mo, Co, V) nanowires show enhanced activity compared to NiP. Especially, NiFeP exhibits the best OER performance with an overpotential of 279 mV (η_{100}) and a Tafel slope of 34 mV dec^{-1}, and this activity was higher activity than that of the IrO_2. The high electrocatalytic activity originated from the low kinetic energy barrier and the large surface active sites. In the HER activity, NiMoP shows improved performance with an overpotential of 68 mV (η_{10}) and a Tafel slope of 87 mV dec^{-1}. Although overpotential was higher than that of Pt in low current density, NiMoP exhibits outperformed activity at high current density. The combining of NiMoP and NiFeP as overall water splitting system requires potential of 1.57 V to generate 10 mA cm^{-2} current density.

5:00 PM EN07.09.03
Iron and Nitrogen Co-doped Agricultural Waste-derived Activated Carbons as Cathode Material for Microbial Fuel Cells Chia-Chieh Hsu and Han-Yi Chen; National Tsing Hua University, Taiwan

Microbial fuel cells (MFCs) are one of the attractive and sustainable energy sources in development while society pays more attention to environmental issues. MFCs are a bio-electrochemical system with the direct conversion from organic matter to electricity via microbes, which can be applied to wastewater treatment, electronic devices, and bio-sensors. However, MFCs tend to have low power output due to the poor oxygen reduction reaction (ORR) on the cathode, which significantly limits the power density. Therefore, platinum has been widely used as a catalyst to improve ORR activity, and this also leads to high cost, poor durability and stability. To deal with the problems, non-noble metal catalysts with high ORR activity and stability are crucial to replace Pt-based catalysts for commercialization in MFCs.
In this study, we developed iron and nitrogen co-doped agricultural waste-derived activated carbons (FeNAC) as cathode material in MFCs. The raw materials and precursors are inexpensive, and the synthesized FeNAC exhibit high surface area and favorable active sites for better electrocatalytic activity on the cathode. The results showed outstanding electrochemical performance, demonstrating that FeNAC is a promising material for MFC.

5:00 PM EN07.09.04
Ultrahigh-Loading Dry-Process for Solvent-Free Lithium-Ion Battery Electrode Fabrication Minje Ryu; Yonsei University, Seoul, Korea (the Republic of)

The current LIB electrode fabrication process relies heavily on the wet coating process, which uses the environmentally harmful and toxic N-methyl-2-pyrrolidone (NMP) solvent. Aside from being non-ecofriendly, this expensive organic solvent substantially increases the cost of battery production, as it needs to be dried and recycled throughout the manufacturing process. Furthermore, NMP is flammable and known to cause male infertility; thus, prolonged exposure can pose health risks to workers and present fire hazards. For this reason, achieving a completely solvent-free process for electrode fabrication is currently a unified goal for many battery researchers and manufacturers. Here, we report an industrially viable and facile dry process for LIB electrodes, namely, the dry press-coating process using multiwalled carbon nanotubes (MWNTs) and polyvinylidene fluoride (PVDF) as a dry powder composite and etched Al foil as a current collector. The MWNT-PVDF dry powder composite uniquely forms a robust 3D conductive scaffold that houses the active materials upon pressing, and the submicron pore-covered etched Al current collector provides remarkable adhesion to the interlayer. Notably, the mechanical strength and performance of the fabricated $LiNi_{0.7}Co_{0.1}Mn_{0.2}O_2$ (NCM712) dry press-coated electrodes (DPCEs) far exceed those of conventional slurry-coated electrodes (SCEs) and give rise to ultrahigh loading (71 mg cm^{-2}, 13.2 mAh cm^{-2}) with impressive specific energy and volumetric energy density of 372 Wh kg^{-1} and 763 Wh L^{-1}, respectively.

5:00 PM EN07.09.05
Facile Synthesis of Hollow-Structured Fe, F Dual-Doped CoS_2 Electrocatalyst for Oxygen Evolution Reaction Hyejin Kim, Kyeongseok Min, Jaeseo Lee and Sung-Hyeon Baeck; Inha university, Korea (the Republic of)

Due to the serious environmental problems caused by excessive consumption of fossil fuels, developing renewable energy sources and sustainable storage process have attracted significant attention from many researchers. The hydrogen is considered as one of the leading options for alternative energy carrier owing to its high gravimetric energy density. Water electrolysis is an efficient way to produce ultra-high purity hydrogen without environmental pollution. However, sluggish reaction dynamics and high overpotential of oxygen evolution reaction (OER) at anode greatly hinders the overall efficiency of water electrolysis. Although precious metal-based materials, such as IrO_2 and RuO_2, are considered as state-of-the-art OER electrocatalysts, their high cost, scarcity and low stability during long-term operation have limited their large-scale applications. Therefore, enormous efforts have been performed for development of highly efficient and stable noble metal-free electrocatalysts. Recently, metal-organic frameworks (MOFs), a class of inorganic-organic hybrid crystalline materials fabricated via the self-assembly of metal cations and organic building blocks, have aroused considerable interest owing to their high porosity, multifunctional properties, large specific surface area. Prussian-blue-analogues (PBAs) with the formula $M^{II}_3[M^{III}(CN)_6]_2$ (M = Fe, Co, Ni, etc) are a class of MOFs with coordinated metal sites linked by the cyano groups. PBA materials can be simply converted to transition-metal based chalcogenides, which are widely explored as efficient OER electrocatalysts. Therefore, they can be utilized as an appropriate precursor for transition metal-based electrocatalysts.
In this study, Fe, F dual-doped CoS_2 nanospheres with abundant active sites using bimetallic CoFe-PBA were fabricated for OER via facile self-templating co-precipitation strategy and subsequent annealing processes with sulfur and fluorine source. First, the monometallic Co-glycerate nanospheres were employed as a self-sacrificial template because of its facile synthetic procedure and low cost. After that, the Co-glycerate was converted to CoFe PBA via simultaneous dissolution and precipitation process at room temperature for 24 h. The self-templating strategy provides a simple synthetic route to prepare hollow-structured bimetallic nanospheres without additional steps of template elimination. The CoFe PBA hollow nanospheres were calcined with sulfur powder to prepare Fe-CoS_2. Subsequently, the prepared samples were pyrolyzed with NH_4F in Ar flow to obtain F, Fe dual-doped CoS_2 hollow nanospheres (Fe-CoS_2-F). The high electronegativity of F (4.0) compared with those of Fe (1.83), Co (1.88), and S (2.58) can partially withdraw electrons from other elements, thereby modulating the surface electronic properties and adsorption energy of oxygen-containing reaction intermediates. Furthermore, simultaneous cation and anion dual-doping can maximize the surface polarity, promoting the infiltration of aqueous electrolytes during OER procedure. As expected, the as-prepared Fe, F dual-doped CoS_2 nanospheres exhibited superior electrochemical performance toward OER with an overpotential of 298 mV to achieve the current density of 10mA cm^{-2}, and a Tafel slope of 46 mV dec^{-1} in 1.0 M KOH, which was much better than the commercial RuO_2 catalysts.

5:00 PM EN07.09.06
ZIF-67 Derived Co_3O_4/CoFe-LDH with Strongly Coupled Interfacial Junction as an Enhanced Electrocatalyst for Oxygen Evolution Reaction Jaeseo Lee, Sojeong Min, Minjung Kim and Sung-Hyeon Baeck; Inha University, Korea (the Republic of)

Development of renewable and clean energy production has become an urgent issue owing to the increasing concerns about depletion of fossil fuels and environmental crisis. Producing hydrogen using water electrolysis is regarded as promising strategy for solving the problem owing to its environmental friendliness and high energy density of H_2. However, the sluggish kinetics and large overpotential of oxygen evolution reaction (OER) at the anode remains a bottleneck in water electrolysis. Until now, noble metal-based oxides, such as Ir/Ru based oxides, are generally used as state-of-the-art electrocatalysts for OER. Unfortunately, their scarcity, high cost and low durability during long-term operation have seriously hindered the large-scale applications of water electrolysis system. Accordingly, development of earth-abundant electrocatalysts with high activity and stability is essential to substitute the expensive electrocatalysts for water electrolysis. Spinel-structured cobalt oxide (Co_3O_4), which is constructed by combination of Co^{2+} and Co^{3+}, is one of the promising electrocatalysts for OER due to rich redox properties and high corrosion resistance. Also, the bimetallic layered double hydroxide (LDH) structure is generally known as highly efficient electrocatalyst owing to its large surface area and flexible open structure.
Based on the above considerations, we synthesized the core-shell structured Co_3O_4/CoFe-LDH composite with abundant oxygen vacancies via co-precipitation, heat treatment, and subsequent sonochemistry method. First, ZIF-67 was prepared by the co-precipitation reaction of Co^{2+} with 2-methylimidazole in methanol solution. Second, the ZIF-67 was annealed and oxidized at high temperature to prepare dodecahedral-shaped Co_3O_4 (Co_3O_4@C). After that, the Co_3O_4 was partially reduced under H_2/Ar flow to induce oxygen vacancies into Co_3O_4 (V_o-Co_3O_4@C). Finally, the Co^{2+} and Fe^{3+} ions (molar ratio of 2:1) dissolved in DI water, and as-prepared V_o-Co_3O_4@C was added into the solution. After stirred for about 30 min to promote adsorption of metal ions on the surface of V_o-Co_3O_4@C, 1M KOH was injected into the above mixture, and ultrasonicated for 30 min. In this step, the adsorbed metal ions react with OH^- ions, resulting in formation of CoFe LDH on the surface of V_o-Co_3O_4 (CoFe-LDH/V_o-Co_3O_4@C). Owing to the electrostatic interaction between oxygen defect sites and metal ions, the CoFe-LDH/V_o-Co_3O_4@C has strongly coupled interfacial junction. Construction of interfacial junction of different phase is effective way to boost charge transfer efficiency. Additionally, it also can prevent the detachment of CoFe-LDH, thereby enhancing the long-term stability of electrocatalyst during OER process. As a result, the CoFe-LDH/V_o-Co_3O_4@C exhibited significantly improved electrocatalytic OER activity with low overpotential and Tafel slope, which are even superior to state-of-the-art RuO_2 electrocatalyst. Moreover, the prepared electrocatalyst showed stable operation over 100 h at a current density of 10 mA cm^{-2} in alkaline solution. We believe that this research will provide a new insight into the preparation of transition metal-based composite materials for energy storage and conversion system.

5:00 PM EN07.09.07
Facile Synthesis of Co, N Dual-Doped Ni_2P Grown on Nickel Foam as Active Electrocatalyst for Oxygen Evolution Reaction Minjung Kim, Hyejin Kim, Kyeongseok Min and Sung-Hyeon Baeck; Inha University, Korea (the Republic of)

Due to the increasingly severe energy depletion and environmental pollution, a lot of studies on efficient and renewable energy have been actively conducted. Recently, Hydrogen is regarded as the most prospective energy source to replace the traditional fossil fuels. Overall water electrolysis, which consists of hydrogen evolution reaction (HER) on the cathode and oxygen evolution reaction (OER) on the anode, is a noticeable technology for producing high-purity hydrogen. The OER has complicated reaction mechanism involving four electron transfer, thereby resulting in high overpotential. To overcome this issue, noble metal-based materials, such as IrO_2 and RuO_2, are generally employed as electrocatalysts owing to their high activity. However, the high cost and poor stability of precious metal-based electrocatalyst have limited widespread application of water electrolysis. Therefore, non-noble metal-based

electrocatalysts with high OER performance have been explored.
Specifically, Ni-, Co-, Fe-, Mn-based electrocatalysts, including their phosphides, sulfides, oxides, chalcogenides, have studied due to their adjustable electronic structure and earth abundance. Among them, transition metal phosphides (TMPs), which have high electrical conductivity, high electrochemical stability, and rich active sites, have been reported as efficient OER electrocatalysts. Furthermore, in order to increase intrinsic OER performance, heteroatom doping strategy has been carried out to modify their electronic configuration structure. The introduction of dual dopants, which have different polarity and electronegativity, can not only modify the electronic state of host species but change the adsorption free energy of reaction intermediates during the OER process.
On the basis of above explanation, Co, N dual-doped Ni_2P grown on nickel foam was synthesized by only two step hydrothermal reaction and subsequent heat treatment. First, a piece of nickel foam (1 cm x 3 cm) (NF) was sonicated with 1.0 M HCl for 15 min to remove the oxide layers and rinsed with DI water and ethanol. Afterward, HCl, $K_3[Co(CN)_6]$, and $Na_3C_6H_5O_7$●$2H_2O$ were put into a Teflon-lined autoclave (130 mL) with NF, and kept at 95 °C for 24 h to synthesize nickel cobalt Prussian blue analogue on NF (NiCo-PBA/NF). Owing to the surface etching of NF by HCl solution, the released Ni^{2+} species immediately react with the $K_3[Co(CN)_6]$, resulting in formation of bimetallic PBA. Finally, the NiCo-PBA/NF was annealed with NaH_2PO_2 at 430 °C for 2 h under NH_3/Ar atmosphere. During the process, the NiCo-PBA was phosphidized owing to PH_3 gases generated by thermal decomposition of NaH_2PO_2. Simultaneously, the nitrogen dopants can be introduced into Co-doped Ni_2P structure under the NH_3 flows and elevated temperature. As a results, the Co, N dual-doped Ni_2P exhibited a notable enhancement of catalytic activity toward the OER compared with Co-Ni_2P, N-Ni_2P, and pure Ni_2P counterparts. Furthermore, the Co, N-Ni_2P/NF showed lower overpotential and superior long-term durability than state-of-the-art RuO_2 electrocatalyst. Undoubtedly, this work will offer a new synthetic insight on the rational design of defect-rich transition metal-based materials with improved catalytic performance for energy storage and conversion system.

5:00 PM EN07.09.08
Simulation of Deformation Mechanisms in Coated and Uncoated Platinum Nanoparticles Muztoba Rabbani[1], Ingrid M. Padilla Espinosa[1], Ruikang Ding[2], Tevis Jacobs[2] and Ashlie Martini[1]; [1]University of California Merced, United States; [2]University of Pittsburgh, United States

Single-digit-nanometer particles are the building blocks for emerging energy technologies, but the complex interrelationships between their size, shape, and mechanical properties are still not fully understood. Particularly, for the smallest nanoparticles, the traditional "smaller is stronger" trend may not apply, and deformation can occur through both atom diffusion and dislocations. Decreasing particle size leads to a greater percent of surface atoms with lower activation energy for diffusion and therefore more diffusion-mediated deformation. Surface energy can be modified by coating nanoparticles, so coatings are expected to affect the relative contributions of diffusion vs. dislocations to deformation. In this study, we used classical molecular dynamics simulation to study the deformation mechanisms of platinum nanoparticles of various shapes and sizes, with and without a surface coating of another metal or oxide. Compression tests were performed on both coated and uncoated nanoparticles to investigate the link between surface energy and deformation mechanisms. Our study contributes to the understanding of nanoparticle deformation which is crucial for designing nanoparticle-based energy systems.

5:00 PM EN07.09.09
Facile Synthesis of CeO_2 Decorated Co_4N Nanoparticles as Highly Active and Durable Electrocatalyst for Oxygen Evolution Reaction Kyeongseok Min, Jaeseo Lee, Sojeong Min and Sung-Hyeon Baeck; Inha University, Korea (the Republic of)

Growing concerns about depletion of fossil fuels and global warming demand the exploration of eco-friendly and efficient energy sources. Recently, hydrogen gas has been considered as a promising candidate for future energy source owing to its environmental friendliness and high energy density. Electrochemical water splitting, involving cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER), is an ideal technology for hydrogen production without any other impurities such as carbon dioxide. Unfortunately, the overall efficiency of water electrolysis is seriously limited by the sluggish kinetics and large overpotential of OER due to the energetically unfavorable four-electron reaction pathway. Therefore, the development of efficient and durable OER electrocatalyst is essential to decrease the reaction energy barrier for OER and enhance the performance of the overall water electrolysis.
Among the noble metal-free materials such as transition metal oxides, sulfides, phosphides, nitrides *etc*., the transition metal nitrides (TMNs) showed promising electrocatalytic activity toward the OER. The TMNs have anti-corrosion stability in alkaline solution and high electrical conductivity due to their metallic feature. Furthermore, the nitrogen atoms in TMNs induce expansion of metal lattice and modify transition metal d-band structure, thereby shifting their d-band center into the optimal energy state for OER. Despite the noticeable progress in TMNs-based electrocatalysts, their unsatisfactory OER performance need to be further improved because of inferior redox reaction kinetics of TMNs.
To boost electrocatalytic OER activity of TMNs, construction of heterostructure with other species which has rich redox properties can be adopted as efficient strategy. The formation of well-defined heterostructure not only offer abundant electrochemical active sites but optimize the electronic properties of catalysts owing to strong interfacial coupling effect between the two components, thus leading to enhanced oxygen evolution performance. Recently, cerium oxide (CeO_2) has been employed as an activating agent for promoting electrocatalytic oxygen evolution, which is attributed to its rich redox property owing to versatile oxidation state between Ce^{3+} and Ce^{4+}. Furthermore, the CeO_2 has abundant empty d orbitals and oxygen vacancy defects, leading to strong electron interaction and introduction of efficient active sites for OER in alkaline solution.
Herein, inspired by above mentioned considerations, we proposed a facile method to prepare heterostructured Co_4N/CeO_2 nanoparticles using bimetallic CoCe-BTC (benzene-1,3,5 tricarboxylate) MOF (metal organic framework). As a self-template and precursor of Co_4N/CeO_2, bimetallic BTC MOF has substantial merits such as chemical and structural tunability, low cost, high surface area and porosity. The CoCe-BTC was converted into heterostructured Co_4N/CeO_2 via simple annealing and selective nitration process. Benefiting from electrical conductive metallic feature of Co_4N and multivalent nature of CeO_2, the synthesized Co_4N/CeO_2 electrocatalyst exhibited exceptional OER performance with a low overpotential of 297 mV to acquire a current density of 10 mA cm^{-2}, small Tafel slope of 88 mV dec^{-1}, and excellent long-term durability over 100 h in alkaline electrolyte. This research will pave the way for development of heterostructured noble metal-free electrocatalyst for various energy storage and conversion system.

5:00 PM EN07.09.10
Hollow Structured N, S Co-Doped Carbon Nanotubes Encapsulating Co/CoS_2 Nanoparticles as Highly Efficient Electrocatalyst for Zinc-Air Battery Sojeong Min, Minjung Kim, Hyejin Kim and Sung-Hyeon Baeck; Inha University, Korea (the Republic of)

The development of sustainable energy conversion and storage systems is crucial owing to the depletion of fossil fuels and energy crisis. Recently, rechargeable Zn-air batteries (ZABs) are regarded as promising energy devices due to their high specific energy density (1084 Wh kg^{-1}), reliable safety and cost effectiveness. However, the ORR and OER involving a four-electron reaction process at cathode always suffer from sluggish kinetic behaviors during the charge and discharge process. Although noble metal-based materials (Pt/C for ORR and RuO_2 for OER) are commonly used as the most excellent catalysts for ORR and OER, their high cost, monofunctionality and low electrochemical durability limit the practical application of ZABs. Consequently, it is essential to develop non-noble metal-based electrocatalysts with superior durability and high electrochemical activity for utilization of ZABs. Transition metal-based materials (alloys/ sulfides/ oxides/ nitrides/ phosphides) have attracted considerable attention as electrocatalysts for rechargeable ZABs benefiting from their low cost, high electrochemical activity, and stable operation. Among the various candidates, transition metal sulfides have superior electrical conductivity compared with other chalcogenides, which is mainly attributed to the shallower valence band generated by S 3p orbital, resulting in

formation of narrower band gap. Moreover, the formation of heterojunction between *n*-type metal sulfides and metals, which is known as Mott-Schottky contact, can further improve the charge transfer efficiency of electrocatalysts.
Inspired by above considerations, hollow structured microsphere with N, S co-doped carbon nanotube shell encapsulating Co/CoS_2 nanoparticles (Co/CoS_2/NSCNT) was prepared via facile polymerization and subsequent pyrolysis steps. First, we synthesized polystyrene (PS) spheres by polymerization, which were used as self-sacrificial template to generate uniform hollow structures. And then, Co^{2+} ions and 2-methylimidazole were mixed in PS solution and ZIF-67 was coated on the surface of PS spheres. Subsequently, the obtained core-shell structured PS@ZIF-67 was pyrolyzed with dicyandiamide at 750°C for 1.5 h under Ar flow. During pyrolysis, PS spheres were completely removed and surface of the spheres became rougher with the growth of N-doped carbon nanotubes owing to the catalytic effect of Co nanoparticle, resulting in the formation of hollow structured Co/NCNT. The well-defined hollow structure can not only reduce ion diffusion length but also increase active surface area. Finally, Co/NCNT was annealed with sulfur at 550°C for 2h under Ar atmosphere to simultaneously conduct partial sulfidation of metal species and sulfur doping into carbon matrix (denoted as Co/CoS_2/NSCNT). Generally, the CNT provide an efficient electron pathway for active species and protect the encapsulated nanoparticles from aggregation and dissolution during the electrochemical reaction. Furthermore, introducing heteroatoms (e.g. N, S, and P) into the carbon materials can affect the electron neutrality of the sp^2 carbon lattice and lead to partial polarization of adjacent carbon, thereby promoting the adsorption of reaction intermediates. As expected, the prepared Co/CoS_2/NSCNT exhibited the excellent ORR activity with half-wave potential of 0.890 V (vs. RHE), outperforming that for the state-of-the-art Pt/C (0.855 V (vs. RHE)). Additionally, it also showed outstanding OER kinetics and low overpotential of 363 mV at a current density of 10 mA cm^{-2}, which was superior to the other prepared electrocatalysts.

5:00 PM EN07.09.12
Feasible Fabrication of Carbon Nanotube-Poly(Acrylic Acid) Network Encapsulating Silicon Microparticle for Lithium-Ion Batteries Gwanghyun Lee and Jong Hyeok Park; Yonsei University, Korea (the Republic of)

Recently, the electrification of personal mobility is accelerating the development of Li-ion batteries. With the demands for a lightweight battery, silicon (Si) is considered a strong candidate to achieve high energy density due to its high theoretical capacity (>3600 mAh g^{-1}). However, the unstable capacity retention of Si anodes is a critical issue for industrial applications. Si particles experience harsh volume changes due to the alloying with the Li ions. This results in the pulverization of Si particles followed by the excessive growth of the solid-electrolyte interphase (SEI) layer. Here, we propose the conductive hybrid network encapsulating Si particles fabricated with a facile slurry-casting method. The functionalized carbon nanotubes (FCNTs) were easily dispersed into water and formed entangled network structures. In addition, poly(acrylic acid) (PAA) enhanced the mechanical properties of the FCNT network and enabled flexible behaviors. This hybrid network uniformly coated Si surfaces and allowed stable connections between the particles providing electron pathways. After the cycle, the pulverized Si particles maintained their morphology with the mechanical supports of the FCNT/PAA network inhibiting the irregular formation of the SEI layer while Si anode with conventional carbon black showed severe destruction of the structure. The electrode with FCNT/PAA network exhibited stable cycle performance during 200cycles and excellent rate capability even at 10C which indicates safe and fast electron transport toward Si particles.

5:00 PM EN07.09.13
Photo-Electrocatalysis (PEC) Enhancement of Anatase TiO_2 Thin Films with [001] Texture for Both Oxygen Evolution Reaction (OER) and Energy-Efficient Applications Luis Esquivel, Andrew Ichimura and Jingjing Qiu; San Francisco State University, United States

The production of hydrogen from water has the potential to be part of the portfolio of renewable energy sources that will help to reduce our dependence on fossil fuels. Splitting water requires catalysts to help drive the hydrogen and oxygen evolving reactions. Photo electrocatalysis (PEC) is a method to split water that employs a light-absorbing semiconductor to produce charge carriers and a catalyst to lower the overpotential of the hydrogen and oxygen evolving reactions (HER and OER, respectively). Typical catalysts for PEC water splitting include nobel metals such as Pt and Pd (HER) and IrO_2 (OER), which are expensive and rare. In order to realize the potential of PEC, less expensive, nontoxic, and earth-abundant materials must be studied to replace these noble metals, especially for the kinetically slow OER.
Anatase titanium dioxide is a well-known functional material with applications in the fields of environment and energy. The band gap value in semiconductors determine the energy requirements for electron transfer and light absorption. Anatase has a band gap of 3.2 eV and valence and conduction band energy levels that are suitable for PEC water splitting and especially the OER reaction. Experimental studies demonstrate that (001) facets are highly oxidizing surface and the [001] orientation imparts a negative flatband potential that makes it ideal for OER and charge transfer. In this work, we combine these two structural characteristics into the semiconductor TiO_2 layer to improve the PEC performance.
Anatase TiO_2 thin films with (001) facets and [001] orientation were synthesized following previous work (Ichimura, et al. 2012) modified for FTO substrate. . First a blocking layer of amorphous titania (a-TiO_2) was first deposited onto clean FTO substrate. Then, anatase with [001] texture was grown hydrothermally from TiF_4 solution. The films were then annealed at 500 C and then any pinholes were sealed by electrochemically by depositing a-TiO2 from a $TiCl_3$ solution. Finally, the NiO/Ni$(OH)_2$ catalyst layer was formed by electrodeposition and monitored by chronoamperometry/chronocoulometry. The resulting thin films are characterized with gracing incidence X-ray diffraction (GI-XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM). These measurements confirm the [001] orientation and (001) faceting at the surface of the thin films. the photoelectrochemical measurements of the thin films were conducted by means of cyclic voltammetry in 0.1 M KOH solution using a 150 W xenon arc lamp as a light source. The PEC OER of anatase thin films before and after Ni2+ deposition was observed under dark and light conditions. Before illumination, only the Ti^{3+}/Ti^{4+} redox couple can be observed with an onset potential of -0.7 V (vs Ag/AgCl) and negligible OER at anodic potentials. Under irradiation, the TiO_2 thin film without Ni^{2+} catalyst exhibits a small photocurrent that saturates at low potentials through the anodic scan. With the NiO(OH)/Ni$(OH)_2$ catalyst present, the photocurrent continues to increase throughout the anodic region. Our preliminary results show a current density of ~1.5 mA cm^{-2} at 0.8 V. This study may lead to improvements in the PEC activity of anatase TiO_2 thin films based on optimizing the film structure for both reactivity and charge transport.

SESSION EN07.10: Energy Storage, Hydrogen Technologies and CO2 Capture II
Session Chairs: Chong Liu and Hua Zhou
Friday Morning, April 14, 2023
Moscone West, Level 2, Room 2007

8:00 AM EN07.10.01
A Recyclable Solid Electrolyte for Li-Ion Batteries Composed of Supramolecular Nanostructures Yukio Cho, Cole D. Fincher, Yet-Ming Chiang and Julia Ortony; Massachusetts Institute of Technology, United States

The recyclability of Li-ion batteries is a critical goal but is technically challenging and often impractical due to the complex structure of mixed materials and the irreversible process of production. We investigated the use of organic small molecule self-assembled nanoribbons as an electrolyte material because they offer precise spatial arrangement, high surface areas, tunable surface chemistry, and most notably here, reversible structural formation. In this study, we synthesized nanoribbons by self-assembly of aramid-containing amphiphiles that overcome structural stability problems, and we systematically modified the surface chemistry to promote Li-ion conductivity. We investigated the performance and transport mechanism of these supramolecular nanomaterials as a solid electrolyte for Li-ion batteries. Furthermore, we show direct recyclability of the end-of-life cell.

8:15 AM EN07.10.02

Ionothermal Upcycling of Spent NMC 111 to Nickel-rich NMC Cathodes in Reciprocal Ternary Molten Salts Tao Wang[1,2], Huimin Luo[1] and Sheng Dai[1,2]; [1]Oak Ridge National Laboratory, United States; [2]The University of Tennessee, Knoxville, United States

The wide use of lithium-ion batteries (LIBs) in portable devices and electric vehicles has changed people's lifestyles, while end-of-life (EOL) LIBs are causing severe environmental risks due to their hazardous components. Thus, properly handling EOL LIBs has become an urgent and promising task. Though the current recycling technology can recover valued metals through the breakdown of cathodes, the added value from the compound structure of cathode materials is lost. Direct recycling stands out as an emerging technology to retrain the added value of the compound structure by healing the compositional and structural defects in spent cathode materials. However, the recovered state of EOL LIB may be outdated, because the recycling of EOL LIBs generally happens years later after production. In this work, beyond direct recycling, direct upcycling of spent cathodes to the next-generation cathodes is realized to maximize the value of EOL LIBs.[1] The directly upcycling of spent NMC 111 to Ni-rich NMCs was achieved in "reciprocal ternary molten salts" (RTMS) by simultaneously realizing the addition of Ni and the relithiation of Li. After flux upcycling in RTMS, the obtained Ni-rich NMCs exhibited very similar performance to that of the pristine NMC 622 including an α-$NaFeO_2$-type layered structure, restored Li content, and excellent electrochemical performance.

Scheme 1. Illustration of the upcycling of D-NMC 111 to Up-NMC 622 in RTMS.

Reference

1. T. Wang, H. Luo, J. Fan, B. P Thapaliya, Y. Bai, I. Belharouak, S. Dai, *iScience*, 2022, 103801.

8:30 AM EN07.10.03

Electrochemical Resource Recovery Using Battery Electrode Materials Seoni Kim; Ewha Womans University, Korea (the Republic of)

Demand for lithium is dramatically increasing due to the rapid growth of secondary battery usage. Lithium is mainly produced via evaporation and precipitation from brine lakes, which requires a long period of time for lithium production. Also, this process can only be applied to limited water sources that contain low amounts of certain ions, and several environmental concerns are arising regarding the evaporation and precipitation method.

Recently developed electrochemical lithium recovery systems, whose operation principle mimics that of lithium-ion batteries, might relieve these concerns. The cathodes (e.g., $LiMn_2O_4$, $LiFePO_4$) for lithium-ion batteries have the suitable channel size for selective Li^+ insertion, which enables selective recovery of lithium from source waters with a wide range of lithium ions (Li^+) concentrations. However, there had been a lack of understanding of the physicochemical behaviors of the Li^+-selective electrode in realistic operation conditions. In addition, the stability and cost of the counter electrodes of this system have been serious issues that impede the practical application of this system.

This talk will cover the physicochemical behavior of the Li^+ selective electrode during the electrochemical lithium recovery process regarding the Li^+ concentration in source water and the operation rate will be covered. On the basis of the understanding based on the characterization of the electrodes using X-ray techniques, increasing the density of the electrode/electrolyte interface is suggested as a realistic and general route to enhance the overall lithium recovery performance and is experimentally corroborated in a wide range of operating environments. Also, new electrode designs for the electrochemical lithium recovery system to improve performance and durability are suggested.

8:45 AM DISCUSSION TIME

9:15 AM EN07.10.06

Circular Economy Strategies for Clean Hydrogen Technologies Taylor Uekert, Hope Wikoff and Alex Badgett; National Renewable Energy Laboratory, United States

Clean hydrogen produced from water electrolysis and powered by renewable electricity is expected to play a critical role in achieving decarbonization goals. Recovery and recycling of the valuable materials contained within electrolyzers and fuel cells will be essential to maintain a resilient supply chain and mitigate environmental impacts. However, research into circular economy strategies for clean hydrogen production lags behind other renewable energy technologies such as lithium-ion batteries or photovoltaics. This quantitative analysis maps electrolyzer and fuel cell components to emerging recycling techniques such as pyrometallurgy and acid- or organic solvent-based recovery. The recycling options are then assessed and compared across environmental impacts, costs, and technical capabilities (e.g., recovery yields). This critical analysis lays crucial groundwork for the development of a circular economy for hydrogen technologies.

9:30 AM EN07.10.07

High Throughput Screening of Cladded Steel Pipelines for Hydrogen Fuel Vijay Shankar Sridharan[1], Varun Chaudhary[1], Siwei Du[2] and Dong Zhili[1]; [1]Nanyang Technological University, Singapore; [2]Advanced Remanufacturing and Technology Centre, Singapore

Many nations have aimed for net zero emissions by 2050. Existing gas pipelines and containers can be upgraded for transport and storage of hydrogen as part of a sustainable energy transition. However, pipeline-hydrogen interaction and its safety need to be established for further use within the operational conditions. In this study, hydrogen embrittlement behavior of alloy gladed API X 60 steel was studied using high throughput methodologies. API X-60 steel is widely used in the oil and gas pipeline for transportation over long networks. The compositionally graded alloy deposition was performed through additive manufacturing technique direct laser deposition. A combination of 316L and In625 powders were used to compositionally deposit in different gradients to identify the optimal composition in terms of depositions that are crack free and at the same time has maximum resistance towards hydrogen embrittlement. The high-resolution Scanning Kelvin Probe Force Microscopy (SKPFM) is used to map the diffusion profiles of hydrogen at cross section of samples after hydrogen charging. The results from SKPFM, electron microscopy, and variation in mechanical behavior before and after HER was correlated and presented as a function of alloying composition. The variations in the resistance to hydrogen embrittlement and hardness, measured using high throughput characterization techniques, were rationalized by recourse to different phases present in the microstructures. Our study showed that the composition gradient coatings through additive manufacturing has improved the resistance to corrosion and hydrogen embrittlement of API X-60 steel.

9:45 AM BREAK

10:15 AM EN07.10.08
Multiscale Hydrogen Chemistry of Direct Iron Reduction in Decarbonizing Steelmaking Xueli Zheng, Lauren Y. Moghimi, Subhechchha Paul, Yi Cui and Leora E. Dresselhaus-Marais; Stanford University, United States

Steelmaking contributes to 8% of the total annual CO_2 emissions globally. One attractive approach to decarbonizing steelmaking is to shift from the conventional coal-based reduction of iron ores in blast furnaces to hydrogen-based direct reduction of iron, preventing CO_2 emissions from coal. Despite its opportunity, hydrogen-based steelmaking has been slow to scale up because iron ore reduction with hydrogen is slow and energy-intensive (i.e. endothermic). While extremely important, the reaction kinetics and mass transfer in hydrogen-based steelmaking are poorly understood. Herein, we measure the kinetics of magnetite (Fe_3O_4) reduction with H_2, comparing industrial Fe_3O_4 to the lab-synthesized nanoscale Fe_3O_4 samples. Using *in situ* synchrotron X-ray diffraction and Rietveld analysis, we obtain the phase fraction of Fe_3O_4, wustite (FeO), and metallic Fe as reduction propagates on the full temperature dependence from 300 ^oC to 800 ^oC. We further map out the reaction kinetics and reveal the associated structural/morphology changes. Using *in situ* small-angle X-ray scattering, we demonstrate how the kinetics evolve simultaneously with mesoscopic structural changes. Ptychographic X-ray computed tomography reveals how evolved nano-/microstructure influence reduction reaction kinetics in H_2-based steelmaking. Our work provides insights on microstructure design to accelerate reduction reaction kinetics, further paving the way for commercializing sustainable steelmaking.

10:30 AM EN07.10.09
A Multi-Scale View of Scalability Challenges in H_2-Based Ironmaking Leora E. Dresselhaus-Marais; Stanford University, United States

Modern metals manufacturing relies on centuries-old techniques that we must now revisit in light of global challenges in environmental and resource sustainability. While steel is ubiquitous, its refinement currently contributes 8% of the global CO_2 footprint, 64% of which originates from ironmaking. Updating ironmaking processes requires careful studies of the fundamental science that complicates scalability and direct integration of those approaches with scale models. I will present my group's work using *in-situ* X-ray and electron probes (diffraction and imaging) to directly resolve the kinetics and multiscale structural dynamics for H_2-based direct iron reduction. By mapping these dynamics from the atomic through µm-scales, we demonstrate we demonstrate the intricate and complex links between mechanics, chemistry, and mass transport give rise to complex chemistry. Our finding shed light on the complex reaction dynamics of this system, paving the way for important insights into the energy-landscape of carbon-free steelmaking that offer an important starting point for process models.

10:45 AM EN07.10.10
The Poisonous Effect of Carbon-Bearing Species on Adsorption of Hydrogen on Pd Alloys Membrane Surfaces Abduljabar Alsayoud[1], Ahmed Abuelyamena[1], Venkateswara Manga[2], Rached Ben Mansour[1] and Mohammed Habib[1]; [1]KFUPM, Saudi Arabia; [2]The University of Arizona, United States

Hydrogen separation through the Pd membrane is one of the most promising technologies for producing pure H_2. This work investigates the effect of gaseous impurities, CO, CO_2 and CH_4 on the adsorption process of hydrogen, i.e. on the physisorption, and the chemisorption of hydrogen on Pd- x (x- Au, Pt) surface using density functional theory (DFT). Specifically, the study aims to sample the energy landscape associated with the hydrogen-adsorption while varying the structural and compositional degrees of freedom. The relative orientations of adsorbing molecules with respect to the surface of the slab, the crystallographic plane of the slab and various configurations of the adsorbed species have been investigated. In the case of compositional degrees of freedom, adsorption as a function of surface coverage, of mainly hydrogen, is studied. The physisorption of H2 on the Pd alloys-surface at different coverages of H-atoms (and without any impurities) has revealed that among the available adsorption sites, the top site with the horizontally oriented gaseous molecule is energetically the most favorable. Among the impurity gaseous species, when investigated for their binding to the Pd-surface and for their effect on the physisorption energies of the H2, CO is found to alter the energetics of the adsorption process, indicating a higher poisoning effect relative to CO2 and CH4. Moreover, the study also showed that at higher coverages of H-atoms, the physisorption energies of H2 decrease.

11:00 AM EN07.10.11
Emission-Free Hydrogen and High-Value Carbon Co-Production from Methane Pyrolysis Marco Gigantino[1], Eddie Sun[1], Alexander Nelson[1], Henry Moise[1], Vasudev Haribal[2], Andrew Tong[2], Jian-Ping Shen[2], Raghubir Gupta[2], Arun Majumdar[1] and Matteo Cargnello[1]; [1]Stanford University, United States; [2]Susteon Inc., United States

Methane pyrolysis is a technology that allows to produce greenhouse-gas-free H_2 along with solid carbon using less energy per mole H_2 than water electrolysis (37 vs. 286 kJ/mol H_2). Catalytic approaches applied to methane pyrolysis are strongly limited by catalyst deactivation from carbon coking. In addition, a system that possesses high and stable H_2 yield while producing high-quality carbon has remained elusive. Here, we report on a novel methane pyrolysis process for the co-production of H_2 and high-value carbon, which contains a large fraction of carbon nanotubes. The process consists of repeated pyrolysis steps followed by in-situ (i.e., within the reactor) regeneration steps of an iron-based catalyst, aimed at dislodging the carbon from the catalyst active surface. In such way, the catalyst can be reused while the carbon can be collected in a semi-continuous fashion. We demonstrated the operation for multiple cycles with high CH_4 conversion, high selectivity for H_2, and carbon dislodging in a fluidized-bed reactor system. Besides methane, we also investigated ethane as a feedstock for this process, since it is another main component of natural gas. Overall, this process demonstrates the production of high-quality carbon and hydrogen without carbon emissions.

11:15 AM EN07.10.12
CO_2 Capture Using Nanomaterials and Low-Energy Requirements Vitaliano Dattilo[1,2], Alexsanthra Rodriguez[1], Dogukan Yazici[1], Michael Bozlar[1,1], Marco Simonetti[2], Forrest Meggers[3] and James Coleman[3]; [1]The University of Texas at Arlington, United States; [2]Politecnico di Torino, Italy; [3]Princeton University, United States

Natural phenomena combined with intense human activities have resulted in a sudden increase in carbon dioxide (CO_2) emissions over the last century, and CO_2 is a major anthropogenic greenhouse gas. The most recent reveal that CO_2 concentration in the atmosphere rose from 378 parts per million (ppm), back in 2005, to 419 ppm in 2022. In order to mitigate CO_2 concentrations in the atmosphere, we propose to focus on different aspects of CO_2 capture and management, from the perspectives of materials science and computational chemistry. The main purpose of this research is to identify adequate materials and optimal processes to accomplish sustainable CO_2 capture and sequestration. In particular, we focus on materials chemistry in order to minimize the energy demands for CO_2 sorption and conversion/sequestration. Using computational techniques including, Density Functional Theory (DFT), as well as Molecular Dynamics (MD) Simulations, we study the electronic properties of the materials (Fermi Level, Density of States, and Charge Density Difference Analysis), as well as their ground states after adsorption and their capacity to capture CO_2. We also analyze the nature of the physical and chemical interactions of the different sorbent materials used. Then, we quantify the energetic requirements for the adsorption and desorption processes. To validate our models, we identify and design sorbents as well as experimental processes to replicate environmental conditions. The results indicate that the proposed sorbents can capture several thousands ppm of CO_2 in 24 hours under stationary diffusion conditions.

SESSION EN07.11: Functional Materials Based on Abundant Elements

Session Chairs: Peter Sushko and Hua Zhou
Friday Afternoon, April 14, 2023
Moscone West, Level 2, Room 2007

1:30 PM EN07.11.01
Engineering the Solid State Synthesis and Processing of Nickel Boride with Enhanced Functionality Jennifer Hong, Paolo P. Pescarmona and Loredana Protesescu; University of Groningen, Netherlands

Nickel boride Ni_xB_y has shown potential as an efficacious catalyst for a broad range of systems (hydrogenations, hydrogen, and oxygen evolution reactions) under challenging conditions (such as high pH or high temperatures). Given the increased surface area and surface optimization, as commonly displayed by other nanosized materials the nanostructured Ni_xB_y remains underdeveloped despite the potential enhanced performance,. The limited development of nano NixBy is mainly due to the notoriously difficult synthetic process. Recent works have shown that synthetic methods at lower temperatures (<400 ^oC) yield amorphous polydisperse nanocrystals (NCs), while phase purity remains an issue at higher temperatures. Here, a simple, scalable synthesis is demonstrated to obtain a phase-pure nanocrystalline Ni_xB_y. Through the solid-state reaction of either metallic Ni^0 or $NiCl_2$ with $NaBH_4$ at a relatively low temperature (400 ^oC) under atmospheric pressure, crystalline nanosized Ni_2B and Ni_3B could be obtained with high yield in pure phase and with narrow size distribution (15-30 nm). Through extensive mechanistic studies, we show that Ni nanoclusters (*approx.* 1 nm) are intermediate in the boriding process, while the halide precursors lower the decomposition temperature of the $NaBH_4$ (used as a reducing agent and B source). We further explore the size control using reaction mediators, and we probe the differential nucleation and growth of Ni (clusters) or Ni_xB_y NCs while using L (amine, phosphine) and X-type (carboxylate) mediators. The synthesized Ni_3B nanopowder can undergo surface functionalization with inorganic ligands in polar solvents, forming a stable ink. Furthermore, the Ni_3B nanocrystals ink can be ligand-exchanged with organic ligands in a non-polar low-boiling point solvent. This work opens the door for the large-scale production of Ni_xB_y nanocrystals solution-processable inks to make it a commercially viable catalyst and pave the way for other metal borides colloidal nanostructures.

1:45 PM EN07.11.03
Nanoscale Iron Redistribution During Thermochemical Decomposition of $CaTi_{1-x}Fe_xO_{3-\delta}$ Alters the Electrical Transport Pathway Jason Luong[1], Xin Wang[1], Alicia Tsung[2], Nicholas Humphrey[2], Huiming Guo[1], Benjamin Lam[1], Shaama M. Sharada[2] and William J. Bowman[1]; [1]University of California, Irvine, United States; [2]University of Southern California, United States

Potential applications of the earth-abundant, low-cost, and non-critical perovskite $CaTi_{1-x}Fe_xO_{3-\delta}$ in electrocatalysis, photocatalysis and oxygen transport membranes has motivated intensive research to tune its chemical composition and morphology. However, investigations on the decomposition mechanism(s) of $CaTi_{1-x}Fe_xO_{3-\delta}$ under thermochemically reducing conditions are limited, and direct evidence of the nano- and atomic-level decomposition process are not available in the literature. In this work, the phase evolution of $CaTi_{1-x}Fe_xO_{3-\delta}$ (x=0-0.4) was investigated in a H_2-containing atmosphere after heat treatments up to 600 °C [1]. The results show that $CaTi_{1-x}Fe_xO_{3-\delta}$ maintained a stable perovskite phase at low Fe content while exhibiting a phase decomposition to Fe/Fe-oxide nanoparticles as Fe content increases. In $CaTi_{0.7}Fe_{0.3}O_{3-\delta}$ and $CaTi_{0.6}Fe_{0.4}O_{3-\delta}$ the phase evolution to Fe/Fe-oxide was greatly influenced by the temperature: Only temperatures of 300 °C and greater were shown to facilitate phase evolution. Fully coherent Fe-rich and Fe-depleted perovskite nanodomains were observed directly by atomic resolution scanning transmission electron microscopy (STEM). Prior evidence for such nanodomain formation was not found and it is thought to result from a near-surface Kirkendall-like phenomena caused by Fe migration in the absence of Ca and Ti co-migration. Density functional theory simulations of Fe-doped bulk models reveal that Fe in an octahedral interstitial site is energetically more favorable than in a tetrahedral site. In addition to coherent nanodomains, agglomerated Fe/Fe-oxide nanoparticles formed on the ceramic surface during decomposition, which altered the electrical transport mechanism. From temperature-dependent electrical conductivity measurements it was found that heat treatment and phase decomposition change the transport mechanism from thermally activated p-type electronic conductivity through the perovskite to electronic conduction through the iron oxide formed by thermochemical decomposition. This understanding will be useful to those who are developing or employing this and similar earth-abundant functional perovskites for use under reducing conditions, at elevated temperatures, and when designing materials syntheses and processes.

[1] Jason Luong, Xin Wang, Alicia Tsung, Nicholas Humphrey, Huiming Guo, Benjamin Lam, Shaama Mallikarjun Sharada, William J. Bowman (In review)

2:00 PM EN07.11.04
Synthesis of Cobalt and Nickel based MOF@MOF configuration for Overall Water Splitting Chandan C. Gudal, Jae Wook Lee and Chan-Hwa Chung; Sungkyunkwan University, Korea (the Republic of)

Human activities in developing a better future consider less or no harm to the environment and climate on the planet Earth. Concerning this, fossil fuel usage is the main cause, these combustion releases harmful gases, which further leads to global warming and air pollution. Among the various alternative energy sources, the production of the hydrogen gas used in place of fossil fuels guarantees a secure and clean energy future. Moreover, hydrogen gas is mass-produced using fossil fuels, which leaves a carbon footprint in the environment as well. Water splitting is a method that produces hydrogen gas without leaving any harmful gases listed in greenhouse gases. The use of a highly efficient catalyst to break down the water molecules into hydrogen and oxygen gas will lead to the betterment of the future. The high overpotential and slow kinetics of two-half reactions during water splitting, such as hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), have necessitated the development of new efficient and porous crystalline electrocatalysts. Due to the high cost and scarcity of noble metal-based materials such as Pt and IrO_2/RuO_2, it has become necessary to investigate alternative electrocatalysts derived from inexpensive metals for water splitting.

The combination of inorganic and organic materials co-exist and perform better than individually by enabling high properties like tunable porous crystallinity, surface areas, and functionality. Metal-organic frameworks (MOFs) are a class of porous crystalline polymeric materials that promise properties that are dependent on their structures with their compositions and architectures. However, the functionalization of MOFs with other kinds of MOFs remains challenging and relatively unexplored. The porous structure and metal-ion in the MOFs act itself as building blocks for the self-assembly of homogenous and/or heterogeneous MOFs generating hybrid structures. Therefore, progressive research on MOFs materials has led to a new family of

MOF@MOF composites developed by two or more MOF units.

MOFs based on the coordination of metal ions and organic ligands have rich porous structures, ultrahigh specific surface areas, and an abundance of adjustable sites and are widely used in a variety of domains, including gas storage, sensors, catalysis, energy storage and conversion, gas separation, and drug release. Furthermore, MOF derivatives made by using MOFs as self-precursor/sacrificing templates to make metal sulfides, metal phosphides, metal oxides, carbon materials, and their composites with micro/nanostructures can inherit the unique structural properties of MOF precursors. The exploration of novel MOF@MOF composite electrocatalysts originated from inexpensive metals and room-temperature synthesizable electrocatalysts for water splitting. Herein, the development of room temperature synthesized Co-MOF@Ni-MOF composite was successful. The obtained Co-MOF@Ni-MOF exhibited high catalytic activity towards HER and OER with the requirement of low overpotentials of 170 and 290 mV to reach a current density of 10 mA cm^{-2}, respectively. In addition, this catalyst showed superior stability for HER and OER, better than commercial Pt/C and RuO_2 products. This benefited from advantageous porous crystalline nanoarchitecture, which provided a large surface area and abundant electroactive sites, leading to remarkable electrocatalytic activity and stability in alkaline conditions. The achieved results excitingly suggested a novel catalyst for effectively producing hydrogen gas via the overall water-splitting process.

2:15 PM EN07.11.05
$Ni_{5-x}Ga_{3+x}$ Catalyst for Selective CO_2 Hydrogenation to MeOH—Investigating the Activity at Ambient Pressure and Low Temperature with Microreactors Filippo Romeggio, Christian D. Damsgaard, Jakob Kibsgaard and Ib Chorkendorff; DTU Physics, Denmark

Methanol obtained from the direct hydrogenation of CO_2 at low pressures and temperatures can be used as a fuel/chemical feedstock and, if paired with renewable energy sources, could strongly contribute to reach a more sustainable society.
We have studied the catalytic performance of the intermetallic compound $Ni_{5-x}Ga_{3+x}$ for methanol production. The catalyst shows outstanding activity and selectivity at low temperatures, outperforming the conventional Cu/ZnO. At higher T, the selectivity promptly shifts towards the production of methane and CO, leading to surface poisoning. Nevertheless, the experiments demonstrate the possibility of full regeneration of the catalyst by hydrogen reduction. Lastly, high stability over time under reaction conditions makes it an interesting candidate for scale-up and future industrial application.
A variety of techniques are used to characterize the surface before and after reaction, including XPS, HR-SEM/STEM, XRD, etc., along with close collaboration with computational theoreticians for DFT calculations. All the experiments are performed in state-of-the-art equipment: microreactors of 256 nL are used for catalytic testing. The inlet flow rate is in the order of magnitude of nanomoles/min, making it possible for all the gases to enter directly the QMS, leading to extremely high product detection sensitivity. This, together with an almost immediate temperature control, makes our system ideal for further fundamental studies about CO_2 hydrogenation.

2:30 PM BREAK

3:00 PM EN07.11.07
Low Thermal Conductivity Micro-fabricated GeSn Thermoelectric as a Potential Energy Harvester Sabur A. Ayinde[1,2] and Maksym Myronov[1]; [1]The University of Warwick, United Kingdom; [2]The Federal Polytechnic, Nigeria

Clean energy from renewables remains the key solution to decarbonisation, but the resources to tap into this are not sufficiently available. Thermoelectric (TE) as a clean energy source still suffers from low efficiency, which has been very challenging over the years. Thermal conductivity, as one of major parameters that determines the figure of merit (efficiency of TE) of a material, is required to be around ~1 Wm^{-1}K^{-1} for optimum performance of TE material.
In this work, we experimentally measure the thermal conductivity of high tin content up to 9% relaxed germanium tin ($Ge_{0.91}Sn_{0.09}$) semiconductor grown epitaxially on a silicon (Si) substrate via a germanium (Ge) buffer toward energy harvesting for low energy consuming device. Suspended microwires of a single layer $Ge_{0.91}Sn_{0.09}$ epilayer were fabricated to isolate the single layer thermoelectric material from the underneath layers thereby eliminating the parasitic thermal effect from the substrate (Si) and a buffer layer (Ge).
Thermal conductivity measurements of relaxed $Ge_{0.91}Sn_{0.09}$ epilayer was obtained at temperatures between ~180 and ~550 K. As a result, thermal conductivity of the undoped 82% relaxed $Ge_{0.91}Sn_{0.09}$ epilayer microwire was found to be 2.5 Wm^{-1}K^{-1} at room temperature. It is comparable to the thermal conductivity of ~1.12 Wm^{-1}K^{-1} of the best thermoelectric material $Bi_2Te_{2.7}Se_{0.3}$ for room-temperature applications. It is a major achievement on a pathway for new high performance thermoelectric materials, which could be manufactured on large diameter silicon wafers and from abundant materials like Ge and Sn to reduce cost of thermoelectric devices and bring them into everyday life.

3:15 PM EN07.11.08
90% Silver Reduction in Silicon Heterojunction Cell Metallization with Reactive Silver Inks Steven DiGregorio[1], Michael Martinez-Szewczyk[2], Subbarao Raikar[1], Mariana I. Bertoni[2] and Owen Hildreth[1]; [1]Colorado School of Mines, United States; [2]Arizona State University, United States

Silver is the most expensive non-silicon component in photovoltaic cells. This is particularly salient for Silicon Heterojunction (SHJ) cells which can consume between 200-400 mg of silver in low-temperature silver pastes. Replacing low-temperature silver pastes with reactive silver ink can reduce silver consumption by producing more conductive fingers and lower contact resistances while avoiding high temperatures that can damage SHJ cells. This work investigates ink formulation and optimization for SHJ cells with a focus on PV performance and reduced silver consumption. We test reactive silver inks with different dominant reduction pathways, additives, and printing temperatures and characterize the silver fingers using electrical measurements and top-down and cross-section microscopy. The best performing ink achieved silver fingers with resistivities of 3.1 μΩcm and contact resistivities of 3.2 mΩcm^2 when printed at 61 °C. A 156 mm × 156 mm SHJ cell metallized with this reactive ink showed similar cell performance to low-temperature silver pastes while consuming 80-90% less silver.

3:30 PM EN07.11.09
Surface Photovoltage Spectroscopy Reveals the Modulating Influence of Water on the GaP-$BiVO_4$ Interface Anna C. Kundmann and Frank E. Osterloh; University of California, Davis, United States

Dual-absorber or "tandem" photocatalysts (PCs) hold promise for generating the large potentials (>1.6 V) needed to drive the overall water-splitting reaction, while using the visible-energy photons available in the solar spectrum. Establishing direct electrical contact between absorbers is advantageous for commercialization due to ease of implementation. Despite the promise of this type of tandem configuration, few functional direct-contact tandem PCs have been demonstrated and solar-to-hydrogen efficiencies remain low. Bismuth vanadate ($BiVO_4$) is a promising oxygen-evolving PC that has been demonstrated in direct-contact tandem configurations. GaP is a known hydrogen-evolving PC that offers improved optoelectronic properties over the metal oxides typically paired with $BiVO_4$, potentially offering an avenue to higher solar-to-hydrogen efficiencies. In the present study, $BiVO_4$ films were prepared on GaP by dropcasting, electrophoretic deposition (EPD), and electrodeposition (ED), and the interfacial charge transfer properties were examined using surface photovoltage spectroscopy (SPS). SPS is a highly surface-sensitive, non-destructive technique providing information about the magnitude and direction of charge separation and the position of energy states within a material. Large surface photovoltages of -1.7 V, -1.2 V, and -1.4 V are achieved in thin dropcast, EPD, and ED films, respectively, under vacuum. These data demonstrate a strong interaction between GaP and $BiVO_4$, resulting in a junction that separates electrons toward GaP and holes toward the $BiVO_4$ surface. SPS further observes sub-bandgap signals ca. 1.2 eV, revealing the presence of mid-gap states at the GaP-$BiVO_4$ interface. These mid-gap states under illumination <1.9 eV consistently generate more than half of the surface photovoltage that is observed in samples under super-bandgap illumination. This demonstrates a prominent role of the sub-bandgap states in the charge separation mechanism. To learn more about this junction under operating conditions, SPS was performed on samples in contact with liquid water. These measurements show an equalizing effect on the surface photovoltages, suggesting that the GaP/water interface takes over the charge separation mechanism. The interaction between interface states and water will also be discussed. This investigation reveals the challenges in directing charge transfer in systems that incorporate multiple electronically active interfaces.

3:45 PM EN07.11.10

Structural Phase Transition from the Stannite to the Wurtz-Stannite Structure Investigated by Neutron Powder Diffraction—The $Cu_2Mn(Ge_xSn_{1-x})S_4$ Solid Solution David C. Matzdorff[1,2], Maxim Avdeev[3,4], Galina Gurieva[1] and Susan Schorr[1,2]; [1]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; [2]Freie Universität Berlin, Germany; [3]Australia's Nuclear Science and Technology Organisation, Australia; [4]School of Chemistry, Australia

The research of quaternary Cu-based chalcogenide semiconductors has caught a large interest for photovoltaic applications, as these materials consist of non-toxic and earth abundant elements. While being environmentally friendly and low cost, materials like Cu_2MnGeS_4 or Cu_2MnSnS_4 are very promising candidates for use in tandem solar cells, because they can cover a wide bandgap range of 1.52-1.72 eV [1, 2]. This study presents new insight into the crystal structure of the solid solution $Cu_2Mn(Ge_xSn_{1-x})S_4$ via neutron powder diffraction.
Since Cu^+ and Ge^{4+} are isoelectronic cations and Mn^{2+} is electronic similar to Cu^+ and Ge^{4+}, they cannot be differentiated in a structural analysis based on X-ray powder diffraction data alone. However, their neutron scattering lengths are considerably different, that is why we apply neutron diffraction to analyze the crystal structure of $Cu_2Mn(Ge_xSn_{1-x})S_4$ mixed crystals. Moreover, the basis of our investigations is a careful determination of the chemical composition of the mixed crystals by WDX spectroscopy. This is important, because it was shown for other quaternary chalcogenides (e.g., Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$) that even small deviations in composition (off-stoichiometry) can have a critical influence on the band gap energy of the material [3].
The endmembers of the $Cu_2Mn(Ge_xSn_{1-x})S_4$ solid solution crystallize in different structure types: Cu_2MnSnS_4 crystallizes in the tetragonal stannite-type structure (space group *I-42m*), whereas Cu_2MnGeS_4 adopts the orthorhombic wurtz-stannite structure (space group $Pmn2_1$). Thus, within the solid solution a structural transition from the tetragonal to the orthorhombic crystal structure can be expected.
In the presented study $Cu_2Mn(Ge_xSn_{1-x})S_4$ mixed crystals were synthesized by solid state reaction of pure elements in evacuated silica tubes at temperatures of 800°C. The chemical composition and homogeneity of the synthesized polycrystalline powder materials were investigated by WDX spectroscopy using an electron microprobe system. LeBail refinement of the powder X-ray diffraction data was used to determine the lattice parameters of the mixed crystals. The final cation distribution in the unit cell was defined by applying the average neutron scattering length analysis method [4], which forms the basis to conclude on the crystal structure and structural disorder and elucidate the mechanism of structural phase transition.
The results of the chemical composition study in combination with structural characterization and optical bandgap evaluation from diffuse reflectance of $Cu_2Mn(Ge_xSn_{1-x})S_4$ mixed crystals will be presented. These investigations enabled us not only to determine the type and concentration of intrinsic point defects, but also to deduce the complex cation re-distribution process within the crystal structure which transfers the stannite- to the wurtz-stannite-type structure. It will be shown that Sn-rich mixed crystals ($0 \leq x \leq 0.29$) adopt the stannite type structure, whereas Ge-rich mixed crystals ($0.68 \leq x \leq 1$) of this series adopt the wurtz-stannite type structure. Within $0.29 > x > 0.68$ two chemically identical but structurally different quaternary phases coexist, adopting the tetragonal and the orthorhombic structure respectively.

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SESSION EN07.12: Virtual Session: Critical Materials for Energy
Session Chairs: Chong Liu and Hua Zhou
Tuesday Morning, April 25, 2023
EN07-virtual

8:00 AM EN07.12.02

A Metastable O6 Phase with Stable Cation and Anion Redox Reactions Yanfang Wang[1,2]; [1]University of Birmingham, China; [2]Southern University of Science and Technology, China

Lithium rich metal oxides (LRMOs) are promising candidates for cathode materials in next generation batteries because of their high capacities (>250 mAh/g) contributed by both cationic and anionic redox reactions (ARRs). Progressive energy (*i.e.* capacity and voltage) loss resulting from oxygen loss and transition metal (TM) migration in LRMOs is the major bottleneck to their development and commercialisation. Previous work to mitigate this has focused primarily on tailoring local cation ordering in O3 structures or using O2-type structures. Despite improvements to the voltage decay, longer-term (> 50 cycles) capacity retention remains relatively poor.

Here, we propose a new approach to obtain stable cationic and anionic redox activity using O6-type structures. Although O6 structures have been captured as intermediate phases formed during de-/lithiation or on thermal treatment of O2-type cathode materials, their metastability makes directly synthesizing O6 phases challenging. By combining ion-exchange with optimized moderate heat treatment, we detail the first report, to the best of our knowledge, of a phase-pure directly-synthesized cobalt-free O6-type material, $Li_{0.693}[Li_{0.153}Ni_{0.190}Mn_{0.657}]O_2$. It presents a reversible capacity of ~250 mAh/g within the potential window of 2.0-4.8 V vs Li/Li^+ at 10 mA/g. Upon long-term cycling in an all-fluorinated electrolyte, it delivers an initial capacity of 195 mAh/g at 100 mA/g, of which 96.0% is retained after 100 cycles with only slight voltage decay; this capacity retention is superior to current state-of-the-art cobalt-free O3- or O2-type cathode materials which utilise ARRs, marking a step-change in lithium-ion cathode chemistry.

The underlying mechanisms responsible for the material's superior performance have been proposed via detailed multimodal characterization, combining *ex situ*/ *in situ* XRD, *ex situ*/ *in situ* Raman, *ex situ* EPR, *ex situ* XANES, *ex situ* XPS, and electrochemical experiments. The O6 phase undergoes first-order phase transformations in both highly-delithiated states and highly-lithiated states, forming O2-phases via facile gliding of TMO_2 slabs. Despite multiple O6-to-O2 phase transformations, the face-sharing geometry of LiO_6 and TMO_6 octahedra is retained. This means that the irreversible TM migration, and thus voltage fade associated with formation of the spinel phase, is suppressed by the strong electrostatic repulsion between adjacent TM ions. The all-fluorinated electrolyte promotes the formation of a stable cathode-electrolyte interphase (CEI) which allows the high-voltage (> 4.5 V) nickel redox reactions and ARR to stabilize immediately after the first cycle; this, along with the ease and stability of the O6/O2 interconversions, is the origin of the excellent capacity retention.

We believe that this work is of sufficiently widespread appeal given (i) the significant advance in addressing the primary roadblock that poor cycle-stability places in the way of development and commercialization of high-capacity cathode materials utilizing ARRs; (ii) the new vein of research into O6-type structures and other metastable cathode structures that is likely to be initiated by this work and; (ii) the demonstration of a dual-pronged approach to achieve cycle stability: the judicious choice of local atomic structure paired with the stable CEIs afforded by advanced electrolyte compositions.

8:15 AM EN07.12.03
Investigation on Gd Doped BFO as a Stabilizer for Capacity Retention of CNT-Sulfur Composite Electrodes of Li-S Batteries Rajesh K. Katiyar, Claudia C. Zuluaga Gomez, Balram Tripathi, Gerardo Morell, Brad R. Weiner and Ram S. Katiyar; University of Puerto Rico-San Juan, United States

In this work, bismuth ferrite powder modified via Gadolinium (Gd) with spontaneous polarization is adopted to modify the carbon nanotube (CNT)-sulfur composite cathode owing to its special interaction with polysulfides. We synthesized these composite cathodes via ball milling of Sulfur and CNTs and Gd-doped BiFeO3 (BFO) was coated on a polypropylene separator. As a matter of fact, Gd-modified BFO in interaction with CNT-sulfur composite acts as a stabilizer to develop a stable cathode. However, carbon nanotubes have distinct qualities like high aspect ratios, increased surface area, and high surface-to-volume ratio. Our results show that Gd-modified BFO in interaction with CNT-sulfur composite cathode can effectively suppress the shuttling of polysulfides and then greatly improve the electrochemical properties of the lithium-sulfur battery in terms of cycle stability, rate performance, reaction kinetics, self-discharge behavior.

8:30 AM EN07.12.04
Abstract Presented (ON-DEMAND ONLY) Aqueous Zn-based Energy Storage Devices Working Under Extreme Conditions Zhixiao Xu and Xiaolei Wang; University of Alberta, Canada

Aqueous zinc-based energy storage devices hold great promise for grid-level energy storage yet are challenged by dendritic growth and low Coulombic efficiency under both normal and extreme conditions. In the past years, we have developed Zn batteries and capacitors working under extreme conditions through engineering electrode, electrolyte, and binder. The first project is the making of ultrafast, stable, high-loading and wide-temperature zinc ion supercapacitors through the incorporation of activated carbon (AC), aqueous binder, and concentrated electrolyte. AC exhibits large surface area, hierarchical porous structures, and abundant heteroatom dopants, aqueous binder enhances electrode-electrolyte wettability enabling high-mass-loading electrode, and concentrated electrolyte gives high Zn stripping/plating efficiency, high ionic conductivity as well as suppressed hydrogen bonding interaction in water realizing ultralow frozen temperature. Three keys combined unlock unprecedented ZICs with a large capacitance of 436 F g −1 (capacity: 200 mAh g −1), ultrahigh rate up to 200 Ag −1 , ultralong cycles (0.3 million), ultrahigh loadings (10 mg cm −2) under lean electrolyte (8.8 µL mg −1), and wide-temperature operation (-60~60 °C), leading to a maximal energy density of 134.8 Wh kg −1 and power density of 118.4 kW kg −1 . A proton/Zn 2+ ion co-interaction mechanism was revealed in the AC electrode. With low cost and extreme functionalities, this work opens an avenue towards practical supercapacitors beyond normal conditions. The second project is the development of Zn-free polymer anode that enables ultrafast rates (100 A g -1), ultralong life (1 million cycles), and ultrahigh-loadings (50 mg cm -2) through DFT calculation, polymer preparation, and electrolyte optimization. The optimal polymer possesses suitable electronic structure and a large π-conjugated structure and its storage mechanism involves reversible Zn 2+ /proton co-storage at the carbonyl site. The polymer-based full cells demonstrate ultrahigh power densities and ultralong lifespans, far surpassing those of corresponding Zn-metal-based devices.

8:45 AM EN07.12.05
Passivation of NCA Cathodes Enables NCA/PEO-LiTFSI/LTO Lithium-Ion Batteries Joseph Sullivan[1], Finn Frankenberg[2] and Arijit Bose[1]; [1]The University of Rhode Island, United States; [2]Technische Universität Braunschweig, Germany

Poly(ethylene oxide) (PEO) with bis(trifluoromethane) sulfonimide (LiTFSI) lithium salt is a well-studied electrolyte system for safer lithium-ion batteries. The PEO-LiTFSI electrolyte does not passivate the aluminum within the cathode, leading to corrosion and severe capacity crash when used with high voltage cathode materials. This study describes a single step method to protect a 4V-class cathode from aluminum degradation and failure. An interfacial investigation of the lithium nickel cobalt aluminum oxide (NCA) cathode material with a PEO-LiTFSI electrolyte follows. We show that a one charge-discharge pre-cycle with liquid electrolyte containing $LIPF_6$ prevents the capacity crash observed without passivation and enables the use of NCA as a cathode with PEO-LiTFSI.

9:00 AM EN07.06.14
Ni-Co-Based Bimetal Organic Framework as Superior Electrode Material for Hydrogen Evolution Reaction and Supercapacitors Shiva Bhardwaj[1,2], Rishabh Srivastava[1,2], Teddy Mageto[1,2] and Ram Gupta[1,2]; [1]Pittsburg State University, United States; [2]National Institute for Material Advancement, United States

Metal-organic framework (MOF) has a uniform crystal structure with adjustable porosity, a large surface area, and a good adsorption affinity. These properties made MOFs suitable materials for energy storage applications. As the requirement for rapid energy increases continuously, it results in the development of supercapacitors (SCs) and electrocatalysts. SC possesses high power density and high charge storage capacity, whereas electrocatalysts can modify the reaction rate for hydrogen production during the water-splitting reaction. This work introduces the highly efficient electrode materials derived from nickel (Ni) and cobalt (Co) compounds and their combination for application in SCs and electrocatalytic activity. The samples were synthesized using the hydrothermal method at 160 degree celsius, where glutaric acid was used as an organic ligand. The Ni-MOF showed the highest specific capacitance (C_{sp}) of 706 F/g at 1 A/g, whereas bi-metallic NiCo-MOF showed a C_{sp} of 978 F/g at 1 A/g. Furthermore, the catalytic activity has been deployed for FC application using hydrogen evolution reaction (HER). The Ni and Co-MOF both show 208 mV overpotential at 10 mA/cm^2, whereas the NiCo-MOF required 182 mV to reach 10 mA/cm^2 with a Tafel slope of 89 mV /dec. These results demonstrate a new method for developing highly efficient electrodes for SCs and electrocatalysts.

9:05 AM EN07.08.03

Techno-Environmental Modelling of Energy Storage Systems for a Remote Telescope Isabelle Viole, Guillermo A. Valenzuela Venegas, Marianne Zeyringer and Sabrina Sartori; UiO, Norway

A new radio telescope in the Atacama desert, Chile, is currently under design and envisaged to be powered by an islanded energy system of photovoltaic arrays during the day-time and a hybrid energy storage system for non-sunny hours. Similar isolated solar energy systems employ Lithium-ion or Lead-acid batteries as storage, which either increase the pressure on critical materials like lithium and cobalt or contain lead which mining brings a set of harmful environmental impacts. Hydrides based on intermetallic compounds are emerging as a viable solution for energy storage in stationary applications and are particularly appealing due to their abundance and non-toxicity. Here, by developing a multi-objective techno-environmental optimization, we size a power system that can fuel the telescope's demand economically while also maintaining a low life cycle carbon footprint. The optimization includes life cycle inventory data of potential components next to costs, including mono- and bifacial monocrystalline photovoltaic arrays, lead-acid and lithium-ion batteries, hydrogen storage in metal hydrides and as compressed gas, alkaline and PEM electrolyzers as well as PEM fuel cells.
Pure techno-economical optimization without life-cycle inventory optimizes towards power systems with up to 32% of curtailed photovoltaic power. Levelized costs of electricity resulted in $100.1/MWh with storage systems using Li-ion batteries and $171.5/MWh for systems relying on hydrogen produced on-site. With our optimization, we propose a system resulting in a low life cycle carbon footprint and acceptable electricity prices, analyzing indirect carbon emissions of the stationary system as well as costs.
The life-cycle carbon footprint optimization performed allows both the remote telescope in question and other off-grid energy systems to make informed decisions on sustainable solutions to fuel their power needs.
The authors acknowledge funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 951815 (AtLAST - Towards an Atacama Large Aperture Submillimeter Telescope).

SYMPOSIUM

April 11 - April 25, 2023

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SESSION EN08.01: Solid-State Battery Devices and Solid Electrolytes I
Session Chairs: Xiaolin Li and Cengiz Ozkan
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2008

10:30 AM *EN08.01.01
High-Performance Solid-State Electrolytes by Ultra-fast High Temperature Sintering (UHS) Liangbing Hu and Qi Dong; University of Maryland, United States

We recently reported an ultrafast high temperature sintering (UHS) for solid state electrolytes (Science, 2020, May Cover). The long sintering time of conventional syntheses can lead to Li loss in garnet SSEs caused by the evaporation of Li and the formation of secondary phases that lead to lower ionic conductivity. In contrast, the UHS technique enables us to tune the sintering time in units of seconds, which provides excellent control in terms of the Li content and grain growth. I will discuss our progress on applying UHS method to sintering various solid-state electrolyte, from compositions to microstructures. By programming the temperature and time (T-t), we can establish process diagrams to sinter porous vs. dense structures. The rapid sintering also allows us to sintering multilayer solid-state electrolytes with significantly reduced interlayer diffusion.

11:00 AM EN08.01.02
Effects of Aluminum Concentration on the Structure and Electrochemical Properties of $Li_7La_3Zr_2O_{12}$ Alexandra C. Moy[1], Alicia Manjon Sanz[2] and Jeff Sakamoto[1]; [1]University of Michigan, United States; [2]Oak Ridge National Laboratory, United States

The need for improved battery performance and safety has created the impetus to replace carbon-based anodes used in state-of-the-art batteries with lithium metal. However, it is generally known that lithium metal anodes cannot cycle with state-of-the-art liquid electrolytes due to dendrite formation. Owing to its stability and stiffness, the solid-state electrolyte lithium lanthanum zirconium oxide (LLZO) is known to physically stabilize lithium during cycling. In order to induce high conductivity, LLZO is commonly doped with aluminum. However, it is not known what other structural and electrochemical effects variable aluminum doping may produce. Additionally, the effect of structure and defects on the conductivity is not yet fully understood in LLZO. Thus, there is a need to better understand the effect of aluminum concentration in LLZO to determine how it may or may not affect its other properties.

LLZO with variable levels of aluminum was fabricated using rapid induction hot pressing. Phase purity, lattice site occupancy, and structural information were determined via neutron powder diffraction as a function of temperature. Electrochemical impedance spectroscopy was used to determine activation energy of bulk lithium-ion conductivity. This work presents a correlation between the structural and electrochemical properties of LLZO as a function of aluminum concentration and temperature, increasing the understanding of the effects of aluminum doping on LLZO and the intrinsic understanding of the relationship between conductivity and structure. With this understanding, optimal design and fabrication of solid-state electrolytes can be determined to allow for the implementation of lithium metal anodes into advanced battery technology.

11:15 AM EN08.01.03
On High-Temperature Thermal Cleaning of LLZO Solid-State Electrolytes Kostiantyn Kravchyk[1,2], Huanyu Zhang[2] and Maksym V. Kovalenko[2]; [1]Empa – Swiss Federal Laboratories for Materials Science and Technology, Switzerland; [2]ETH Zurich, Switzerland

The deployment of $Li_7La_3Zr_2O_{12}$ (LLZO) garnets as Li-ion solid-state electrolytes in Li-metal solid-state batteries is partially hindered by their chemical reaction with water and carbon dioxide, leading to the formation of a Li_2CO_3/LiOH contamination layer on the LLZO surface.[1, 2] The latter causes high Li/LLZO interfacial resistance, voltage polarization at the Li anode, and induces the formation of Li dendrites.[3] To address this issue, in this work, we investigate the applicability of high temperature annealing (600 – 900 °C) as a method for thermal cleaning of LLZO. Through an in-depth analysis of the LLZO surface using X-ray photoelectron spectroscopy, hard X-ray photoelectron spectroscopy, *in-situ* grazing incidence synchrotron X-ray diffraction and Raman spectroscopy, we have found that high-temperature thermal cleaning has an inherent issue. On the one hand, heat-treatment allows a significant reduction in Li_2CO_3/LiOH contamination. On the other hand, the use of high temperatures of 600 − 900 °C leads to the formation of the $La_2Zr_2O_7$ phase on the LLZO surface as a result of Li losses. The effect of both factors on the Li/LLZO interfacial resistance, voltage polarization and critical current density of Li/LLZO/Li symmetrical cells have been thoroughly investigated by electrochemical impedance spectroscopy and galvanostatic cycling measurements.

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11:30 AM EN08.01.04
Electrochemical Effects of Proton Exchange and Contamination Formation on LLZO Solid Electrolytes Sunny Wang, Edward Barks, Celeste Melamed, Xin Xu and William C. Chueh; Stanford University, United States

Cubic Lithium Lanthanum Zirconium Oxide (LLZO) and its aliovalently doped counterparts are amongst the most promising solid electrolyte candidates due to their high bulk ionic conductivity and stability with Lithium metal. However, its performance as a solid electrolyte is significantly hindered by detrimental side reactions. LLZO readily undergoes Li+/H+ exchange in the presence of protic solvents such as water. In air, the exchanged Li+ can subsequently undergo surface reactions that result in the formation of lithophobic contaminants such as Lithium carbonate. These surface reactions detrimentally affect the electrochemical performance of LLZO by removing Li+ from the bulk electrolyte and exasperating current constriction phenomena at the Lithium metal interface.

In this work the surface chemistry of LLZO under different treatment conditions is systematically examined and correlated to the interfacial electrochemistry. The impact of surface contaminants and proton exchange on Lithium plating dynamics, bulk ionic conductivity, constriction impedance and charge transfer are discussed.

SESSION EN08.02: Solid-State Batteries Devices and Solid Electrolytes II
Session Chairs: Cengiz Ozkan and Hongli Zhu
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2008

1:30 PM EN08.02.02
Sulfide-Based Hybrid Solid Electrolytes for All-Solid-State Lithium-Ion Batteries Young-Jun Lee, Seung-Bo Hong, Han-Jo Lee, Hui-Tae Sim and Dong-Won Kim; Hanyang University, Korea (the Republic of)

All-solid-state lithium batteries (ASSLBs) with sulfide electrolytes have attracted considerable attention owing to their enhanced safety and high energy density. The successful development of ASSLBs relies on resolving the many issues related to solid electrolytes. The brittleness of solid electrolyte pellets prepared by pressing sulfide powder makes it difficult to prepare a thin sheet. Therefore, typical sulfide-based solid electrolytes used in ASSLBs have a thickness of more than 500 μm to prevent mechanical breakage of the pellet, which leads to a decrease in the ionic conductance and energy density of the ASSLB. Moreover, making an electrolyte pellet by cold pressing results in formation of numerous voids in the solid electrolyte, which blocks ion transfer in the electrolyte. In addition, the high interfacial resistance between the solid electrolyte and composite electrodes caused by poor solid-solid interfacial contacts deteriorates the cycling performance of ASSLB. To date, rubber-based polymer binders have been commonly used to prepare sheet-type thin electrolyte sheet. However, rubber-based binders significantly reduce the ionic conductivity. Herein, we prepared thin and robust sheet-type electrolytes using an ion-conducting cross-linking agent. The cross-linking reaction allowed the three-dimensional network structure of sulfide electrolyte, resulting in enhancement of mechanical strength of the electrolyte. In addition, a cross-linked sheet exhibited high flexibility that enables roll-to-roll processing. The sheet-type cross-linked solid electrolyte was applied to all-solid-state lithium-ion cell (graphite/$LiNi_xCo_yMn_{1-x-y}O_2$), and its electrochemical performance was evaluated and compared with that of a cell employing a sheet-type solid electrolyte treated with rubber-based binders.

1:45 PM EN08.02.03
Preparation of Thin Halide Electrolyte by Tape Casting and Li Metal/Halide Interlayer Exploration Fengyu Shen[1], Michael McGahan[2], John D.

Pietras[2], Marca M. Doeff[1], Vincent S. Battaglia[1] and Michael Tucker[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]Saint-Gobain, United States

Halide solid-state electrolytes attract significant attention due to their high room-temperature ionic conductivity (>10^{-3} S/cm), low processing temperature, and good compatibility toward oxide cathode materials. Similar to sulfide electrolytes, the halide electrolytes can be densified through pressing, which can lower the cost of electrolyte manufacture. The scale-up of halide electrolytes by tape casting is challenging as halide materials are reactive with most of the traditional solvents in the battery industry. Moreover, halide materials are incompatible with Li metal, and interfacial layers (ILs) between Li metal and halide electrolytes are needed if Li metal is used as an anode. Our study shows non-polar solvents, such as toluene, are compatible with the Li_3YBr_6 halide material. An electrolyte with thickness <50 µm is prepared by tape casting, with a small amount of binder. It's room temperature ionic conductivity is higher than 10^{-4} S/cm. We also explore various ILs, such as Li_3N, for mitigating the reaction between Li metal and halide electrolyte. Li/IL/halide/IL/Li symmetric cells show good stability even at current density of 0.5 mA/cm^2. The performance of the interlayer is also evaluated in full cells with a high voltage cathode.

2:00 PM EN08.02.04

Lithium Thioborate Solid-State Electrolytes for Practical, High-Energy All-Solid-State Lithium Metal Batteries Sarah Holmes; Stanford University, United States

Solid-state batteries (SSBs) using a lithium metal anode have the potential to transform the energy density and safety of rechargeable batteries for EVs, consumer electronics, and the grid. There is a strong need to improve the chemical/electrochemical stability, ionic conductivity, and fundamental understanding of new materials for the solid-state electrolyte (SSE) before commercialization. Lithium thioborates (LBS) are a new class of SSEs with ionic conductivity predicted to be up to 80 mS cm^{-1}, making them exciting SSE candidates with unexplored potential. Our work focuses on developing and studying LBS compounds for application in all-solid-state batteries.

Through careful optimization, we have developed a multigram-scale, solvent-free synthesis for high-purity LBS compounds. We have synthesized and fully characterized pure-phase LBS materials $Li_2B_2S_5$, Li_3BS_3, and $Li_{10}B_{10}S_{20}$ using X-ray diffraction, FTIR, and electrochemical analysis. Of all LBS stoichiometries, $Li_{10}B_{10}S_{20}$ is the most promising candidate for SSBs, with experimental Li^+ conductivity of 0.34 mS cm^{-1} and negligible electronic conductivity. $Li_{10}B_{10}S_{20}$ demonstrates an exceptional voltage window of 1.3-3.0 V vs. Li/Li$^+$, wider than most sulfur-based SSEs. At room temperature, in Li-LBS-Li symmetric cells, $Li_{10}B_{10}S_{20}$ has shown high critical current density of 1.0 mA cm^{-2} and stable cycling for hundreds of hours at reasonable current densities as high as 0.3 mA cm^{-2}. In NMC-LBS-Li full cells using a solid composite cathode, we have demonstrated cycling at C/10 rates with minimal capacity degradation at room temperature and reasonable pressure. These initial results using $Li_{10}B_{10}S_{20}$ are highly encouraging for future studies on this exciting new class of electrolytes.

2:15 PM EN08.02.05

Succinonitrile-Lithium Salt Composite as a Solid Catholyte for LLZO-Based All-Solid-State Batteries Wooseok Go, Michael Tucker and Marca M. Doeff; Lawrence Berkeley National Laboratory, United States

All-solid-state batteries (ASSB) have come into the spotlight as next-generation batteries because of their potential high energy density and low flammability. LLZO ($Li_7La_3Zr_2O_{12}$) is a prominent solid electrolyte material for ASSBs due to its high ionic conductivity (>1 x 10^{-4} S/cm at room temperature) and compatibility with Li metal. However, for its use in ASSBs, there are challenges including forming intimate contact with the active electrode material. Because both LLZO and the cathode active material are rigid, employing a soft solid catholyte between them can be a solution to ensure intimate contact. The solid catholyte must be ionically conductive, and stable for oxidation (> 4.5 V vs. Li/Li$^+$).

Organic Ionic Plastic Crystals (OIPC) are a class of materials that are soft and waxy at room temperature. When the OIPC is mixed with Li salts, the mixture has high ionic conductivity and a wide electrochemical window. Succinonitrile (SN) is an OIPC material, and SN with Li salts is reported to have high ionic conductivity (> 1x10^{-4} S/cm) and good oxidation stability (>5 V vs. Li/Li$^+$) [1]. Despite the favorable properties of the SN-Li salt composite as a solid catholyte, studies for their use with LLZO are still limited. For example, the investigation of compatibility with LLZO, and contact formation between the composite and LLZO has rarely been reported.

In this talk, Succinonitrile-Lithium salt composites are investigated for their use as a solid catholyte in LLZO-based ASSBs. The properties of composite with different Li salt concentrations, their compatibility with LLZO, and their contact formation with LLZO will be shown. The performance of all-solid-state cells with the mixtures will also be demonstrated at room temperature. It is hoped that this work can motivate efforts toward forming intimate contact between the LLZO and cathode using OIPC materials.

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3:00 PM EN08.02.06

Investigation of the Stability of the Poly(ethylene oxide)|$LiNi_{1-x-y}Co_xMn_yO_2$ Interface in Solid-State Batteries Yuriy Yusim[1], Dirk Hunstock[1], Raffael Ruess[1], Alexander Mayer[2], Dominic Bresser[2], Stefano Passerini[2], Jürgen Janek[1] and Anja Henss[1]; [1]Justus Liebig University Giessen, Germany; [2]Karlsruhe Institute of Technology, Germany

Solid-state lithium batteries (SSLBs) are known to provide superior safety and increased energy density compared to conventional lithium metal batteries (LIBs) with liquid electrolytes. However, for commercial applications SSBs based on poly(ethylene oxide) (PEO) have only been combined with $LiFePO_4$ (LFP), a low-voltage active cathode material (CAM).[1] Using high voltage CAM such as $LiNi_{1-x-y}Co_xMn_yO_2$ (NCM), cells experience fast capacity fading, the cause of which is not fully understood.[2] According to electrochemical impedance measurements in a three-electrode setup, we show that the NCM/PEO interface is still the Achilles' heel in PEO-based SSBs at high voltages. We demonstrate that the electrochemical cycle stability depends on the cut-off potential and the molecular weight of PEO. This is supported by impedance measurements. In addition, using X-ray photoelectron spectroscopy (XPS), we confirm the formation of C=O bonds due to the oxidative degradation of the solid polymer electrolyte (SPE) at high potentials, which is consistent with previous reports.[3] Considering the structure of PEO, the formation of C=O in the main chain indicates chain breakage, in turn resulting in a decrease in viscosity. Using PEO with high molecular weight (8 Mil g mol^{-1}), secondary electron microscopy (SEM) shows that after cycling to 4.3 V vs. Li$^+$/Li the pores of the composite cathode are filled by PEO. This indicates that the mechanical properties deteriorate due to the oxidative degradation of the SPE at the cathode side.

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3:00 PM BREAK

3:15 PM EN08.02.07

Hydrophobic Polymer Coatings for Enhanced Air Stability of Inorganic Solid Electrolytes for All-Solid-State Batteries Kyu Tae Kim, Jehoon Woo, Hiram Kwak and Yoon Seok Jung; Yonsei University, Korea (the Republic of)

Achieving improved safety in energy storage devices has been intensively pursued as the demand for electrification increases. All-solid-state Li batteries (ASLBs) employing inorganic solid electrolytes (SEs) are considered the Holy Grail because of the possibility to achieve not only enhanced safety but high energy/power density. Sulfide and halide-based SEs are considered promising because of their superionic conductivity and deformability. However, they suffer from poor air stability, which hinders the commercialization of ASLBs. Sulfide-based SEs react with humid air and release H_2S gas with rapid structural degradation. Halide-based SEs also suffer from irreversible degradation to form MCl_3-H_2O and LiCl-H_2O. The poor chemical stability of these inorganic SEs causes not only the degradation of the electrochemical performance of ASLBs but drastically increased processing costs because the strict exclusion of moisture is required. Thus far, several strategies to enhance air stability of inorganic SEs have been proposed: i.e., elemental substitution, functional additives, and surface treatment. However, those strategies have limitations, such as limited applicability, severe decrease in ionic conductivity, and insufficient air stability.
In this study, we report on our universal hydrophobic polymer coating strategies for enhanced air stability of inorganic SEs. The hydrophobic coating layer impedes the diffusion of moisture into the SEs and enhance the air stability. Furthermore, the structural degradation mechanism in humid air is discussed. Finally, to investigate practical application, dry room compatibility of the protected SEs will be presented.

3:30 PM EN08.02.08
Development of a New Generation High-Energy Lithium Metal Polymer Battery Jean-Christophe Daigle, Ki Seok Koh, Annie-Pier Larouche, Frédéric Roussel, Francis Barray, Zhang Xuewei and Kim Chisu; Hydro-Québec, Canada

In the race for the electrification of transportation, many companies are competing to develop more efficient solid-state batteries for commercial applications. Since the landmark discovery of using polyethylene oxide (PEO) as a lithium-ion carrier for lithium metal batteries by Armand in 1978, solid-state batteries based on polymer electrolytes have been deeply scrutinized;[1] Viable commercial applications have been provided by Blue Solutions since 2011.[2] Despite their many advantages, such as the ability to use lithium metal as a negative electrode as well as reduced cell weight and enhanced overall safety, the use of polymer electrolytes remains limited. Additionally, the low overall ionic conductivity and transport number (t+), poor high-voltage stability, and elevated operating temperature remain obstacles for their wide implementation in electric vehicles (EVs).

In this presentation, we outline our efforts to develop a high-energy and long-life cycle NMC – Polymer Electrolyte - Li metal pouch cell. Major challenges are addressed in this pursuit, including stability of polymers with NMC, stable interface between all components, preventing dendrite growth, and developing a scalable process.

Using a star-shaped polymer as electrolyte, we developed a specific formulation to accommodate high C-rate cycling. This polymer is easily scalable for the industrialisation and requires only a negligible amount of solvent to be processable. Considering the need to minimise the process cost and diminish the ecological footprint, this feature provides meaningful advantages for the commercialisation.[3-4]

Another major achievement was the development of new Organic Ionic Plastic Crystal (OIPC), which was implemented as catholyte in the electrode formulation. Our new formulation allows the continuous production of cathode electrode using conventional coating machines used in Li-ion battery industry. Based on the unique properties of the new OIPC family, we achieved high C-rate with a good capacity retention more than 500 cycles at C/6 – 1 C.[5]

This technology was successfully scaled up at the format of 1 Ah pouch cell, and will be further scaled up to large format cells > 20Ah using our in-house pilot line in 2023.

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3:45 PM EN08.02.10
Investigation of Exothermic Reaction Pathways in Solid-State Batteries: Implications for Safety Megan Diaz, Alex Bates, Yuliya Preger, Loraine Torres-Castro and Randy Shurtz; Sandia National Laboratories, United States

It has been assumed that replacing the liquid electrolyte (LE) in a Li-ion battery (LIB) with a nonflammable solid electrolyte (SE) provides inherent safety. However, results from prior thermodynamic modeling[1] show that batteries containing a SE still have the potential to reach high temperatures during certain failure scenarios. Even if these temperatures do not lead to ignition of the battery contents, they could ignite surrounding flammable packaging material. The reaction pathways leading to thermal runaway are not well understood.

This work investigates those pathways for battery materials undergoing external heating and compares the results with thermodynamic modeling. The following battery configurations were explored: all solid-state batteries (ASSBs), solid-state batteries (SSBs) containing some amount of LE, and LIBs. A Ta-doped LLZO SE was used in the ASSB and SSB configurations. Differential scanning calorimetry (DSC) was used for thermal characterization of individual and combinations of battery components as well as complete microcells to differentiate between contributing factors in heat release scenarios. Calorimetry was halted and materials characterization completed at each distinct exotherm to isolate specific reaction pathways. Microstructure changes were characterized in a scanning electron microscope (SEM) and crystal structure transitions and chemical compositions were obtained through x-ray diffraction (XRD). Avoidance or mitigation of critical component-level interactions leading to thermal runaway will help pave the way towards improving SSE battery safety.

1. Are solid-state batteries safer than lithium-ion batteries? Bates AM, Preger Y, Torres-Castro L, Harrison KL, Harris SJ, Hewson J. Joule. 2022;6(4):742-55

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. SAND No. 2022-15109 A.

4:00 PM EN08.02.11
Combining 3D Printing and Field Assisted Sintering to Process Garnet-based Solid-state Electrolyte and Composite Cathode Bor-Rong Chen[1], Asa Monson[1], Arin S. Preston[1], Spencer Doran[1,2], Jorgen F. Rufner[1], Donna P. Guillen[1] and Eric J. Dufek[1]; [1]Idaho National Laboratory, United States; [2]Oregon State University, United States

Garnet-based lithium-ion conductors have been investigated as a promising solid electrolyte material exhibiting superior conductivity and stability compared to sulfur- and polymer-based ones. However, the fabrication of garnet-based solid-state batteries is challenging due to the high temperature (1000-1250 °C) and long duration (~12 hr) necessary for densification as well as the brittle nature of ceramics when processing thin layers below millimeters. To achieve thin and dense garnet layers using an energy efficient approach, we combine two advanced manufacturing technologies, digital light processing (DLP) and field assisted sintering (FAS), to produce $Li_7La_3Zr_2O_{12}$ (LLZO) electrolyte layer and $LiCoO_2$ (LCO)–LLZO composite cathode.

DLP is a unique 3D printing technology capable of layer-by-layer printing of multiple components in a single print [1]. In this work, we demonstrate that LLZO layer and LLZO/LCO composite cathode stacks printed with controllable solid mass loading, dimension, and composition. The ceramic prints are subsequently densified using FAS, during which an electric field is applied to the sample to create local Joule heating that aids densification to near theoretical density [2]. Using FAS, LLZO can be densified with a significantly shorter dwell time (<10 min) and lower temperature (900-1100 °C) compared to conventional routes. DLP-printed workpieces with controlled mass and homogeneous distribution of ceramic particles also enable FAS to produce objects thinner than its traditional limit at a millimeter-scale. By establishing the DLP-FAS process flow, we produce free-standing, sub-millimeter-thick LLZO layers. The thickness is further reduced when co-sintered with LLZO-LCO composite cathode serving as a support layer. The LLZO/cathode stack is then coupled with Li metal anode and full battery performance is evaluated.

This DLP-FAS workflow not only saves the energy and time during sintering, but also introduces several other advantages in solid-state battery processing, including reduced number of processing steps, preservation of grain and interface structures, and minimizing interdiffusion during co-sintering of LLZO and cathode material. Using DLP, fine adjustments of layer thickness and compositions, such as multi-layer structures or graded mixtures, are also achievable. In the future, this DLP-FAS process flow will provide more opportunities to fabricate various designs and chemistries of solid-state batteries.

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SESSION EN08.03: Poster Session
Session Chairs: Cengiz Ozkan and Hui Wang
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN08.03.01
Assessing Mesoscopic Chemo-mechanical Coupling Effects on Effective Transport Properties of Solid Electrolytes based on a Fourier Spectral Method Bo Wang, Kwangnam Kim, Liwen Wan, Marissa Wood, Tae Wook Heo and Brandon Wood; Lawrence Livermore National Laboratory, United States

The geometrically complex microstructures of solid electrolytes have profound impacts on the macroscopic behavior and performance of all-solid-state Li-ion batteries. To understand such processes, it is critical to accurately evaluate the effective ionic transport properties across a highly inhomogeneous microstructure with known materials properties of individual homogeneous domains, a process also known as the homogenization. For liquid electrolytes in porous electrodes, the most common approaches include simple analytical methods such as the Bruggeman model that correlates microstructural factors (*e.g.*, tortuosity, porosity) and transport properties; and numerical methods for directly solving the transport equations over a digital representation of the complex porous microstructures. However, solid electrolytes exhibit distinct microstructural features, which are significantly different from the porous electrode counterparts. In addition, conductive Li ions transport through the host solid electrolytes often give rise to highly heterogeneous and anisotropic strain/stress fields via the chemo-mechanical couplings, which bring challenges to accurately evaluating the effective transport properties using the existing methods. Here, we present a thermodynamically consistent mesoscopic model for quantifying the chemo-mechanical coupling effect on the transport properties of arbitrary inhomogeneous microstructures. We also discuss its numerical implementation to efficiently solve the coupled steady-state transport and mechanical equilibrium equations incorporating fully anisotropic local materials properties. Specifically, the chemo-mechanical effects enter the coupled equations by a stress-gradient-driven drift term in the transport equation and a chemical expansion term in the mechanical equilibrium equation. To achieve numerical efficiency for the strongly inhomogeneous materials properties, we combine the Fourier spectral-based superposition method and the iterative perturbation method. As a representative example, we will show how we apply our model to computing the effective ionic diffusivity of polycrystalline $La_3Li_7Zr_2O_{12}$ (LLZO) solid electrolytes and porous LLZO-$LiCoO_2$ composites with local materials parameters derived from atomistic simulations. We will also discuss the impact of the chemo-mechanical coupling on the effective properties systematically and quantitatively using our established modeling framework.
This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

5:00 PM EN08.03.02
PEO/LLZTO Composite Electrolytes for Li-S Batteries Ai-Yin Wang, Chun Han Kuo and Han-Yi Chen; National Tsing Hua University, Taiwan

Lithium-sulfur batteries (LSBs) have the advantages of high specific capacity and high energy density, which attracted attention in the past decade.

However, poor safety and polysulfide shuttle phenomenon are the two most criticized reasons for liquid LSBs. Using solid-state electrolytes can overcome those problems, but compared with liquid electrolytes, solid electrolytes have lower ionic conductivity and poorer electrode/electrolyte interface contact in all-solid-state LSBs. Herein, we combined polymer polyethylene oxides (PEO), Li-ion conducting ceramic powder, $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO), dispersant, and plasticizer to form PEO/LLZTO composite electrolyte. The ionic conductivity of PEO/LLZTO composite electrolyte is approximately 10^{-4} S cm^{-1} at room temperature. Furthermore, the capacity of the all-solid-state LSB assembled with the sulfur cathode, Li metal anode, and PEO/LLZTO composite electrolyte can reach up to >1000 mAh g^{-1}. After 100 cycles at a current density of 0.2C at room temperature, the S//PEO/LLZTO//Li batteries still exhibited high capacity retention of up to 70%, showing high potential for all-solid-state LSB applications.

5:00 PM EN08.03.03
Development of Operando X-Ray Diffraction-Raman Dual System for a Solid Battery Hyuksang Kwon and Yong-Il Kim; KRISS, Korea (the Republic of)

Li-ion batteries (LIBs), becoming one of the daily necessities in human lives, have been widely used primarily for the achievement of carbon neutrality, toward which the replacement of fossil-fuel-based vehicles with eco-friendly electric vehicles are progressing rapidly. In addition, if the urban air mobility market opens within the next 10 years, the environmental safety and stability of these batteries will become key issues. Currently, there is significant enthusiasm for research on solid batteries using solid electrolytes owing to the safety issues of batteries using liquid electrolytes. Thus, the research and development of advanced batteries utilizing the chemical and electrical stability of solid batteries, high-voltage anode materials, and lithium anode materials have been an extensive. For the measurement technology, challenges arise on spatial tracking of non-uniform electrochemical and interfacial chemical reactions in a cell, and understanding the cause of such reactions for the pursuance of safe battery design. The non-uniform lithiation/delithiation upon battery material location also requires the development of advanced measurement systems that incorporate two or more specialized techniques.
In situ/operando Raman spectroscopy is a technique that characterizes dynamic battery materials. Moreover, X-ray diffraction (XRD) is an essential technique for conducting secondary battery research to understand a crystal structure and perform multiphase quantitative analysis. Both techniques are a part of the state-of-the-art technologies that aim for a highly realistic environmental system with the most confidential measurements toward the characterization and development of next-generation materials. We have developed the XRD-Raman dual system, which is advantageous in assessing the non-uniform electrochemical reaction of the active material. Home-made fiber-type Raman system was unified with the conventional XRD system. The excitation laser can be irradiated to the sample in variable angles. The Raman signal, scattered from that, was collected into an off-axis parabolic mirror, which directs it to the spectrometer and detector. In addition, we developed a special coin cell to observe the dynamic behavior of the battery material in the assembled device. First, we chose transparent materials and attached them to the holed coin cell lid, so that the X-ray and visible light source can simultaneously transmit and reflect. Second, we fabricated the coin cell with a gap between the chosen transparent film and cathode materials to reduce the unwanted background. This coin cell enabled for XRD-Raman measurements to be performed during the battery operation under the same environmental conditions. The XRD-Raman dual operando measurement technology for material diagnosis in real systems will be of great help in improving the performance of secondary batteries.

5:00 PM EN08.03.04
Comparison of Different Cathode-Solid Electrolyte Interface Solutiuons for High-Voltage All-Solid-State Sodium Batteries Xiaochen Yang[1,2], Yu Chen[1,2], Yingzhi Sun[1,2] and Gerbrand Ceder[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Lab, United States

The use of inorganic solid-state electrolytes in composite cathodes is challenging due to their rigid nature and poor interfacial contact with the active electrode material. Various cathode-solid electrolyte modifications have been proposed to minimize the interfacial resistance, but they vary in their high-voltage stability. We will present results on Na-solid-state batteries using a sodium super ionic conductor (NASICON)-type solid-state electrolyte and the high-voltage $Na_3(VOPO_4)_2F$ cathode charged up to 4.3V. The high-voltage stability of three different interfacial engineering concepts is compared: 1) liquid electrolyte addition; 2) a cathode composite with solid-state polymer electrolyte; 3) or a layer of plastic-crystal electrolyte. We find that the addition of both liquid electrolyte and polymer electrolyte leads to a rapid capacity loss within 10 cycles due to their oxidation at high voltage. In contrast, the plastic-crystal interface exhibits a vastly improved electrochemical performance with more than 90% capacity retention after 200 cycles. In addition, the plastic-crystal interface maintains similarly good high-voltage cycling stability at both room temperature and elevated temperate (50°C), which demonstrates its compatibility for operating at high-voltage.

5:00 PM EN08.03.05
Ionic Transport Across Disordered Interfaces with Atomic-Scale Simulations Oskar K. Garcia[1,2], Kwangnam Kim[2], Liwen Wan[2] and Nicole Adelstein[1,2]; [1]San Francisco State University, United States; [2]Lawrence Livermore National Laboratory, United States

The solid state battery material Li7La3Zr2O12 (LLZO) is one of the most promising solid
electrolytes. If improvements can be made to this material and its interfaces with the cathode, it may be possible to replace current liquid electrolyte batteries with this safer, more energy dense alternative. To better understand LLZO at the interface with the common cathode material LiCoO2, we calculate the elastic and electronic properties of Co-doped LLZO.

5:00 PM EN08.03.08
An Advanced Impedance Analysis for Interfacial Reaction of Sulfide-Based Solid-State Batteries in Rapid Cycling Sung Soo Shin[1,2] and Hyoungchul Kim[2]; [1]Kumoh National Institute of Technology, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)

Interfacial features are primary factors of the overall electrochemical performance in solid-state electrochemical devices. They mainly influence ionic resistance as well as electronic conduction depending on their shape and distribution. So far, researches have been focused on strengthening the interfacial structure by various architecturing methods (e.g., multiscale structuring, core-shell coating, micropatterning) to enhance the mechanical stability and increase energy density. Furthermore, analytical approaches to demonstrate this enhancement in interfacial structure are also gaining interest. Electrochemical impedance spectroscopy (EIS) with the conventional fitting approach for Nyquist plot has mostly been utilized for quantitative investigation of each electrochemical response in electrodes and electrolytes without damaging cells. However, as the complexity of the cell's electrochemical reaction rises, so does the degree of freedom in circuit layout, which limits the precision of the measurement of individual resistance components.
In this study, we suggest an advanced analysis tool based on the distribution of relaxation times (DRT) method to accurately determine the electrochemical components of the complicated solid-state interfacial properties in sulfide-based solid-state batteries. Based on the advanced approach, we constructed precise equivalent circuit for the composite cathode of solid-state batteries. It also confirmed that the conventional fitting approach overestimated one of the electrode resistance by 40%, and identified the new resistance component from the lithium depletion layer. Finally, we validated that our results are in good agreement with the computational methods, and we established that this method is appropriate for quantitatively analyzing complicated interfacial

reactions in solid-state batteries.

5:00 PM EN08.03.09
Improving Lithium Metal Deposition in Solid Polymer Electrolyte Batteries with Thin Alloying Anodes Michael J. Counihan, Pallab Barai, Anil Mane, Jeffrey W. Elam, Venkat Srinivasan and Sanja Tepavcevic; Argonne National Laboratory, United States

Solid-state lithium metal batteries (SSLMBs) are the key to high energy density storage for electric vehicle applications. Solid polymer electrolytes (SPEs) used in SSLMBs offer the advantage of low manufacturing cost and provide soft interfaces for battery electrodes to keep contact without high pressures required for other solid electrolytes. However, lithium metal anodes in conjunction with SPEs have numerous chemical and mechanical challenges that limit the cycle-to-cycle efficiency and lifetime of the battery. Most notable is dendrite formation, which leads to cell shorting and dead lithium and can be caused by uneven plating on the anode surface, whether it be lithium metal or another current collector like copper in anode-free cell designs. Here, we investigate how adding a thin layer (<100 nm) of a metal or metal oxide can improve the performance characteristics of lithium metal batteries based on poly(ethylene oxide) (PEO)-based SPEs. If the metal is capable of alloying with lithium, the thin layer converts to a lithiophilic Li_xM alloy that provides a better surface for more uniform lithium metal deposition and limits dendrite formation compared to the non-alloying copper anode. We systematically detail the alloy phases, overpotentials, and reversibility of numerous alloying metals like Al, Zn, and Au and show that Coulombic efficiencies over 95% with no external pressure are possible. This thin film alloy design maintains the high energy density of lithium metal and could also be used with other solid-state and liquid electrolytes to help remedy dendrite formation and lithium metal loss.

5:00 PM EN08.03.12
Hierarchical Interface Modeling of All-Solid-State Lithium Metal Battery Based on Energy Band Theory Heebae Kim[1], Jinil Cho[1], Seonmi Pyo[1], Heejun Yun[1] and Youn Sang Kim[1,2]; [1]Seoul National University, Korea (the Republic of); [2]Advanced Institute of Convergence Technology, Korea (the Republic of)

Development of practical all-solid-state Li-metal batteries (ASSLB) is essential for a breakthrough in battery technology. Compared to conventional lithium-ion batteries using liquid electrolyte, ASSLBs have higher energy density, superior safety, and wider operating temperature range. However, fabrication of all-solid-state battery with Li-metal anode (LMA) and inorganic solid-state electrolyte (SSE) is a far challenge. Two critical issues are hindering the development of ASSLBs as following: large impedance of non-conformal electrode-electrolyte contact and electrochemical instability at the interface. Solid materials, being composed into all-solid-state battery, possess their own distinctive electrochemical and physical properties. When these materials in the forms of electrode or electrolyte are assembled into an electrochemical cell configuration, solid–solid interfaces are subsequently built inside the energy storage system. For realization of practical ASSLBs, interfacial stability at the LMA–SSE contact must be assured because the direct contact causes interfacial reactions leading to battery failure. Therefore, intrinsic instability of inorganic SSE against LMA is required to be prevented. Preceding researches have focused on developing the interface modification methods to enhance ASSLB's long-term cycling stability. But it is confined to a phenomenological solution if modification strategy is established without in-depth understanding of the interface. Also, the fact that rechargeable batteries are operated by behavior of charges inside electric field is often overlooked. The LMA-SSE interface of ASSLB is under in situ electric field during charging process, and the SSE possesses semiconducting properties unlike liquid electrolytes. Consequently, governing mechanism of interface stabilization cannot be identified by using only the conventional electrochemical techniques or by considering solely the material science perspective. For these reasons, solid-state physics concepts of electrical contacts and conduction are necessary to be discussed in ASSLB research.

This study demonstrates the significance of interface stabilization strategy via energy band alignment. The intrinsically unstable LMA–SSE interface is effectively improved by nanoscale titanium deposition on the electrolyte’s surface. And the pure transition metal nanolayer is transformed into an ion-conducting crystal structure through electrochemical interactions with Li-metal. The Li symmetric cell with titanium compound self-induced interlayer (TSI) has successfully maintained its constant overpotential over 1000 cycles and the significantly reduced impedance, whereas the cell having no interface modification exhibits erratic voltage profiles and is easily failed by repetitive charge–discharge process. Subsequently, the cell components can preserve their functions during the repetitive charge–discharge process. Such improvements are achieved by the formation of TSI functioning as stable Li-ion conductor and electron buffer at the anode-electrolyte interface, which is demonstrated by in-depth electrochemical analyses and is fully supported by widely accepted energy band theory. XRD analysis has confirmed the formation of self-induced interlayer, EDS analysis has shown its structural robustness and uniform elemental distribution, and depth-profiling XPS measurement has confirmed the effect of electron blocking phenomenon across the interface. The revealing results provide not only comprehensive understanding of the interfacial phenomena, but also fundamental interface modification method applicable to various types of all-solid-state battery. Furthermore, rigorous stability requirements of automotive applications are expected to be satisfied by the innovative interface modeling.

5:00 PM EN08.03.13
Structural Changes in the Silver-Carbon Composite Anode Interlayer in Solid-State Batteries Varnika Agarwal, Dominic S. Jolly and Peter Bruce; University of Oxford, United Kingdom

Solid-state batteries, in which a lithium foil anode is used in conjunction with a ceramic solid electrolyte, promise to improve the energy density and safety of cells. However, charging solid-state batteries at practical rates on the order of 1-10 mA cm^{-2} can lead to cell failure. Solid-state batteries fail at high rates of charge because, as Li metal is plated to the anode, dendrites (filaments of Li metal) penetrate through the ceramic electrolyte, short-circuiting the cell. One approach to mitigate this problem has been to introduce an interlayer between the ceramic electrolyte and the lithium anode to facilitate homogeneous Li deposition and protect against dendrite penetration; with inorganic, metal, and carbon-based interlayers having been shown in the literature to increase charging critical currents.
In this work, we study the structural changes of interlayers in cells pairing a lithium metal anode and a Li_6PS_5Cl solid electrolyte by a combination of techniques including electrochemistry and *operando* powder X-ray diffraction. In addition, the relationship between the rate of charge, the Li-ion diffusivity of the interlayer, and the effectiveness of the interlayer in protecting against dendrite growth are discussed.

5:00 PM EN08.03.14
Prelithiated Ga_2O_3/C Nanocomposites as Self-Healing Host Materials for Stable Lithium Metal Anodes in Solid-State Batteries Sungwoo Park, Kyubin Shim, Hyun Woo Kim and Hae Jin Kim; Korea Basic Science Institute, Korea (the Republic of)

To achieve safe and high energy density rechargeable batteries, it is essential to adopt lithium metal anodes (LMAs) in solid-state batteries (SSBs). Because, lithium metal has excellent electrochemical properties including both high theoretical capacity (3860 mAh/g) and exceptionally negative potential (-3.04 V vs. NHE), which provides for increasing energy density by reducing total space and/or weight of SSBs. However, Li dendrites or filaments growth caused by unstable interfacial reactions and contact between Li metal and solid electrolytes during electrochemical cycling are obstacles hindering solid-state Li-metal batteries.
In the aspect of anodes engineering, rational design of 3D host materials decorated with lithiophilic sites is one of reasonable approach to suppress the

growth of Li dendrites or filaments by effectively regulating Li deposition. Among the various lithiophilic materials, gallium (Ga) has been considered as a self-healing anode material due to its low melting point (29.8 °C). This unique property can facilitate form a conformal electrode-electrolyte interface in SSBs. However, its fluidic feature at close to room temperature, makes it difficult to realize nanostructured design.

In this study, Ga_2O_3/C nanocomposites were simply synthesized via microwave-induced hydrothermal reaction for 20 min and subsequent carbonization. The nanocomposites exhibited that Ga_2O_3 nanodots with diameter of ~ 10 nm are densely embedded in thin carbon matrix. To evaluate stable Li plating ability of Ga_2O_3/C nanocomposites, coulombic efficiency (CE) was obtained in liquid electrolytes after specific prelithiation process. The composite electrodes presented low initial Li nucleation overpotential of 20.0 mV, and initial high CE was stably maintained over 200 cycles under the conditions of 1.0 mAh/cm^2 at 1.0 mA/cm^2. It could be confirmed by in-situ XRD analysis that the excellent performances of Ga_2O_3/C electrodes are attributed to prelithiation process resulting in lithiophilic Ga phase in electrodes. The effects of Ga phase on stable interface contact between electrode-solid electrolyte during electrochemical cycling were evaluated by controlling cell measurement temperature (above and below Ga melting point) at solid-state half-cell assembled by using PEO-based solid electrolytes. Furthermore, cell performances of carbon matrix without Ga_2O_3 were also compared at same temperature to identify the effects of cell operating temperature on PEO-based solid electrolytes in LMAs.

5:00 PM EN08.03.15

Revealing the Roles of Interface Design for Ga-Doped Garnet/Polymer Composite Electrolyte of Solid-State Lithium Batteries Purna C. Rath[1], Wei-Lun Hsu[2], Tai-Chou Lee[2] and Jeng-Kuei Chang[1,2]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]National Central University, Taiwan

$Li_7La_3Zr_2O_{12}$ (LLZO)-based composite solid electrolyte (CSE) are considered to be the most promising electrolytes in solid-state lithium metal batteries (SSLMBs) due to the advantages of high safety and potentially high energy density. However, unsatisfactory interfacial connections of LLZO at both cathode and anode solid junctions are the key bottlenecks. To reduce the internal resistance of SSLMBs, three strategies have been employed in this work. First, Ga concentration in $Li_{7-3x}La_3Ga_xZr_2O_{12}$ (LGLZO) was optimized. The significant impacts of the Ga stoichiometry on the battery performance are investigated. Second, an LGLZO CSE layer is fabricated directly on top of a $LiFePO_4$ (LFP) cathode using a spin-coating technique. The CSE slurry infiltrates the cathode layer, forming a Li^+ conduction network and ensuring intimate contact between the CSE and the cathode. The advantages of a spin-coated CSE over a conventional freestanding CSE in terms of the charge transfer resistance and the battery charge-discharge properties are disclosed. Third, an ionic liquid (IL) connectivity layer is added at the Li/CSE interface to improve wettability. The IL interlayer homogenizes Li^+ flux throughout the interface and prevents hot spots for Li dendrite formation, thus suppressing interface-side reactions. The optimal ionic conductivity of the CSE is ~1 × 10^{-3} S cm^{-1} at 60 °C. With such an ingenious arrangement, a satisfactory LFP capacity of 141 mAh g^{-1} at 1 C and a great cyclability of 96% capacity retention after 300 cycles are achieved. We believe that the proposed dual interface design is simple and affordable and is an efficient strategy to significantly improve practical SSLMB performance.

SESSION EN08.04: Cathode Design and Materials for Solid-State Batteries
Session Chairs: Xiaolin Li and Hongli Zhu
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2008

8:00 AM *EN08.04.01

Designing Cathode Materials and Composite Electrolytes for Li-ion Batteries and Beyond Lianzhou Wang; University of Queensland, Australia

Li-rich layered oxides (LRLOs) are ones of the most promising cathode materials for next generation high-energy-density lithium-ion batteries (LIBs) because of their extraordinary specific capacity over 250 mA h/g. Such high capacity originates from the “activation” of Li from transition metal layer in the Li_2MnO_3 phase. However, the activation process is kinetically slow, and the relevant phase transformation as well as the electrode /electrolyte side reactions at high voltage region cause serious capacity and voltage decay. In this talk, we present our recent studies on the electrochemical activation mechanism and capacity/voltage decay challenges. A series of *ex-situ* and *in-situ* characterisations reveal the structural evolution mechanism of the cathode materials, and the optimised materials deliver a high capacity of ~270 mA h/g and with good capacity retention of >98% over 300 cycles. We will also discuss our recent works on the atomic layer protection of a new high-voltage cathode material with excellent cycling stability of over 1000 cycles, the design of integrated printable solid-state battery systems for flexible electronics, and the development of new gradient composite electrolytes for solid-state sodium ion batteries.

8:30 AM EN08.04.02

Designing Zero-Strain Li-Ion Cathodes Xinye Zhao, Yaosen Tian, Zhengyan Lun, Zijian Cai, Tina Chen, Bin Ouyang and Gerbrand Ceder; University of California, Berkeley, United States

Cathode materials for Li-ion batteries (LIBs) commonly suffer from chemo-mechanical structural degradation during cycling. The repeated (de-)lithiation processes induce severe volume change and deteriorate the structural integrity of cathode particles, cathode coatings, and the cathode/electrolyte interface [1]. Especially for all-solid-state batteries, solid electrolytes lack the mechanical compliance to tolerate the structural change of the cathode particles. The local expansion and contraction of the cathode particles push the solid electrolyte away, resulting in increased cell impedance and capacity loss [2-4]. Therefore, to improve the capacity retainability and cycle life of all-solid-state Li-ion batteries, it is crucial to develop cathodes that exhibit low volume strain to minimize the structural degradation during cycling. We have used well-calibrated computational techniques to systematically investigate the roles that redox chemistry, structure, disorder, inactive elements, and metal coordination play in determining the volume change of cathode upon delithiation, leading to the exciting conclusion that zero strain compounds are possible. Based on our design rules, we have experimentally synthesized $Li_{1.3}V_{0.4}Nb_{0.3}O_2$ and $Li_{1.25}V_{0.55}Nb_{0.2}O_{1.9}F_{0.1}$ with low volume change upon cycling [5]. In this presentation, we will present our established guidelines in detail and discuss the significance of zero-strain for advancing all-solid-state batteries.

Reference:

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8:45 AM EN08.04.03
Surface Coating by Mechanofusion Modulates Bulk Charging Pathways and Battery Performance of Ni-rich Layered Cathodes Dong Hou and Feng Lin; Virginia Tech, United States

Alkali metal-based batteries (e.g., lithium batteries) are considered the most effective energy storage candidate for portable electronics, power grids, and electric vehicles due to their considerable energy density, power density, cycle life, safety, and competitive prices. The Ni-rich Co-less ternary $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC) (Ni>80%) is considered one of the most promising cathode materials due to its high discharge capacity (>200 mAh g^{-1}) and high energy density (>750 Wh kg^{-1}). Common issues in these Ni-rich NMCs are poor cycling performance and undesired degradation at high voltages. Surface coating is considered an effective way to mitigate performance degradation for polycrystalline cathodes in batteries. However, the synergic effect between surface modification, bulk charge distribution, and particle microstructural evolution has not been systematically studied. Moreover, many coating methods are practically expensive, require intermediate processing steps, and have high standards for precursors, etc.

We utilize a dry surface modification method, mechanofusion, to achieve enhanced battery stability. The simplicity, high yield, and flexibility make it cost-effective and highly attractive for processing at an industrial scale. The underlying mechanisms responsible for performance improvement are unveiled by a systematic study combining multiple probes, e.g., 3D nano-tomography, spectroscopic imaging, in situ synchrotron diffraction, and finite element analysis. Mechanofusion affects bulk crystallography by introducing partially disordered structure, microstrain, and local lattice variation. Furthermore, the crack initiation and propagation pattern during delithiation are regulated and the overall mechanical fracture is reduced after such surface coating. We validate that mechanofusion can alter the bulk charging pathways. Such a synergic effect between surface modification and bulk charge distribution is fundamentally important for designing next-generation battery cathode materials.

Reference: Hou, D., Han, J., Geng, C., Xu, Z., …& Lin, F., Surface Coating by Mechanofusion Modulates Bulk Charging Pathways and Battery Performance of Ni-rich Layered Cathodes, *Proceedings of the National Academy of Sciences of the United States of America (PNAS)*, accepted.

9:00 AM EN08.04.04
Improved Electrochemical Performance of Co-free Li-rich Layered Oxides Caused by Temperature-driven Chemical Segregation Dries De Sloovere[1,2], Kunkanadu Rajappa Prakasha[3], Jekabs Grins[4], Aleksander Jaworski[4], Thomas Thersleff[4], Gunnar Svensson[4], leif Olav Jøsang[5], Anne Dalager Dyrli[5], Andreas Paulus[1,2], Jan D'Haen[1], Hemesh Avireddy[3], Joan Ramon Morante[3], Marlies K. Van Bael[1,2], An Hardy[1,2] and Jordi Jacas Biendicho[3]; [1]UHasselt and Imec, Belgium; [2]EnergyVille, Belgium; [3]Catalonia Institute for Energy Research, Spain; [4]Stockholm University, Sweden; [5]Ceramic Powder Technology AS, Norway

While solid-state lithium batteries are regarded as a promising technology because of their potential safety and electrochemical stability, the gravimetric energy density of the positive electrode material remains a limiting factor for the cell energy density.[1] The current lithium-ion battery technology is dominated by the use of layered, cobalt-containing oxides with general stoichiometry $LiNi_xMn_yCo_zO_2$ (NMC, with x + y + z =1) as positive electrode material.[2] The large-scale production of these materials therefore relies heavily on cobalt, which raises concerns because of the latter's high cost, scarcity, and vulnerable global supply chain. Recent research efforts therefore focus on the elimination of cobalt from the active positive electrode material, while simultaneously increasing its energy density.

More specifically, extensive efforts are placed on the development of lithium-rich layered oxides, as they can combine a high specific capacity with a high operating potential and lower cost. Generally, these materials can be represented by the formula $[xLiMO_2{*}(1 - x)Li_2MnO_3$ (M = Mn, Co, Ni, etc.)], where the monoclinic (*C*2/*m*) Li_2MnO_3 structure closely resembles the rhombohedral (*R*-3*m*) $LiMO_2$ structure, but with a different cation ordering. Their high energy density results from the combination of traditional cationic redox processes with anionic redox processes of the oxygen sublattice. Further, the high manganese content of these materials implies that they are relatively cost-effective.

This presentation will focus on the synthesis and electrochemical performance of $Li_{1.1}Ni_{0.35}Mn_{0.55}O_2$ as a cobalt-free, lithium-rich layered oxide for (solid-state) lithium-ion batteries. The oxides were synthesized by spray pyrolysis of an aqueous precursor followed by calcination. Performing the latter at 900 °C caused an increase in particle size. Furthermore, powder neutron diffraction, and HAADF-STEM combined with EDX and EELS showed that calcination at this temperature led to a pronounced structural segregation between the aforementioned rhombohedral and monoclinic phases, where the former corresponded to nickel-rich facets, and the latter corresponded to manganese-rich regions. In half cells, this material delivered a discharge capacity of 160 mAh g^{-1} at C/3, with a capacity retention of 80% after 150 cycles. This contrasts with the material calcined at 700 °C, which showed no appreciable capacity retention in the same conditions. At 1 C, the former material had a discharge capacity of 100 mAh g^{-1}. Furthermore, it showed a slower voltage decay than is observed for the oxides calcined at lower temperatures.

The formation of larger, structurally segregated particles was shown to mitigate degradation reactions within the cathode, thereby improving its electrochemical performance in various aspects. This work therefore provides a simple but effective strategy to improve the performance of cobalt-free, lithium-rich layered oxides which can be used in solid-state lithium-ion batteries.

This work was supported by Horizon 2020 LCBAT-5 COBRA project 875568.

References:
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9:15 AM EN08.04.05
Novel Polymer Binder with Superior Performance in the Composite Cathode for Sulfide All-Solid-State Lithium Batteries Seung-Bo Hong, Yoo-Rim Jang, Young-Jun Lee and Dong-Won Kim; Hanyang University, Korea (the Republic of)

The safety concern of commercialized lithium-ion batteries (LIBs) is a critical problem to be solved. Accordingly, all-solid-state lithium batteries (ASSLBs) with non-flammable solid electrolytes have been considered promising alternatives. Among various types of solid electrolytes, the sulfide electrolytes with high ion conductivity are received a lot of attention. However, the realization of sulfide-based ASSLBs is still challenging due to the difficulty of producing composite cathodes with high active mass loading. To avoid the delamination of cathode components and mitigate mechanical stress generated during cycling, a small amount of polymer binder should be incorporated into the composite cathode. Acrylonitrile-butadiene rubber (NBR) is the most common binder used in preparing composite cathode. In our study, we investigated a new polymer binder that can improve the cycling performance of ASSLBs. The composite cathode prepared with new binder enables the realization of an ASSLB with better cycle life than the case of an ASSLB employing a composite cathode with NBR.

9:30 AM EN08.04.06
Micro-Architected Lithium Cobalt Oxide Electrodes toward 3D Solid-State Batteries Yuchun Sun and Julia R. Greer; California Institute of Technology, United States

Lithium-ion batteries (LIBs) are the primary candidates for advancing energy storage needs, but current LIBs suffer from energy-storage and power limitations of their slurry electrodes, as well as the safety concern from liquid electrolytes. Thickness of commercial slurry electrodes is highly limited by Li ion transport. This constraint on electrode thickness limits the mass ratio between active materials and current collectors, and thus the energy and power density of LIBs. One approach to overcome this limitation is to fabricate 3D architected electrodes using additive manufacturing techniques. In this work, lithium cobalt oxide (LCO) is fabricated into 3D micro-architected structure through a novel hydrogel infusion process. In this process, a blank 3D architected organogel is printed through vat photopolymerization and soaked in water to form a blank hydrogel, where lithium and cobalt ions in an aqueous solution are then swelled into the 3D hydrogel structure. After calcination, LCO micro-lattice with 50 μm beam diameter is obtained, giving a crucial lithium-ion diffusion length of 25 μm. This approach enables LCO cathode to be flexibly architected into 3D geometries, for example the interdigitated plate configuration, toward the realization of 3D Li-ion batteries with high energy and power density. A carbon anode of the same 3D architecture can be fabricated and combined with the LCO cathode, followed by conformal coating and in-situ polymerization of a photo-polymerizable oligo(ethylene glycol)-based gel polymer electrolyte resin on 3D electrodes, giving a 3D solid-state lithium-ion battery.

9:45 AM EN08.04.07
New Hybrid Nano-Architecture of Sulfur Electrode for Lithium-Sulfur Batteries. Mariam Ezzedine, Fatme Jardali, Ileana Florea and Costel-sorin Cojocaru; Ecole Polytechnique, France

Lithium-Sulfur batteries have the potential to provide a much greater energy storage capacity than current Lithium-ion batteries. However, Lithium-Sulfur batteries are hampered by challenges arising from the cell level, such as poor conductivity of sulfur, its volume expansion, and the lithium polysulfides shuttle effect. The technology developed in our lab overcomes these fundamental challenges by implementing an innovative electrode architecture that exploits the properties of vertically aligned carbon nanotubes (VACNTs). The hierarchical-assembled-nanostructured battery positive electrode is based on carbon nanotube carpets grafted by 100% sulfur nanomaterial. Coupling it with metallic lithium as negative electrode results in high energy and power, and long-life Lithium-Sulfur battery (Figure 1). The positive electrode topology enables to store more electrical charge more rapidly than any other commercial electrode, positively impacting the power and energy storage capacity of the battery. The Lithium-Sulfur batteries exclude inactive components (such as binders/additives essential for traditional Lithium-ion batteries), thus eliminating the “dead weight” found in the today’s batteries.
Electrochemical performance tests have shown that the Lithium-Sulfur batteries developed in our work have substantially improved capacity performance, stability and cycle life compared to conventional Lithium-Sulfur batteries. At a discharging rate of 2C (i.e., 30 minutes), the cells have shown a stable specific capacity of 400 mAh g^{-1} over 1000 cycles.

10:00 AM BREAK

SESSION EN08.05: Interface Design and Studies in Solid-State Batteries
Session Chairs: Cengiz Ozkan and Hui Wang
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2008

10:30 AM EN08.05.02
The Electrostatic and Elastic Conditions for Quasi-static Dendrite Propagation in Solid-State Electrolytes Cole D. Fincher[1,2], Yet-Ming Chiang[1,2], Brian Sheldon[3] and Craig Carter[1,2]; [1]MIT, United States; [2]Massachusetts Institute of Technology, United States; [3]Brown University, United States

We have demonstrated that dendrite propagation possesses a marked dependence upon the mechanical state of the electrolyte and upon the applied overpotential [1]. The conditions for the arrest or propagation depend on a trade-off between energy released during infinitesimal growth against the infinitesimal increase due to surface energy. The released energy has at least two sources: elastic relaxation and the change in the electrostatic field due to the growth of a conducting dendrite. The implications of these results for electrolyte design are illustrated with general stability diagrams. Extension to dendrites propagating with finite velocities will be discussed.

[1] CD Fincher, CE Athansiou, C Gilgenbach, MJ Wang, BW Sheldon, WC Carter, YM Chiang, “Controlling dendrite propagation in solid-state batteries with engineered stress,” *Joule,* in press. DOIs: 10.1016/j.joule.2022.10.011

10:45 AM EN08.05.03
Pitfalls of Critical Current Density Tests to Investigate Alkali Metal Electrodes Till Fuchs, Felix Richter and Jürgen Janek; Justus-Liebig-University Giessen, Germany

Using lithium metal as anode material promises a drastic increase in energy and power density in solid-state batteries. However, morphological challenges such as local contact loss of the metal electrode or dendrite growth occur during cell cycling,(1) limit the applicable current density. Designing reliable and reasonable testing protocols is of utmost importance to ensure an error-free analysis of the Li|Solid Electrolyte(SE) interface.

Testing the so-called “critical current density” (CCD) via a stepwise increase in applied current density in an alternating direction is often applied. These CCD tests should determine the maximum current density a cell can withstand before undergoing critical failure, which suggests that the CCD is a material property of the SE itself. However, our analysis shows that the CCD is neither an inherent cell nor an SE property. It highly depends on several external factors, such as the used current profile, exact interface conditions, applied pressure and temperature and even the cell geometry and size. This is evident from the spread of CCD values over orders of magnitude obtained on very similar materials in different studies.(2)

Therefore, to interpret the results obtained by CCD tests, it is necessary to know the microscopic mechanism that causes cell failure. This could be a direct failure of the SE, e.g. by cracking and dendrite formation, or it could also be a pore formation that precedes the growth of dendrites and acts as a precursor for short-circuiting by focusing the current at remaining contact spots. As all these effects overlap and gradually worsen and influence each other during a CCD test, data interpretation is quite challenging. We therefore suggest a differentiation between the different failure mechanisms by carefully tailoring the test protocol to induce the desired case, being either a direct short-circuiting or a short-circuiting as a result of pore formation.

For example, we suggest using an intermediate pressure and a waiting time between the current steps of a test to close potentially forming pores when investigating the SE. If instead the SE is a constant during the experiment and the interface conditions are changed, e.g. by interlayers or surface treatments, we suggest the omission of stack pressure and instead concentrate on longer current steps to not miss voiding at the interface. Generally, we hope our guidelines on how to investigate the Li|SE interface will help to streamline the efforts made by the community and ensure a better comparability between the results of different groups.

(1) Krauskopf, T.; Richter, F. H.; Zeier, W. G.; Janek, J. Physicochemical Concepts of the Lithium Metal Anode in Solid-State-Batteries. *Chem. Rev.* **2020**, *120 (15)*, 7745-7794.
(2) Flatscher, F.; Philipp, M.; Ganschow, S.; Wilkening, H.M.R.; Rettenwander, D. The Natural critical current density limit for $Li_7La_3Zr_2O_{12}$ garnets. *J Mater. Chem. A.* **2020**, *8*, 15782-15788

11:00 AM EN08.05.04
Elucidating Interfacial Stability of the Electrolyte/Cathode Interfaces in Solid-state Batteries Yi-Tzu Wu, Jing-Sen Yang and Ping-Chun Tsai; National Taiwan University of Science and Technology, Taiwan

Emerging solid-state electrolytes (SSEs) with superior ionic conductivity have been developed for all-solid-state batteries (ASSBs). However, most SSEs experience noticeable interfacial incompatibility with most conventional cathodes, so ASSBs are subject to significant cycling degradation. Through experimental characterization techniques, it is hard to clarify the main interfacial degradation factors, identify the decomposition products, and allow an atomic scale visualization of interfacial reactions. In this study, *ab-initio* calculations are used to determine phase, chemical and electrochemical stability of various prominent SSEs and cathodes as a function of the state-of-charge (SoC). Specifically, SSE/cathode interfaces of superior oxide-, sulfide-, and halide-based SSEs and conventional layered-, spinel-, and olivine-structure cathodes are investigated. Factors controlling interfacial stability are revealed and stable SSE/cathode interfaces are identified. The *ab-initio* understanding of the SSE/cathode interfacial stability allows the development and design of a variety of stable solid-to-solid interfaces.

11:15 AM EN08.05.05
Theoretical Understanding of the Deposition and Growth of Lithium in a Solid State Lithium-ion Conducting Electrolyte Xiao-Dong Zhou, Yudong Wang and Anil Virkar; University of Louisiana at Lafayette, United States

All-solid-state lithium batteries have been extensively pursued for next-generation energy storage, in which the state-state electrolyte (SSE) is a key component. The deposition of metallic lithium inside an SSE has been observed and is a concerning issue for development of the forefront all-solid-state lithium batteries. Unlike lithium dendrites that form and grow from the surface of Li-metal anode, metallic lithium can nucleate and propagate directly inside the bulk SSE, which can cause an instant failure of SSE.

In this work, we first present a theoretical model that is built based on non-equilibrium thermodynamic theory while taking consideration of the electronic conduction in an SSE. The electronic conductivity is a key variable to determine the chemical potential of lithium. The distribution of chemical potential of lithium is then calculated based on transport properties of an SSE. When the lithium chemical potential is higher than the sum of the elastic energy and surface energy, the change of Gibbs free energy for lithium formation is less than zero, which is the thermodynamic criterion for the deposition of lithium in an SSE. We will present our ongoing experimental research, as well as the electrochemical and materials characterization, to elucidate the approaches to control the deposition of lithium in an all-solid-state battery.

Acknowledgement: We would like to thank the supports from NASA under 80NSSC21M0333 and NSF under NSF-2119688.

SESSION EN08.07: Advanced Characterizations and Modeling in SSBs I
Session Chairs: Hui Wang and Hongli Zhu
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2008

8:00 AM *EN08.07.01
Nanoscale Imaging of Li-ions Through Ion Mass Spectroscopy Marina S. Leite; University of California, Davis, United States

Determining where Li ions preferentially accumulates during charging/decharging is critical for understanding and controlling undesired chemical reactions that ultimately lead all-solid-state batteries to fade. Here, we implement time-of-flight secondary ion mass spectroscopy (ToF-SIMS) in oxygen free and controlled environment to image the distribution of Li-ions in all-solid-state batteries formed by Si/LiPON/$LiCoO_2$, with nanoscale spatial resolution. Specifically, we resolve Li ions distribution within all active layers of the batteries upon cycling, and identify the formation of a solid-electrolyte interphase (SEI) at the LiPON-$LiCoO_2$ interface after the first charging. Our method is extended to energy-storage devices with $Li_xV_2O_5$ anode and V_2O_5 cathode, as will be discussed.

8:30 AM EN08.07.02
Real-Time Solid Interface Observation Using Synchrotron X-Ray Computed Tomography for All-Solid-State Battery Seongjun Kim[1], Michael Wang[2], Cole D. Fincher[2], Yet-Ming Chiang[2], Tim Fister[1], Alan Kastengren[1] and Paul Fenter[1]; [1]Argonne National Laboratory, United States; [2]Massachusetts Institute of Technology, United States

For a few decades, the lithium-ion batteries (LIB) have changed the numerous aspects of modern industry. Particularly, the vehicle industry is the one of the most affected areas as rising of the LIB. Despite the rapid expansion of the market, the state-of-art LIBs are still not getting full trust from the public because of anxiety about safety, cost, and environmental issues. All-solid-state batteries (ASSB) are a novel battery system that can change the paradigm of the battery ecosystem in the future. This solid-state system is making people look forward to them because they can overcome the problems of conventional LIBs. However, it has still many steps to achieve the commercial ASSBs as always. Therefore, possessing deep scientific and engineering knowledge on the new system is essential.

Exploration for searching solid electrolyte has been found various types of electrolytes including argyrodites, garnets, and LISICON/NASICON-type structure. Among them, some doped garnet-type solid electrolyte (i.e., $Li_7La_3Zr_2O_{12}$ or LLZO) have high ionic conductivity (~ 1 mS cm^{-1} at 298 K) and high shear modulus (60 GPa) along with high stability against Li metal and air atmosphere. However, existing suggested ASSB model have been limited by the contact of the solid interfaces. The rigidity of solid state along with volume changes of the electrodes lead a degradation of interface contact from void evolution and dendrite formation. The degradation eventually increases the interfacial resistance resulting in cell failure. Therefore, observation of dynamics on the solid interfaces and electrolyte becomes necessary procedure to achieve the high performance ASSBs.

Synchrotron X-ray computed tomography (XCT) is a non-destructive method that can characterize the solid-solid interfaces with varying scales, ranging from sub-micron to centimeters. The three-dimensional (3D) morphological variation can be detected by the XCT technique, which is helpful to identify the transformation on the electrolyte interface. Despite the great advantages, the high Z-element (i.e., La, Ta, and Zr) of the garnet-type electrolyte absorbs a large amount of x-ray, as a result, the tomography images with clear phase contrast is difficult. Contrary, the contrast sensitivity of low Z-element like Li can be decreased at high-energy x-rays for high Z-elements. Taking into account the x-ray attenuation of the atomic weight materials, the proper cell design and measurement strategy are critical for the interface characterization.

Several strategies and cell construction for tracking the morphological transformation of high Z materials will be discussed. With calculation on the tolerable x-ray beam pathway that can travel through the solid electrolyte, the multiple mechanical factors such as dimension and morphology of the cell is modified for high quality x-ray tomography imaging. Additionally, the void or defect appearance and crack evolution by different current densities in Li|LLZO|Li symmetric cell are investigated along with the discussion the interfacial behavior on the solid interface.

This presentation provides much information to build a measuring technique for solid state interface of ASSB and insights on the phenomenon of cell failure from interface deterioration.

8:45 AM EN08.07.03

Recent Advances in *Operando* X-Ray Photoemission/Absorption Spectroscopy to Probe the Electrified Electrolyte/Electrode Interfaces in All-Solid-State Batteries Mario El Kazzi; Paul scherrer Institute (PSI), Switzerland

All-solid-state batteries (ASSBs) are a rising alternative for boosting the volumetric energy density and promising a superior safety. However, Li-ion transport across the solid electrolyte (SE)/active materials (AMs) interfaces is limited by poor mechanical contact and parasitic (electro-)chemical side reactions. The fundamental understanding of such interface has not been fully achieved yet mainly due to the limitations in current surface-sensitive analytical techniques, especially in *operando* mode.

In this contribution, we will review the recent developments in *operando* X-ray photoemission (XPS) and absorption (XAS) spectroscopy, to monitor in real-time the interface evolution of operational ASSB working electrodes (WE). *Operando* measurements are made possible thanks to the unique and versatile electrochemical custom-made cell designed to operate in ultra-high vacuum, providing reliable electrochemistry.[1] We will highlight how the combination of in-house *operando* XPS and synchrotron-based *operando* XAS using soft and hard X-rays can provide a reliable platform to investigate (i) the (electro-)chemical evolution of the SE/AMs interfaces, (ii) the surface modifications of the AMs and (iii) the electronic properties across electrified solid-solid interfaces. Different examples will be presented describing in a novel way the interface degradation mechanism observed in real time upon cycling.

Specifically, we show results from *operando* XPS performed on $LiCoO_2$ (LCO) and $(Li_2S)_3$-P_2S_5 (LPS) WE, where we identified LPS oxidation byproducts and its onset oxidation at 2.3 V vs. InLix followed by Co-ions diffusion into the LPS forming CoS_x species at 2.9 V. Consequently, negative localized charges have been detected embedded into the LPS at the interface with LCO. Furthermore, we demonstrated the presence of a sharp potential drop, confirming previous theoretical predictions of a narrow space layer charge at the interfaces between WE and SE in ASSB.[2,3]

In *operando* XAS performed at the Mn, Ni and Co L-edges, as well as at the S and P K-edges of the $LiNi_xCo_yMn_zO_2$ (NCM) and LPS WE, we evidenced a surface chemical reaction when LPS comes in contact with NCM, leading to the formation of sulfates and reduced Co and Ni. These chemical and electrochemical interface reactions are further enhanced upon the first charge, while after several cycles the interface reaches a self-passivation regime where the degradation reactions are highly attenuated resulting in relatively stable cycling performance.

[1] X. Wu, C. Villevieille, P. Novák, M. El Kazzi, Physical Chemistry Chemical Physics, **20** (16), 11123-11129 **(2018)**
[2] X. Wu, M. Mirolo, C. A. F. Vaz, P. Novák, M. El Kazzi**,** ACS Appl. Mater. Interfaces, 13 (36), 42670-42681 **(2021)**
[3] M. Mirolo, X. Wu, C. A. F Vaz, P. Novák, M. El Kazzi, ACS Appl. Mater. Interfaces, **13** (2), 2547–2557 **(2021)**

9:00 AM EN08.07.04

A Study of the Li-LLZO Interface via Plasma Focused Ion Beam Marco Siniscalchi and Chris Grovenor; University of Oxford, United Kingdom

Despite the considerable interest that lithium garnet ceramic solid electrolytes have attracted, their application in solid-state batteries is still limited by the penetration of lithium filaments through the electrolyte resulting in short circuits at small critical current densities. It is still not fully understood how these lithium filaments nucleate and propagate through the solid electrolyte. In this study, we show that during cycling lithium metal can deposit in the sub-surface porosity of the solid electrolyte. We demonstrate that this sub-surface lithium is present in occluded pores and has no apparent electrical connection path to the plated lithium electrode. As a consequence, large pressures develop within the solid electrolyte and lead to internal cracks, along which more lithium can plate and eventually short-circuit the cell. Such degradation mechanism was visualized at the interface between a lithium electrode and LLZO solid electrolyte via focused ion beam (FIB) milling and scanning electron microscopy. In addition, we obtained detailed three-dimensional reconstruction of interface features such as spallation cracks, which are possible sites for the nucleation of lithium filaments. These results elucidate the formation mechanism of lithium filaments and suggest effective surface engineering strategies for their prevention.

9:15 AM EN08.07.05

In-situ 4D-STEM Biasing of Model Lithium-Sulfur Batteries Hadas Sternlicht[1], Benjamin Savitzky[1], Alpesh K. Shukla[2], Colin Ophus[1] and Andrew M. Minor[1,3]; [1]National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory, United States; [2]ZoNexus, LLC, United States; [3]University of California, Berkeley, United States

While Sulfur has been reported as a promising cathode material given its high capacity and energy density, practical use of Lithium-Sulfur batteries is impeded by challenges such as the low electric conductivity of Sulfur. This work aims to determine the structure-chemistry relationship in Lithium-Sulfur batteries upon biasing, which is crucial for identifying the mechanisms that alter Lithium-ion transport and affect battery performance. To do so, Lithium-Sulfur micrometer length-scale solid state batteries are fabricated, biased and studied entirely *in-situ* using 4D-STEM. This approach allows focus on a single controllable interface. A full air-free setup was developed and is being used to transfer samples to and from the glove box during sample preparation and characterization. Carbon is introduced to and coated on the Sulfur cathode, in order to exploit the improved properties associated with the

Sulfur(Carbon) cathode compared to Sulfur. These include improved conductivity, and prevention of Sulfur loss via vapor pressure. Variations in the microstructure are studied by tracking the reaction products, Li_2S and other Li_xS compounds.

9:30 AM BREAK

SESSION EN08.08: Advanced Characterizations and Modeling in SSBs II
Session Chairs: Xiaolin Li and Cengiz Ozkan
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2008

10:00 AM *EN08.08.01
Modeling of the Potential Distribution and the Electrical Double Layer in Solid-State Batteries Yue Qi; Brown University, United States

The electrical double layer (EDL) is a key feature of all electrochemical interfaces, controlling the kinetics and thermodynamics of both electron transfer and ion transfer reactions, and therefore the performance of all solid-state batteries (ASSB). Unlike in a liquid electrolyte with an EDL made of solvated ions, the EDL in a solid electrolyte is made up of charged point defects. Thus, the well-known Poisson-Boltzmann equation at electrode/liquid-electrolyte interfaces no longer holds in SSBs. This problem is even more challenging, as ion insertion and/or reaction with the electrode alters the material and thus band alignments at the electrode/solid-electrolyte interfaces.

In this talk, a density functional theory (DFT)-informed theoretical framework was established to predict the interface potential profiles. We first assumed the electrochemical potential for Li^+ ions reached a constant at the open circuit equilibrium condition, then derived the relationship among the electrostatic potential, the lithium chemical potential, Fermi level, ionization potential, and the work function. This relationship yielded quantitative profiles of the electrostatic potential and electronic energy level alignments across the entire solid-state batteries.

The electrostatic potential jump at the electrode/electrolyte interface creates intrinsic barriers for Li^+ transport across the interface. The predicted potential jump was directly compared to the Kelvin probe force microscopy (KPFM) measurements and correlated with the interfacial impedance. The interfacial potential jump was then predicted for 48 ASSBs made of different electrolyte and electrode materials. A number of cathode/electrolyte pairs with low "intrinsic" potential barriers were identified, suggesting these promising interfaces will most benefit from engineering efforts to reduce "extrinsic" interfacial impedance, such as increasing the interface contact area.

To obtain the electrostatic potential variation as a function of the distance to the interface, a more general model for the EDL at a solid-state electrochemical interface based on the Poisson-Fermi-Dirac equation was developed. The EDL structure is presented in various materials that are thermodynamically stable in contact with a lithium metal anode. The model further allows designing the optimum interlayer thicknesses to stabilize the interface without introducing additional electrostatic barriers for lithium ion transport at relevant solid-state battery interfaces.

10:30 AM EN08.08.02
Multiscale Modeling of Ion Transport Phenomena at Interfaces in All Solid-State Batteries Liwen Wan, Kwangnam Kim, Aniruddha M. Dive, Bo Wang, Tae Wook Heo and Brandon Wood; Lawrence Livermore National Laboratory, United States

Ion transport at interfaces dictates the performance of all solid-state batteries. For example, it has been routinely observed that in many superionic oxide conductors, lithium-ion transport kinetics are orders of magnitude slower at the interfaces, such as grain boundaries or interfaces with common electrode materials, compared to the bulk phases. The ability to understand, predict and precisely control ion transport kinetics at these interfaces are therefore critical and would have a transformative impact on the development of solid-state battery technologies for practical applications. Here, I will address the need for a multiscale and multiphysics modeling framework to unravel the mechanisms of ion transport at complex interfaces and predict the kinetics of ion transport in solid-electrolyte/cathode composite architectures that are relevant for all solid-state lithium batteries. I will use the garnet-type solid-electrotype and lithium cobalt oxide cathode as an example to demonstrate the predictive power of such a multiscale, multiphysics modeling framework towards establishing the correlations between ion transport and local atomic structure, chemical environment, and mesoscopic microstructure features in the cathode/electrolyte composites.

This work was sponsored by the Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office and was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. An award of computer time was provided by the Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program. This research used resources of the Argonne Leadership Computing Facility, which is a DOE Office of Science User Facility supported under Contract DE-AC02-06CH11357.

10:45 AM EN08.08.03
Small Correlation Between P-S Building Block and Ionic Conductivity in Amorphous Li–P–S Super-Ionic Conductors Byungju Lee[1], KyuJung Jun[2] and Gerbrand Ceder[2]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]University of California, Berkeley, United States

Amorphous Li-P-S materials have been widely used as solid-state electrolytes for all-solid-state batteries because of their high ionic conductivity (10^{-4}–10^{-3} S cm^{-1}) as well as good synthetic accessibility and processability. Despite the potential of these materials, their amorphous structures have made it challenging to quantify the relation between structure and conductivity. In this paper, we use *ab initio* molecular dynamics simulations to investigate the role of the local structure and density in determining the conductivity of amorphous Li–P–S structures with different polyanion units. We observe similar rates for Li-ion hopping regardless of the local P–S polyanion environment in these amorphous materials, indicating that the path connectivity at a larger length scale may be controlling the overall Li conductivity. This finding will serve as an important guideline in the continued development of amorphous solid electrolytes for advanced all-solid-state batteries.

11:00 AM EN08.08.04
Phase-field Simulations of Failure in LLZO: How Flaw Size and Distribution Affect Electrochemical Tolerance Scott Q. Monismith[1], Remi Dingreville[2] and Jianmin Qu[3,1]; [1]Tufts University, United States; [2]Sandia National Laboratories, United States; [3]Stevens Institute of Technology, United States

The solid electrolyte, $Li_7La_3Zr_2O_{12}$ (LLZO), is a promising next-generation candidate material for lithium metal batteries. However, LLZO-based cells exhibit crack growth and subsequent Li metal plating, leading to short circuit and failure. In our work, we develop a coupled electrostatics-mechanics phase-field model which characterizes the growth of cracks; this model comprises deterministic and stochastic frameworks to describe the failure of LLZO with a single crack and multiple randomly distributed cracks respectively. Our single-crack model demonstrates that crack propagation under applied electrostatic loads follows an inverse-square law of failure, analogous to classical fracture mechanics. Multiple-crack simulations show that the Weibull model applies to both constant voltage and constant current conditions. Furthermore, an interfacial region of flawless crystal leads to substantial increases in both critical overpotential and critical current. The totality of these results provide some guidance for the rational operation of LLZO-based cells in an industry setting as well as some possible routes for improvement of the material's microstructure for long-term operability.

11:15 AM EN08.08.05
Probing Interfacial Degradation at $Li_7La_3Zr_2O_{12}$|$LiCoO_2$ Interfaces in All Solid-state Batteries Using Machine Learning Interatomic Potential
Kwangnam Kim[1], Aniruddha M. Dive[1], ShinYoung Kang[1], Nicole Adelstein[2], Brandon Wood[1] and Liwen Wan[1]; [1]Lawrence Livermore National Laboratory, United States; [2]San Francisco State University, United States

All solid-state batteries (ASSBs) are emerging next-generation energy storage technologies that promise improved safety with potentially higher energy density compared to conventional Li-ion batteries. However, the interfacial instability between the solid electrolyte (SE) and electrodes hinders their practical applications. For example, cation interdiffusion across the interface can alter the composition and atomic structure of the interface as well as the bulk phases that affect Li-ion transport. Severe interfacial degradation may also occur that lead to the formation of undesired secondary phases that can block Li diffusion. To mitigate this issue, fundamental understanding of the intrinsic physico-chemical properties of the SE/electrode interfaces is required, which necessitates advanced computational methods that can accurately predict the chemical processes that govern the early-stage of interfacial degradation and the reaction products as well as dynamic properties at the interfaces.

In this talk, we will present the direct probing of structural and chemical evolution at the $Li_7La_3Zr_2O_{12}$SE/$LiCoO_2$ cathode interfaces by a machine learning (ML) interatomic potential. The ML potential was developed based on artificial neural network trained by the energies and atomic forces of structure data sampled from ab-initio molecular dynamics (AIMD), which was proved to reproduce the structural and dynamic properties of the interfaces and bulk phases similar to AIMD. Using this ML potential, we performed large-scale MD simulations on a series of interface models varied by initial compositions and atomic arrangements. We will discuss interfacial disordering propensities with different interfacial chemistry as well as observations of cation interdiffusion and its implication towards Li-ion diffusion. We emphasize the critical need of accurate large-scale atomistic simulations, which can be enabled by ML potential, to resolve the atomic details of the interface and unravel the structure-property relationship at the interface that governs Li-ion transport and dictates the performance of ASSBs.

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

11:30 AM EN08.08.06
Understanding the Physical and Mechanical Properties of Solid Electrolyte and Protective Layer on the Inhibition of Li Dendrite Growth by Phase-Field Method Yao Ren[1], Bharat Pant[1], Yue Zhou[2] and Ye Cao[1]; [1]The University of Texas at Arlington, United States; [2]The University of Texas at Dallas, United States

Lithium (Li) dendrite growth in Li batteries is a long-standing problem, which causes critical safety concerns and severely limits the advancement of rechargeable Li batteries. Replacing a conventional liquid electrolyte with a solid electrolyte of high mechanical strength and rigidity, or introducing a protective layer at the electrode-electrolyte interface (EEI) have become potentially approaches to mitigate the Li dendrite growth. However, there still lacks an accurate understanding of the roles of the physical and mechanical properties of the metal electrode, the EEI, and the electrolyte in the Li dendrite growth. Recently, phase-field model which uses a field variable to capture the evolutions of complicated microstructures in materials, has been successfully employed to investigate the Li dendrite growth in Li metal batteries. However, most models do not fully consider the effects of the elastic and plastic properties of the electrode and electrolyte, the complicated microstructure of the solid composite electrolyte, or the existence of a physical protective layer at the EEI on the Li dendrite growth. In this talk, I will discuss our recent works on the development of a phase-field model coupled with multi-physics behaviors to understand the mechanism of Li dendrite growth. It is revealed that Li dendrite can also be effectively inhibited by solid electrolytes of high elastic modulus and initial yield strength. Meanwhile, the role of the yield strength of the Li metal is also critical when the yield strength of the electrolyte becomes low. It is also discovered that the introduction of the nanofibers to form nanochannel arrays in polymer composite electrolyte confines the Li-ion transport along uniaxial direction, reduces the Li-ion concentration gradient across the electrode/electrolyte interface, and inhibits the Li dendrite growth. Finally, introducing a protective layer of lower Li ion diffusion barrier than the electrolyte results in a much smoother electrode/electrolyte interface during the electrodeposition. The simulation results are compared with experimental results from our collaborators to validate the model. Our work thus provides a deeper understanding of the mechanism of Li dendrite growth and its suppression, as well as a design strategy for solid electrolyte and protective layer for improved Li anode stability. Our model can potentially be extended to other electrode-electrolyte interfacial problems in energy storage materials beyond Li metal batteries.

SESSION EN08.09: Advanced Characterizations and Modeling in SSBs III
Session Chairs: Ye Cao and Hui Wang
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2008

1:30 PM *EN08.09.01
Dedicated Forcefields for Efficient Simulation of Electrode:Electrolyte Interfaces in Solid State Batteries Stefan N. Adams; National University of Singapore, Singapore

A transition to ceramic all-solid-state batteries is widely expected to achieve safer energy storage systems with higher energy density. To overcome hurdles slowing down the development of such energy storage systems, it is necessary to understand more in detail the key processes at their buried interfaces. This should allow for a more rational design and tailored evolution of the interfaces, which largely govern the device performance and cycle life. In order to gain such a deeper understanding we need both experimental operando probing and advanced simulation approaches, but both remain so far challenging. High

fidelity ab initio calculation methods offer high accuracy and transferability, but their computational cost severely limits the size and complexity of models that can be analysed as well as the periods over which processes can be monitored by ab initio molecular dynamics simulations. Classical molecular dynamics (MD) simulation methods using empirical “reactive” forcefields reduce the computational cost for a comparable system size or simulation period by many orders of magnitude and have a more favourable scaling behaviour, so that more complex structure models can be handled. Here “reactive” refers to forcefields that are able to describe ion transport and chemical reactions, where atoms change their bonding partners over the runtime of the simulation.
A crucial matter of concern especially for screening applications is the transferability of such empirical forcefield. We demonstrated how our bond-valence based transferable softBV forcefield successfully enables the design of new solid electrolytes or insertion-type electrode materials and the analysis of ion transport processes therein [1,2].
As a two-body forcefield, it enables fast simulations for complex structures over long periods, but inevitably shares the tendency of two-body forcefields to maximize coordination numbers if free volume facilitates a reorganization of the atoms. This vulnerability of two-body forcefields is overcome in a computationally efficient way by introducing an embedded-atom-method(EAM)-inspired bond valence sum(BVS)-based new class of transferable forcefields with machine-learning optimised parameters [3]. With the help of several application examples it will be discussed how the high computational efficiency (due to a linear scaling of the computational effort with system size) as well as the availability of parameters for most inorganic compounds renders our softBV-EAM forcefield suitable for simulating electrode:electrolyte interfaces, entire electrochemical cells, or neuromorphic devices. Thereby the approach enables a systematic high throughput screening in the search for high compatibility electrode:electrolyte materials combinations or in the rational interface engineering by suitable coatings. The next step will be to enable also the description of redox reactions and systems with alkali metal electrodes.
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2:00 PM EN08.09.02
Quantitative Phase Field Modeling of Dendrite Growth of Lithium Metal Anode Jin Zhang, Alexander F. Chadwick and Peter W. Voorhees; Northwestern University, United States

Dendrite growth is one of the main challenges to the success of using lithium metal anodes in solid-state batteries. The ability to simulate detailed dendrite growth in 3D under experimental conditions will benefit the community by providing a fundamental understanding of the growth mechanism and interfacial stability. This opens new possibilities to explore and design application-dependent battery materials and structures to suppress dendrite growth. Here, we developed a quantitative phase field model based on nonequilibrium thermodynamics in a fully variational and thermodynamically consistent way. The proposed model reproduces the Nernst equation, captures reaction kinetics like Butler-Volmer and Marcus-Hush, and can also include elastic stress. We verify our model against analytical solutions from sharp interface models with simple geometries to demonstrate that our model can give quantitative predictions. The proposed model enables the simulation of systems of experimental size with realistic materials parameters in three dimensions. We show simulations of dendrite growth as a function of applied voltage/current, demonstrating the effects of nucleation density and the mossy-to-dendritic lithium transition. The model can be easily extended to model other alkali metal anodes.

2:15 PM EN08.09.03
Reaction and Ionic Migration at the Electrode-electrolyte Interface in Solid State Batteries from Machine Learning Molecular Dynamics Jingxuan Ding and Boris Kozinsky; Harvard University, United States

Understanding the interfacial reactions between the Li-metal anode and solid-state electrolyte (SSE) and the Li ion diffusion mechanism are keys for developing stable and efficient solid-state batteries. Yet, theoretic studies are hindered by the high computational costs of ab initio molecular dynamics in both spatial and temporal dimensions. We combine on-the-fly active learning based on Gaussian Process regression (FLARE) with local equivariant neural network interatomic potentials (Allegro) to construct a symmetric battery of Li-metal anode and SSE and perform machine-learned molecular dynamics (MLMD) of tens of thousands of atoms over several nanoseconds with ab initio accuracy. Prominent reactions are observed at the interface with product phases forming a transition layer spanning a few tens of angstroms. Li ions near the interface are observed to migrate from the anode into the electrolyte and eventually diffuse within the SSE. Finally, we examine how off-stoichiometry affects the reaction rate of the interface and enhances Li ion diffusion.

2:30 PM BREAK

3:30 PM EN08.09.04
Computational Insights into Interfacial Effects on Li-Ion Diffusivity in $Li_7La_3Zr_2O_{12}$ and $LiCoO_2$ Nicole Adelstein[1], Oskar K. Garcia[1], Kwangnam Kim[2], Brandon Wood[2] and Liwen Wan[2]; [1]San Francisco State University, United States; [2]Lawrence Livermore National Laboratory, United States

The garnet $Li_7La_3Zr_2O_{12}$ (LLZO) is one of the most promising solid electrolyte candidates due to its large electrochemical stability window against a lithium anode, reasonable ionic conductivity, from 10^{-4} to 10^{-3} S/cm, and mechanical strength. However, the effect of its interface with the cathode requires investigation. We picked the common cathode $LiCoO_2$ (LCO) and simulated the effect of interdiffusion of Co into LLZO. Co-doping in LLZO and Co-vacancies in LCO will affect the electronic, elastic, and diffusion properties of the materials. Nudged elastic band calculations were used to calculate the change in the activation energy barrier for Li-diffusion due to a Co-vacancy in LCO and a Co-dopant in LLZO. While these defects show Li-ion diffusivity, our results show that diffusion is still possible through these non-stoichiometric compositions that we expect to find at the interface of LLZO and LCO.

This work was sponsored by the Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office and was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. In addition, the work *was supported in part by the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists (WDTS) under the Visiting Faculty Program (VFP).* This research was performed using computational resources sponsored by the Department of Energy's Office of Energy Efficiency and Renewable Energy and located at the National Renewable Energy Laboratory and the Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program from the Argonne Leadership Computing Facility, which is a DOE Office of Science User Facility supported under Contract DE-AC02-06CH11357.

3:45 PM EN08.09.06
Current Collectorless Transparent Thin Film Lithium Ion Batteries Ji-Won Choi[1,2]; [1]Korea Institute of Science and Technology, Korea (the Republic

of); [2]KIST-School of the Korea University of Science and Technology (UST), Korea (the Republic of)

The next-generation transparent energy sources are required with the acceleration of development of smart lenses, glasses, smart windows, transparent displays and the body sensors. A battery with fully transparent materials has not yet been reported since conventional battery components, except from the electrolyte, are opaque. All of the transparent battery research reported so far has a structure using active materials with a fine line width, and this method is a battery made to appear opaque but transparent by creating a micro-pattern below the human eye resolution. This approach includes drawbacks like such a complex process, low energy density, and a packaging system that takes up a lot of space. Therefore, by stacking transparent battery materials, we have created a battery whose materials are all transparent.
In previous research, we have developed transparent cathode, $LiFeMPO_4$. Its wide bandgap of 3.7 eV, high transparency over 70% makes it promising candidate for cathode of transparent battery. However, a full-cell has never been fabricated due to the absence of a transparent anode. Therefore, we developed a transparent anode that does not require an anode current collector for full cell production.
In this study, we developed an Zn doped SnO_2(ZTO)/$AgTi_xCr_y$ (ATC)/Zn doped SnO_2 (ZTO) multilayer anode that exhibits high transmittance (90%), low sheet resistivity (8.8 Ω/sq), and high discharge capacity (1036.9μAh/cm^{2}μm). Due to the high electrical conductivity of the anode itself, anode current collector is not required, therefore the fabrication process can be simplified.
All-solid-state full cell was fabricated with $LiFeMPO_4$ cathode and ZTO/ATC/ZTO anode, LiPON with radio frequency (RF) sputter. Using glass substrate with ITO deposited as a cathode current collector, we created a cell with a total thickness of 1.5 µm excluding substrate. Electrochemical analysis is done in the glove box, checking charge/discharge profiles with 100 cycles. The transparency of full cell was verified by UV Spectroscopy in 550 nm.

4:00 PM EN08.09.07
SiN_x Anode for Transparent Thin Film Battery by CCS Sputtering Yaelim Hwang[1,2], Ho Won Jang[2] and Ji-Won Choi[1,3]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of); [3]KIST-School of the Korea University of Science and Technology (UST), Korea (the Republic of)

In recent years, as the development of smart paper, smart windows, medical diagnostic smart lenses, and transparent displays is accelerated, the development of next-generation energy sources with flexibility or transparency is required. The only transparent component used in lithium-ion battery construction is the electrolyte, making it challenging to manufacture transparent batteries. The transparent anode of all-solid-state batteries has not been studied. We have created the transparent cathode $LiFePO_4$ in previous study. It is a promising candidate for the cathode of a transparent battery due to its wide bandgap of 3.7 eV and great transparency (76.3%). However, since a transparent anode is not present, a full-cell transparent battery has never been created.
In this study, we report the optimized composition of Ag-doped SiN_x to improve the electrical conductivity of SiN_x. The effect of Ag doping on electrical conductivity and electrochemical characteristics in transparent SiN_x anode is investigated using the continuous composition spread (CCS) method. By utilizing two 90° off-axis RF sputtering guns facing each other, the CCS approach allows for the simultaneous study of a large number of compositions. Here, we investigate the optimal transparent SiN_x-Ag anode composition in terms of their optical absorption spectra, electrical performance and lithium storage capacities. The results come out very clear that doping Ag into SiNx can improve not only the electrical conductivity, but also the performance of the electrochemical system. Ag doped SiN_x transparent anode is successfully approached to thin film battery and we have optimized SiN_x-Ag content with high electrochemical properties balanced with the transmittance.

SESSION EN08.10: Anode Design and Anode-Free in Solid-State Batteries
Session Chairs: Hui Wang and Hongli Zhu
Friday Morning, April 14, 2023
Moscone West, Level 2, Room 2008

8:30 AM EN08.10.02
Stable Li Plating in "Li^0-free" Solid-state Batteries Enabled by Seeded Li Nucleation Catherine Haslam and Jeff Sakamoto; University of Michigan, United States

Solid-state batteries utilizing Li metal anodes have the potential to offer increased safety and higher energy density compared to state-of-the-art Li-ion batteries. To achieve this increase in energy density, the Li metal anode must be thin (<25 µm). Manufacturing of thin Li metal anodes is complicated by the reactivity of Li metal, which forms a thin passivation layer even in controlled environments. The "Li^0-free" cell manufacturing approach provides an alternative to these challenges. "Li^0-free" cells are manufactured with a bare anode current collector (CC) and the Li metal anode is plated in-situ at the CC/solid-state electrolyte (SSE) interface during the first charging step using the Li stored in the cathode active material.
Thus far, all demonstrated "Li^0-free" cells rely on high pressure or temperature formation steps to achieve intimate contact at the CC/SSE interface. Sulfide SSE "Li^0-free" cells utilize high-pressure pre-forming steps (490 MPa) and/or high-pressure cycling (15 MPa) to maintain CC/SSE contact, while oxide SSE "Li^0-free" cells require high-temperature (900 °C) bonding of the CC to the SSE surface. Previous studies of oxide SSE "Li^0-free" cells have suggested that the uniformity of the Li plating can be improved by decreasing the CC/SSE adhesion strength. This encourages debonding between the CC and SSE as opposed to fracture of the CC during Li plating. However, when the CC is placed on an oxide SSE instead of bonded at high temperatures, Li penetration of the SSE causes short-circuiting. Enabling stable Li metal plating in cells with no CC/SSE bonding would both simplify the manufacturing of "Li^0-free" cells by eliminating high-pressure or high-temperature pre-forming steps, and possibly improve the uniformity of the plated Li. This study evaluates the feasibility of in-situ Li anode plating in "Li^0-free" cells with no CC/SSE adhesion utilizing the oxide SSE $Li_7La_3Zr_2O_{12}$ (LLZO). It is shown that stable Li metal plating can be achieved with no CC/SSE adhesion strength by seeded nucleation of Li metal on the SSE surface. The in-situ formed Li anode morphology is characterized during both plating and stripping using cross-sectional scanning electron microscopy and electrochemical impedance spectroscopy. These results illustrate the importance of controlled Li nucleation during in-situ Li plating, as well as demonstrate the feasibility of stable Li metal plating in "Li^0-free" cells without the requirement of CC/SSE bonding.

8:45 AM EN08.10.03
Understanding Alloy Interlayer Evolution in Anode-Free Solid-State Batteries Stephanie E. Sandoval, Douglas L. Nelson, John Lewis and Matthew T. McDowell; Georgia Institute of Technology, United States

To achieve high energy density and high specific energy in solid state batteries, "anode-free" battery configurations have garnered a great deal of interest. With no active material at the anode current collector, anode-free systems substantially increase volumetric energy density compared to standard Li-ion batteries and lithium metal batteries with excess lithium. The anode-free configuration additionally simplifies manufacturing by removing the need to process lithium metal. To advance this technology, however, it is critical to understand Li growth and stripping on current collectors while also investigating methods to spatially control these processes. Previous work which probed the effects of alloy interlayers in liquid electrolyte systems using *operando* optical microscopy has found that silver thin films enable higher CE than bare current collectors and cause different deposition and stripping dynamics[1]. Silver layers have also shown beneficial effects in enabling long-term cycling of solid-state batteries (SSBs)[2], but there is a lack of knowledge regarding the mechanisms by which they improve performance. Here, we investigate the structural and morphological evolution of alloy interlayers in SSBs using cryogenic and plasma focused ion beam (cryo-FIB, PFIB) methods correlated with electrochemical measurements. Improved Coulombic efficiency and cycling stability are observed when using silver and gold interlayers compared to bare copper. The origin of these performance improvements are investigated using cryo-FIB and PFIB to uncover morphology evolution at the solid-state interface. We observe non-uniform lithium growth on bare copper throughout cycling, while uniform lithium growth is observed in silver- and gold- modified interfaces. Interestingly, the silver and gold interlayers undergo different morphological evolution, which affects cycling behavior. Electrochemical impedance spectroscopy (EIS) is used to understand and investigate the influence of the alloy interlayers on interfacial impedance during cycling, which is correlated to morphology evolution. Over the first five cycles, bare copper electrodes exhibit a relatively large increase in impedance while the alloy-modified interfaces exhibit only minor increases in impedance throughout cycling. Furthermore, *operando* EIS measurements show distinct signatures due to contact loss for the bare copper. This work provides new understanding of the mechanisms governing the behavior of alloy interlayers in anode-free SSBs, which is important for engineering high-performance and high-energy devices.

1. Sandoval, S. E. *et al.* Understanding the Effects of Alloy Films on the Electrochemical Behavior of Lithium Metal Anodes with Operando Optical Microscopy. *J. Electrochem. Soc.* **168**, 100517 (2021).
2. Lee, Y. G. *et al.* High-Energy Long-Cycling All-Solid-State Lithium Metal Batteries Enabled by Silver–Carbon Composite Anodes. *Nat. Energy* **5**, 299–308 (2020).

9:00 AM EN08.10.04
Lithiated ZnO Nanorods into Li Anode for All-Solid-State Batteries with High Rate Capability by Enhancing Li Replenishing Rate Joonhyeok Park, Jaeik Kim, Jiwoon Kim, Seungwoo Lee, Ungyu Paik and Taeseup Song; Hanyang University, Korea (the Republic of)

Recent advances in all-solid-state batteries (ASSBs) based on sulfide-based electrolytes raise hope for the practical use of the Li anode as it is likely to suppress dendritic growth. However, their practical use has been limited by a poor rate capability caused by the Li dendrite growth. And the Li migration rate at the interface between the anode and solid electrolyte (SE) is faster than the Li replenishing rate by atom diffusion inside of Li bulk, resulting in void formation at the interface between the anode and SE under the operation with high current density. These voids increase the localized current density, leading to the Li dendrite growth. Here, we demonstrate an ASSB system with high rate capability by employing lithiated ZnO nanorods into Li anode. Lithiated ZnO nanorods, capable of Li-ion conduction, provide the passage for Li transportation from the Li bulk to the interface between the Li and SE, improving the replenishing rate. The lithiated ZnO nanorods in Li enable interfacial integrity by suppressing the void formation at the Li/SE interface even under the high current density. ASSBs employing Li anode with lithiated ZnO nanorods exhibit stable cyclability without short circuit at 0.3 C during 300 cycles and a superior rate capability.

9:15 AM EN08.10.05
Rational Design of Si-based Anode Material for High Performance All-Solid-State Batteries Jaeik Kim, Jiwoon Kim, Minsung Kim, Joonhyeok Park, Ungyu Paik and Taeseup Song; Hanyang University, Korea (the Republic of)

Silicon is a promising anode material for all-solid-state batteries due to its high theoretical capacity and low working potential. However, the poor cycle stability caused by electrical and ionic contact loss resulting from the significant volume change of the Si associated with Li should be addressed. Here, we report Si nanoparticles embedded in carbon nanofiber (CNF) coated with solid electrolyte (LPSCl) (Si/CNF@LPSCl) as anode material to achieve high energy density and cycle stability for all-solid-state batteries. By embedding Si in the CNF, more favorable strain release and robust electronic pathways are available. The uniform coating of LPSCl on the surface of Si/CNF composite enhances the interfacial stability between the active material and the solid electrolyte, which improves electrochemical properties by maintaining the contacts. The Si/CNF@LPSCl composite electrode shows a reversible capacity of 1172 mAh g−1 at 0.1C and a stable cyclability of 84.3% at 0.5C after 50 cycles. Especially, the concentration of active material (Si/CNF@LPSCl) in the electrode could be increased without apparent performance degradation due to the improved interfacial stability, which enables a reduction of the fabrication cost and the increase of the energy density.

10:00 AM BREAK

SESSION EN08.11: Solid-State Batteries with Li/Na Metal I
Session Chairs: Hui Wang and Hongli Zhu
Friday Morning, April 14, 2023
Moscone West, Level 2, Room 2008

10:30 AM *EN08.11.01
Nanomaterials for Lithium-Sulfur Battery Applications Jackie Y. Ying, Ayman A. AbdelHamid and Jian L. Cheong; Institute of Materials Research and Engineering, Singapore

We have synthesized high surface area nanomaterials of transition metal nitride, carbonitride and carbide nanoparticles that are highly dispersed on 3D carbonaceous structure. Taking advantage of their high electronic conductivity and surface properties, we have developed the nitrides and carbides as polysulfide (PS) regulators to tackle problems in lithium-sulfur (Li-S) batteries (e.g. shuttle phenomena, insulating sulfur). In particular, V_2CN/C nanocomposite has shown a greater redox activity than TiN/C and NbC/C. It has also demonstrated a superior performance with an initial specific capacity of 1055 mAh g^{-1} at 0.2 C and sulfur loading of 4.5 mg cm^{-2}, and a practical areal capacity and capacity retention of ~ 4.2 mAh cm^2 and 89%, respectively, after 300 cycles.

We have also designed a hybrid quasi-solid electrolyte (HQSE) comprised of $Li_7La_3Zr_2O_{12}$ (LLZO) sheet-based solid framework imbibed with liquid electrolyte. The LLZO HQSE has good contact with electrodes, high mechanical stability and Li-ion conductivity, excellent compatibility with Li metal anode, and impressive thermal stability. It results in a high-performance Li-S hybrid quasi-solid system with a very good safety profile. A remarkable rate capability (~515 and ~340 mAh g^{-1} at 1 and 2C, respectively) has been achieved at a loading density of 1.5 mg cm^{-2}.

11:00 AM EN08.11.02
Mechanisms Understanding and Kinetic Enhancements of All-Solid-State Li Sulfur Batteries Hongli Zhu; Northeastern University, United States

All solid-state lithium-sulfur batteries (ASSLSBs) are believed to deliver high energy density and remarkable safety than conventional Lithium-Sulfur batteries using liquid electrolytes. However, the low utilization of active material (sulfur) caused by sluggish reaction kinetics greatly hindered the development of ASSLSBs. It is significant to fabricate an advanced electrode where sulfur has efficient electron/ion accessibility.
Porous carbon host, which has been widely used in liquid cells, is proposed to address the challenges. However, the conventional porous carbon host used in liquid cells can not be directly used in ASSLSBs, because the nonmobile solid electrolytes can not reach the sulfur confined in the pores buried deeply inside the carbon. An ideal porous carbon host should own a large specific surface area to provide sufficient sites for sulfur, but it is critical that the pores should only locate at the out surface of the carbon. Till now, though many works reported the application of porous carbon in ASSLSBs, but none of them discussed the structure requirement of porous carbon. Here, for the first time, we discussed the ideal structure of the porous carbon and developed a polyacrylonitrile-derived porous carbon fibers (named PPCF) with a unique core-shell structure where a layer of micropores cover on dense core contributing to a high specific surface area. As a result, the ASSLSBs employing this PPCF showed an outstanding electrochemical performance.
Furthermore, we grew MoS2 nanosheets and applied it in ASSLSBs. The chemical and electrochemical compatibility among MoS2, sulfur, and sulfide SSE can greatly improve the stability of the cathode and therefore maintain pristine interfaces between the different compositions for stable ion and electron transport. The presence of electrical-conductive metallic 1T MoS2 and its uniform distribution on carbon fiber without aggregation benefit the electron transfer between carbon and sulfur. Meanwhile, the unique layered structure of MoS2 can be intercalated by a large amount of Li atoms and therefore facilitate both ionic and electronic conductivity. In consequence, the charge transfer and reaction kinetics were greatly enhanced, and the decomposition of SSEs was successfully relieved. As a result, our ASSLSB delivered an ultrahigh initial discharge capacity of 1456 mAh g-1 with ultrahigh initial coulombic efficiency and maintained high-capacity retention of 78 % at 0.1 C after 220 cycles. The batteries also obtained remarkable rate performance of 1069 mAh g-1 at 1 C. This study pioneered new idea that fabricating the high performance ASSLSBs through developing surface functionalized and stabilized conductive carbon additives with metal sulfides.
Last, we revealed that the Li-S redox reaction in ASLSBs undergoes a two-step transformation. First, the active material S8 converts into a short-chain polysulfide intermediate Li2S2 and further reacts into the final product Li2S during discharging process. During the charging process, Li2S converts back to Li2S2 first and then to S8, resulting in a reversible reaction. The sluggish reaction kinetic in the ASSLSBs will cause incomplete reaction and generation of Li2S2.

11:15 AM EN08.11.03
Characterization of the Deposition Behaviour of Sodium at the Copper | Solid Electrolyte Phase Boundary for Reservoir-Free Solid-State Sodium Batteries Till Ortmann[1], Till Fuchs[1], Ziming Ding[2,3], Qianli Ma[4], Frank Tietz[4], Christian Kübel[2,3,3], Marcus Rohnke[1] and Jürgen Janek[1]; [1]Justus Liebig University Giessen, Germany; [2]Technische Universität Darmstadt, Germany; [3]Karlsruhe Institute of Technology (KIT), Germany; [4]Forschungszentrum Jülich GmbH, Germany

Reservoir-free battery concepts have gained attention in literature due to simpler cell manufacturing, lower material and energy consumption, lower cost, and higher energy density. Instead of using a sodium metal foil as anode, a metal anode is formed in situ by plating sodium on a current collector (CC) by extraction of Na^+ from a fully sodiated cathode active material during first charging of the cell. Beside the columbic efficiency, one of the major challenges for reservoir-free sodium batteries is the homogeneous cathodic deposition of sodium metal on a CC.[1] The cathodic deposition of sodium on CC in contact with liquid electrolyte has been analyzed in several studies while for solid electrolyte no study exists.
For the first time, we analyzed the cathodic deposition of sodium on copper CC in contact with $Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$ solid electrolyte. Using a combined approach of galvanostatic electrochemical impedance spectroscopy (GEIS) and cryogenic electron microscopy, we analyzed the evolution of the deposition behavior at different current densities and external temperatures. For vapor deposited copper films, inhomogeneous plating with partial delamination at the $Cu|Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$ is observed. Additionally, a penetration of sodium whiskers through the CC is likely for thin copper films (~ 200 nm), while this can be prohibited by using thicker films (~5 μm).
Inhomogeneous deposition was confirmed by in situ SEM experiments revealing a preferential growth at surface flaws and defects. In a first step, the thin film CC is penetrated by a large whisker which grows continuously. After a certain time, small nucleation spots underneath the CC can be observed. The shape of the penetrated whiskers shows a pronounced dependency on the applied external current and temperature. At low current densities, facet structures are observed while increasing the current density led to a random shape of the whisker. The presented results highlight the importance of external conditions on the deposition behavior of sodium which are essential for reservoir-free solid-state sodium batteries.
[1] Wang, M.J., Carmona, E., Gupta, A., Albertus P., Sakamoto J., *Nat Commun* **2020**, *11*, 5201.

11:30 AM EN08.11.04
Molten Sodium Penetration Through Solid-State NaSICON Electrolytes Under High Current Ryan C. Hill[1], Amanda Peretti[2], Adam M. Maraschky[2], Leo J. Small[2], Erik D. Spoerke[2] and Yang-Tse Cheng[1]; [1]University of Kentucky, United States; [2]Sandia National Laboratories, United States

High conductivity solid electrolytes, such as NaSICON, are poised to play an increasingly important role in safe, reliable battery-based energy storage, enabling a new class of sodium-based batteries. Coupled demands of high current densities (≥0.1 A cm^{-2}) and low temperature (<200 °C) operation, combined with increased discharge times for long duration storage (>12 h), challenge the limitations of solid electrolytes. Here, we explore the penetration of sodium into NaSICON at 0.1 A cm^{-2} in a symmetric molten sodium cell. Previous studies of β''-alumina proposed that Poiseuille pressure-driven cracking (Mode I) and recombination of ions and electrons within the solid electrolyte (Mode II) can cause metal accumulation within solid electrolytes, but a comprehensive study at high current density is necessary. To understand and differentiate these modes in NaSICON, this work employs unidirectional galvanostatic testing of Na|NaSICON|Na symmetric cells at 0.1 A cm^{-2} over 23 hours at 110 °C. While galvanostatic testing shows a relatively constant, yet increasingly noisy voltage profile, electrochemical impedance spectroscopy (EIS) reveals a significant decrease in cell impedance which can be correlated with significant sodium penetration, as observed in scanning electron microscopy (SEM). Metal accumulation from the stripping-side electrode suggests that Mode II failure may be far more prevalent than previously considered. Further, these findings suggest that total charge transported per unit area (mAh cm^{-2}), as opposed to current density (mA cm^{-2}), may be a more critical parameter when examining solid electrolyte failure. Together, these results provide a better understanding of the limitations of NaSICON solid electrolytes under high current density and can guide the design of coatings to improve electrode-electrolyte interfaces.

This work was done in collaboration with Sandia National Laboratories and was supported through the Energy Storage Program, managed by Dr. Imre Gyuk, within the U.S. Department of Energy's Office of Electricity. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

11:45 AM EN08.11.05
Scalable Manufacturing of Selenide Solid-state Electrolytes for Sodium-ion Batteries Saeed Ahmadi Vaselabadi[1], Katie J. Palmer[2], William Smith[1] and Colin A. Wolden[1]; [1]Colorado School of Mines, United States; [2]Rose-Hulman Institute of Technology, United States

Sodium-ion batteries are garnering enormous attention for large-scale energy storage applications due to their low cost, enhanced sustainability, and decent performance. Moreover, their energy density and innate safety could be further improved by substitution of solid-state superionic conductors for conventional liquid electrolytes. Among the various classes of electrolytes, inorganic Na-based solid-state electrolytes, and specifically ternary chalcogenides and their derivatives are promising candidates that can achieve high ionic conductivity and low mechanical stiffness. Replacement of sulfide with selenide anion can provide larger channel size for ionic transport and lower binding energy between the anionic lattice framework and Na ions, leading to higher ionic conductivity. Conventional synthesis routes of selenides include mechanochemistry and high-temperature solid-state reactions which are energy-intensive and not amenable to scale-up. Herein, we employed solution chemistry through precursor and solvent engineering to design a scalable and cost-efficient solution route for the production of air-stable Na_3SbSe_4. Specifically, we showed a simple pseudo metathesis route toward the production of binary Sb_2Se_3 as a precursor that could further be extended to the formation of ternary Na_3SbSe_4 in two different synthetic routes: alcohol-mediated redox and alkahest amine-thiol approaches.
For Sb_2Se_3 preparation, elemental Se was reduced using $NaBH_4$, a common reducing agent, and further reacted with $SbCl_3$ via metathesis reaction to form Sb_2Se_3 and NaCl as a byproduct in an aqueous solution. Recovered amorphous Sb_2Se_3 was crystalized through mild heat treatment and used as is with no apparent impurities in the electrolyte reactions. In the alcohol-mediated route, the electrolyte was successfully synthesized in ethanol using a similar redox solution coupled with Sb_2Se_3 and NaOH as a basic agent. In the other approach, an amine-thiol solvent mixture is utilized as an alkahest system for the dissolution of elemental Se and Na and further reaction with the binary precursor to obtain Na_3SbSe_4. The electrolyte recovered from the alcohol solution without any post-reaction treatment has remarkable ionic conductivity (0.19 mS cm^{-1}) and low electronic conductivity ($1.6*10^{-6}$ mS cm^{-1}) at room temperature on par with reported performance from other conventional routes. Electrolytes obtained from the amine-thiol route produced a similar performance ($\sigma_{Na+} = 0.26$ mS cm^{-1}) via heat -treatment at 300 °C. These novel solution-phase approaches showcase the diversity and application of wet chemistry in producing selenide-based electrolytes for all-solid-state sodium batteries.

SESSION EN08.12: Solid-State Batteries with Li/Na Metal II
Session Chairs: Hui Wang and Hongli Zhu
Friday Afternoon, April 14, 2023
Moscone West, Level 2, Room 2008

1:30 PM EN08.12.01
Visualization Li Through Neutron Images in Sulfide-Based All-Solid-State Batteries Hongli Zhu; Northeastern University, United States

Lithium-metal (Li0) anode is considered the holy grail for all-solid-state lithium batteries (ASLMBs) owing to its exceedingly high energy density; in practice, most reported ASLMBs deliver unsatisfactory stability, mainly stemming from the incompatibility between the solid-state electrolyte (SE) and Li0 anode. To stabilize the interface, one strategy is introducing an interlayer between SE and Li0. Ideally, this interlayer should meet high ion conduction and electron insulation to avoid the direct deposition of Li0 at the SE|interlayer interface. Yet, there have been reported the use of mixed ionic-electronic conductors (MIEC), like the silver-carbon composite and graphite, can suppress the dendrite issue successfully. It seems the electron insulation is optional. A deep understanding of MIEC is critical for interlayer design and stable cycling life. Therefore, in our work, we investigated the mechanochemistry and mechano-electrochemistry behavior of a graphite interlayer, a typical MIEC, in the ASLMB by using operando neutron imaging and operando Raman spectroscopy. This work aims to provide insight into the design of the interlayer for the development of high-performance all-solid-state lithium metal batteries.
We believe that the following four highlights of this work will make it attractive to the broad readership of MRS:
1) For the first time, operando neutron imaging and Raman spectroscopy were coupled to investigate the mechanochemical and mechano-electrochemical reaction mechanisms of the interlayer in ASLMBs. Operando neutron imaging was used to effectively visualize the evolution of Li (either Li0 or Li+) during the battery test, and operando Raman spectroscopy was supplementarily used to distinguish the Li behaviors between intercalation and plating, at the MIEC interlayer.
2) The mechanochemistry and mechano- electrochemistry is studied individually step by step to well understand the Li evolution before and after charging, which is critical because the composition in MIEC after the mechanochemical reaction determine the Li evolution pathway in the following mechano-electrochemical reactions.
The MIEC interlayer was first proved with a complex composition but not the pristine pure material after the mechanochemical reaction. Under a high stacking pressure, the graphite interlayer did not remain pure graphite but transformed into a complex Li-graphite interlayer composed of Li0, diluted graphite intercalation compounds, and SE. The subsequent battery performance was highly determined by the chemistry of this Li-graphite interlayer.
3) We proved the lowest overpotential at the Li0 side is the most critical condition for the interlayer. We fundamentally investigated the mechano-electrochemical behavior at the MIEC interlayer. During the battery charging, the Li+ behavior at the interlayer was the result of three competing mechanisms: transport, intercalation, and deposition. Our results indicate the preferential deposition of Li0 is the Li-graphite|SE interface first and then plate at the Li-graphite interlayer, with no intercalation occurring. The lowest nucleation energy at the interface and the preexisting Li-metal filament trigger the Li-plating behavior.
4) We discussed the working mechanism of the interlayer in ASLMBs and proposed a new criterion for the required characters for the interlayer: a lower nucleation overpotential at the Li meal and MIEC interface. The conventional view that the interlayer should be electron insulation is not comprehensive, limiting many alternative materials owning electronic conductivity, i.e. MIEC, to be used as the interlayer.
5) Continuum modeling was conducted to explain the Li behavior in the graphite. The Li extrusion-intercalation under high pressure leads to the formation of the unique Li-graphite interlayer during the mechanochemical step. The MIEC dominates the Li transport during the electrochemical step, which leads to Li plating instead of Li intercalation.

1:45 PM EN08.12.02
Revealing the Hidden Dopant Effect on the Driving Force of Li Conduction and Dendrite Formation Mechanism in Cubic LLZO Solid Electrolytes Feye-Feng Lu and Hong-Kang Tian; National Cheng Kung University, Taiwan

Garnet-type oxide cubic LLZO (c-LLZO) with doping of super-valent cations is a promising solid electrolyte because of the enhanced ionic conductivity of around 10^{-3} S/cm. Different dopants have been proposed, such as Al, Ga, and Ce. However, the ionic conductivity is still limited and is not simply determined by the charge of dopants or the Li vacancy concentrations. The interaction between the Li and dopants and the complicated local environment due to various configurations of Li is still unclear. To comprehensively reveal the dopant effect in c-LLZO, we have investigated the c-LLZO bulk and surfaces with different dopants (Al, Ga, and Ce) via First-principle-based Density Function Theory (DFT) calculations. For screening out the energetic-favorable atomic structures, we have excluded the electrostatically-unfavorable Li configurations. It is found that the dopant atom tends to occupy the empty 24d sites (*tetrahedral*) in c-LLZO and results in three Li vacancies at the nearby 96h sites (*octahedral*) after doping. To further understand the dopant effect on the driving force of Li conduction, we calculated the vacancy formation energy of all the Li atoms as an indication of the Li chemical potential. The Li chemical potential increases and decreases by around 0.05 eV after doping with Ga and Al, respectively. It indicates that the Li atoms are thermodynamically more "mobile" when Ga is introduced, which agrees well with experimental results. Moreover, by calculating the Density of States (DOS) and Bader charge, it appears that Ga attracts more electrons than Al, resulting in a "more positive" environment for Li atoms that enhance Li conduction. Besides, the effect of different dopants on the surface electronic properties has been investigated, and the "trapping electron" tendency is evaluated to connect to the Li dendrite formation. We have also proposed a possible dopants/replacement that may be able to enhance the Li conduction and surpass the Li dendrite formation altogether.

2:00 PM EN08.12.03
The Impact of Li Surface Heterogeneity and Morphology on Performance in Solid-State Batteries Andrew S. Westover[1], Ritu Sahore[1], Erik Herbert[1,2], Sergiy Kalnaus[1], Robert Sacci[1] and Wan-Yu Tsai[1]; [1]Oak Ridge National Laboratory, United States; [2]Michigan Technological University, United States

Solid-state Li metal batteries have the potential to enable both fast charging and more than a 30% increase in energy density. Two of the most pervasive and limiting challenges in these materials are the interface between the Li metal and the solid electrolyte and the formation of Li filaments that penetrate the solid electrolyte leading to cell shorting. Currently, most efforts to solve these problems are focused on solid electrolytes. Here we present our work investigating the Li side of the equation. This work compares four thin Li sources (<40 µm), three rolled Li from commercial suppliers, and a fourth prepared in-house using thermal evaporation. Using X-ray photoelectron spectroscopy (XPS) and attenuated total internal reflection infrared spectroscopy (ATIR), we determined that the surface layers on these different Li films varied significantly in composition and thickness. Subsequent electrochemical testing of these films in liquid, polymer, and ceramic solid electrolytes, showed that variation in the surface thickness and chemistry significantly impacted the interfacial resistance. Furthermore, an analysis of cell failure due to shorting led to the clear conclusion that in addition to the surface contamination, the Li microstructure also had a significant impact in determining when failure will occur.**Acknowledgments:** Simon Thompson and the DOE EERE Vehicle Technology office Battery Material Research Program for funding supporting this work.

2:15 PM BREAK

2:45 PM EN08.12.05
Organic-Additive-Derived Cathode Electrolyte Interphase Layer Mitigating Intertwined Chemical and Mechanical Degradation for Sulfide-Based Solid-State Batteries Chanhyun Park[1], Juho Lee[1,2], Sangpyo Lee[1], Yu Jin Han[2], Jinsoo Kim[2] and Sung-Kyun Jung[1]; [1]Ulsan National Institute of Science and Technology, Korea (the Republic of); [2]Korea Institute of Energy Research, Korea (the Republic of)

Keeping both the chemical and physical state of the electrode–electrolyte interface intact is one of the greatest challenges in achieving solid-state batteries (SSBs) with longer cycle life. Herein, we demonstrate the use of organic electrolyte additives in the cathode electrolyte interphase (CEI) layer to mitigate the intertwined chemical and mechanical degradation in sulfide-based SSBs. Lithium difluorobis(oxalato)phosphate (LiDFBOP) and argyrodite (Li_6PS_5Cl) is used as a model system, with the LiDFBOP-derived CEI layer induced by irreversible oxidation above 4.12 V (*vs.* Li^+/Li) during the formation cycle exhibiting dual functions. This CEI layer retards the rate of chemical degradation between the cathode active particles and solid electrolyte at high charging potential and helps maintain intimate physical contact even at a low stack pressure of 0.75 MPa. The improved physical contact enables delivery of a high initial capacity, while chemical stability suppressing the sulfite or sulfate formation has a more dominant effect on the long-term cycle stability. This study presents a new perspective and strategies for designing cathode coating materials for sulfide-based SSBs beyond the typically used inorganic oxide materials.

3:00 PM EN08.12.06
Chemical Vapor Treatment on High Nickel Cathode Towards Improved Battery Performance Rajesh Pathak, Anil Mane and Jeffrey W. Elam; Argonne National Laboratory, United States

One of the recent strategies to improve battery performance is to remove the residual lithium compounds (RLCs) from the cathode surface. Ni-rich cathode materials easily absorb moisture and CO_2 that forms RLCs such as LiOH and Li_2CO_3. Such RLC deteriorates the active material's integrity and reduces the Li-ion diffusion coefficient which leads to poor battery cycling performance. Development of Li_3PO_4 as a robust cathode electrolyte interphase (CEI) is another strategy that can provide a physical barrier between the cathode and liquid electrolyte to prevent a solid-liquid interfacial reaction, prevent intergranular cracking and phase transformation, and enable fast lithium-ion transport and high Young's modulus. We reported chemical vapor treatment on NMC811. The surface impurities such as lithium carbonate (Li_2CO_3) and lithium hydroxide get removed after the reaction with an atomic layer depostion-precursor forming Li_3PO_4, releasing CO_2, CH_4, and O_2. In addition, the strong covalent bonding of the PO^{4-} group contributes to high thermal stability, low charge transfer resistance, and high voltage performance. As a result, CVT on NMC811 showed improved electrochemical performance and better rate capability compared to bare NMC811.
Keywords: chemical vapor treatment, high nickel cathode, cathode electrolyte interphase, longer, and high-rate capability

3:15 PM EN08.12.07
Pair Distribution Function Analysis of Local Motion in Double Paddlewheel $Na_2NH_2BD_4$ Megan Murphy[1], Bernadette Cladek[2], Matthew G. Tucker[2] and Jordi Cabana[1]; [1]University of Illinois at Chicago, United States; [2]Oak Ridge National Laboratory, United States

Global concerns over the need for clean sources of renewable energy have motivated research into next generation battery science. Solid-state batteries can be employed in place of traditional, liquid electrolyte batteries, to increase energy density and safety. Recently, $Na_2NH_2BH_4$ (NNB) has been identified to have an ideal structure, and vacancies needed to be employed as a solid electrolyte in Na-ion batteries. NNB is a defect antiperovskite with double paddlewheel anions, that demonstrates high ionic conductivity following a complex, Na-disordered transitional phase change. Currently, there is poor understanding of the pathways Na moves through, within the structure, that cause the intrinsic, high conductivity seen with NNB.
This study uses in-situ neutron PDF measurements of NNB to elucidate local disorder of the polyanions that promote Na migration due to their free rotation. In depth determination of translational, rotational, and bond disorder within both the polyanions and the local structure is performed. Large-box modeling of the data using reverse Monte Carlo profiling is also used to study this double paddlewheel effect and view snapshots of Na ion pathways within the structure. Through this work, insights into local ion disorder within the solid electrolyte lattice are illuminated and will play a key role in furthering solid-state battery technology.

SESSION EN08.13: Virtual Session: Solid-State Batteries
Session Chairs: Cengiz Ozkan and Hui Wang
Tuesday Morning, April 25, 2023
EN08-virtual

10:30 AM *EN08.14.01
Development of High-Capacity Anodes Toward Practical All-Solid-State Batteries Employing Sulfide Solid Electrolytes Yoon Seok Jung; Yonsei University, Korea (the Republic of)

Solidification of electrolytes with inorganic superionic conductors is considered to significantly improve the safety of lithium-ion batteries. Moreover, inorganic solid electrolytes (SEs) have the potential of stabilizing high-capacity electrode materials. Currently, Li metal and Si anodes are considered promising to achieve the high energy of all-solid-state batteries. Although it has been revealed that most SEs also suffer from side reactions (reduction) in contact with Li metal anodes, various interfacial engineering has proved to be effective in improving the performance. Specifically, it was shown that an introduction of Ag-C interlayer in Li-free all-solid-state cells enabled reversible cycling of in situ formed Li metal anodes. However, the use of nanoparticles of Ag may act as a hurdle for the practical application. Besides, high-capacity Si anodes have also been investigated for all-solid-state batteries. The SE-free Si anodes demonstrated drastic outperformance over the conventional Si anodes including SEs. This result was indebted to the absence of parasitic side reactions caused by SEs in the anodes. However, the electrochemical performance was obtained under unrealistically high operating pressures.
In this presentation, we report on our recent results of the strategies to develop high-capacity anodes of Si and Li metal for all-solid-state batteries. Specifically, it will be discussed how interlayer engineering for Si anodes enables stable operation at mild operational pressures, which is critical for practical all-solid-state batteries.

11:00 AM *EN08.13.02
Moisture Stability of Sulfide Solid-State Electrolytes Yubin Zhang[1], Fang Hao[1] and Thomas A. Yersak[2]; [1]Optimal Inc., United States; [2]General Motors Global R&D, United States

In this presentation we will detail a comprehensive study on the moisture stability of sulfide solid-state electrolytes in dry room environments. Although sulfide SSEs have many favorable attributes, this class of materials suffers from poor stability with water. Sulfide SSEs react with water to form gaseous H_2S and a variety of solid byproducts like Li_3PO_4 and LiOH, which go on to increase the interfacial impedance of solid-state batteries. Lab-scale research typically utilizes gloveboxes with < 1 ppm water, however, the large-scale manufacturing of Li-ion batteries occurs in -40 °C dewpoint dry rooms with around 126 ppm water. Consequently, the moisture stability of sulfide SSEs must be addressed if the manufacture of solid-state batteries based on sulfide SSEs is to be scaled up. Here, we are the first to characterize the moisture stability of sulfide SSEs according to both H_2S and the degradation of ionic conductivity at different moisture setpoints ranging from -76 °C to -40 °C dewpoint. A variety of different SSE compositions are studied; namely, $(Li_2S)_{75}(P_2S_5)_{25}$, $(Li_2S)_{70}(P_2S_5)_{30}$, $(Li_2O)_7(Li_2S)_{68}(P_2S_5)_{25}$, $(Li_2O)_7(Li_2S)_{63}(P_2S_5)_{30}$, and $(Li_2S)_{75}(P_2S_5)_{25}$ + 20 mol% LiI. We find that moisture stability improves with 75 mol% Li_2S modifier content and the introduction of a Li_2O co-modifier. After a 30 minute exposure in a -40 °C dewpoint dry room environment we found that $(Li_2S)_{75}(P_2S_5)_{25}$ + 20 mol% LiI powder generated 0.1 cc/g H_2S and its ionic conductivity decreased by over 50%. However, when SSE powder was exposed as a slurry in a dodecane carrier the same SSE composition generated 0 cc/g H_2S and its ionic conductivity only dropped by 14%. Our results show that sulfide SSEs have acceptable moisture stability when appropriately processed in a dry room environment.

11:30 AM *EN08.13.03
Li Metal Anodes for All Solid State Batteries—The Role of Unrecoverable Voids Kelsey B. Hatzell; Princeton University, United States

Alkali metal anodes (e.g.; Li) are energy dense alternatives for conventional anode materials (e.g. Graphite). However, Li metal undergoes significant volume change during electrochemical cycling which can lead to catastrophic cell failure due to irreversible dendrite formation and/or delamination. Recently, there have been numerous reports which demonstrate large degrees of voiding at high stripping rates and capacities which can drive discontinuities at the lithium metal-solid electrolyte interface. Therefore, a major challenge is finding operating conditions to suppress void formation during dynamic operation. There has been a lot of work focusing on how stack pressure can be used to recover interfacial properties upon cycling but contradictory reports demonstrate varying degrees of success. In this work, we studied the creep-induced interfacial aspects of Lithium metal and garnet LLZO solid electrolytes that impact the high-capacity stripping/plating (5 mAh/cm^2) of Li. Due to its intrinsic chemical stability against Li metal, LLZO is an excellent model system to evaluate the chemomechanics of Li metal. Via combining imaging, electrochemistry, and advanced pressure monitoring tools we can start to discuss how voids form and potential pathways for mitigation.

12:00 PM EN08.13.04
Enhanced Ionic Conductivity of Protonated Antiperovskite via Tuning on Paddlewheel Effect Chaohong Guan, Yu Yang, Ouyang Runxin, Huirong Jing, Jieqiong Yang and Hong Zhu; Shanghai Jiaotong University, China

The thermodynamically more stable lithium halide hydroxide, Li2OHCl, is experimentally easier to synthesize than Li3OCl. However, the protonated antiperovskite has the low ionic conductivity at room temperature due to the limited reorientation of OH anions. Here, density functional theory calculations were performed to determine the stability, elastic properties and Li diffusions of brominated Li2OHCl (Li2(OH)0.9Br0.1Cl and Li2OHCl0.9Br0.1). The Br substitution weakens the local bonding interactions and promotes the reorientation of OH anions, then increasing the ionic conductivities. Based on this, the reorientation of OH anions is further accelerated by substituting Cl by BH4 anions, and this novel protonated antiperovskite, Li2OHBH4, exhibits the high ionic conductivity of 2.8 mS/cm at room temperature. Our work highlights combining multi-factors, the overall soft lattice and the soft rotation mode of anion groups correlated to Li migrations, can effectively optimize the Li ionic conductivity, which might be a universal descriptor to further screen or design other classes of solid state electrolytes.

12:15 PM EN08.13.05
Heavily Se-Doping Influence on the Structure and Properties of Na_3SbS_4 Selim Halacoglu, Xiaolin Guo, Varun Shreyas, Yang Li, Badri Narayanan and Hui Wang; University of Louisville, United States

Solid-state sodium metal batteries using sulfide-based solid electrolytes (SEs) have attracted considerable attention in terms of their high theoretical specific capacity, safety, and abounding resources. Sodium chalcogenide ionic conductors are great candidates as solid electrolytes in solid-state sodium batteries. Their high ionic conductivity of 10^{-4}~10^{-2} S cm^{-2} at room temperature, and their attractive chemical stability in the air give them great advantages. However, the synthesis method of chalcogenide solid electrolytes is required to be simple, efficient, and with a scalable approach. In this presentation, we will introduce a solvent-free and low-temperature synthesis method for heavily Se-doped Na_3SbS_4 chalcogenides with compositional control and doping contents. Se-doping in Na_3SbS_4 results in a substantial change of Sb-S bonding in Raman spectra, and enhanced ionic conductivity at room temperature. Furthermore, the electrochemical stability of heavily Se-doped Na_3SbS_4 is also demonstrated in solid-state Na||FeS_2 battery within the voltage window of 1.0-2.7 V. This technique is promoting the practical applications of chalcogenide SEs in solid-state batteries.

SYMPOSIUM

April 11 - April 26, 2023

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SESSION EN09.01: Electrolytes and Interphases I
Session Chairs: Jeffrey Lopez and Guihua Yu
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2009

10:30 AM *EN09.01.01
Understanding Molecular Design for a Stable Lithium Metal Electrolyte Interface Zhenan Bao; Stanford University, United States

Lithium (Li)-metal batteries are attractive due to their high energy density. However, the drastic reactivity of Li metal limits its battery performance due to the formation of a naturally heterogeneous solid-electrolyte interphase (SEI) on the surface. In this talk, I will discuss understanding of molecular design concepts for electrolyte solvents and artificial SEIs to enable stable cycling of Li metal batteries.

11:00 AM *EN09.01.02
Ionic Peltier Effects and Thermal Conductivities of Battery Electrolytes: Studying Factors Controlling Heat and Ion Transport Zhe Cheng, Arghya Patra, Patrick Kwon, Jarom Sederholm, Beniamin Zahiri, David Cahill and Paul V. Braun; University of Illinois at Urbana Champaign, United States

Quantitative measurements of the thermal conductivity and ionic Peltier effect of common organic battery electrolytes can provide new insights into ion solvation and the barriers encountered by ions moving through battery electrolytes as well as how the flow of heat is controlled by the composition of battery electrolytes. Measurement of ionic Peltier effects required developing an ultrasensitive temperature difference metrology approach which we show has with a temperature difference resolution up to ±4 μK. This approach enables the probing of mK-level temperature responses of ionic Peltier effect, even in the presence of parasitic Joule heating using symmetric coin cell with Li metal or $Li_{0.75}CoO_2$ electrodes. We observed large ionic Peltier coefficients (up to 408 mV) in liquid electrolytes which are only weakly dependent on temperature but strongly dependent on ion concentration and electrolyte chemistry. The large ionic Peltier coefficient is related to the enthalpy barrier for ion hopping, providing insights to the mechanism of ion transport. While ions carry some heat, the majority of heat carried by a battery electrolyte is carried by phonons, and how this varies with battery electrolyte composition can be provided via measurements of thermal conductivity performed in conjunction with electrochemical and Peltier effect studies.

11:30 AM *EN09.01.03
Design Wide-Temperature and Fast Charging Battery Electrolyte Zheng Chen; University of California, San Diego, United States

Improving the wide temperature operation of rechargeable batteries is vital to the operation of electronics in extreme environments, where systems capable of higher energy, high-rate discharge and long cycling are in short supply. In this talk, we will show electrolyte designs to achieve high-energy density and stable cycling performance in wide temperature range. We will first demonstrate the holistic design of dual-ion batteries, which circumvent the sluggish ion desolvation process found in typical lithium-ion batteries during discharge. These batteries are enabled by a novel ester electrolyte, which simultaneously provided high electrochemical stability and ionic conductivity at low temperature. The dual-ion cells, when compared to industry-type graphite || $LiCoO_2$

full-cells demonstrated an 11 times increased capacity retention at -60 °C for a 10 C discharge rate, indicative of the superior kinetics of the “dual-ion” storage mechanism. More importantly, the fundamental understanding developed for dual-ion cells was then extended to search for other high-capacity, high-rate electrodes, which leads to further improved energy density and stability for both high and extremely low temperatures, demonstrated by rechargeable Li metal batteries using both high-Ni oxide and sulfur cathodes.

SESSION EN09.02: Electrolytes and Interphases II
Session Chairs: Jeffrey Lopez and Guihua Yu
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2009

1:30 PM *EN09.02.01
Synergistic Impact of (Multi)-Functional Electrolyte Components on Interfacial Chemistry and Phenomena in Lithium-Based Batteries Isidora Cekic-Laskovic; Forschungszentrum Juelich, Germany

Although considered as the systems of choice for many portable, mobile and stationary applications, existing battery technologies still face diverse challenges limited by the fundamental behavior of the active and inactive materials used. More precisely, electrolyte and its *ad hoc* interfacial chemistry are often identified as the main limiting and critical factors. Being the component bridging while interacting with all other active and inactive battery parts, electrolyte plays a key role in terms of design and control of the redox processes as well as regarding material interactions, performance, long-term stability, cost and safety of a battery. Due to the complexity of interactions taking place, the advancement of existing and development of novel electrolyte formulations is non-trivial and often leads to situations where specific targeted properties can only be improved at the expense of other relevant ones. For liquid electrolytes, a special focus is set on implementation of innovative, commercially available as well as newly synthesized ultrapure electrolyte components in optimum amount, particularly (multi)- functional additives/co-solvents/salt additives as effective approach towards desired advancements of electrolyte formulations. Although different classes of molecules have found their application in advancing the electrolyte performance, many questions regarding their role and effectiveness still remain unanswered. Comprehensive characterization by means of selected complementary electrochemical, analytical and structural methods enables establishment of structure-property-performance relationships that provide understanding and elucidation of main operation and failure mechanisms taking place comprising electrolyte│electrode interfaces and interphases.
This talk is an invitation to a journey through the design, development and extensive study highlighting synergy between targeted (multi)-functional electrolyte components advancing resulting formulations and lithium-based battery chemistries for targeted application(s).

2:00 PM EN09.02.02
Understanding Organic Components of Solid Electrolyte Interphase on the Lithium Metal Anode Jeffrey Lopez; Northwestern University, United States

Lithium ion batteries have become the dominant form of energy storage used in consumer electronics and, recently, electric vehicles. However, high costs have prevented widespread deployment of lithium ion batteries for applications other than portable electronics, and the safety issues associated with liquid organic electrolytes remain to be addressed. In order to enable the greater utilization of electric vehicles, allow for grid scale energy storage, and meet the demands of new electronic applications, new materials for high energy density batteries must be developed. High capacity electrode materials like lithium metal have the potential to facilitate these technologies, but lithium metal electrodes are presently limited by significant side reactions, poor quality deposition, and the potential to form hazardous dendrites. Therefore, it is important to develop a clear understanding of the surface reactivity and growth behavior of the lithium metal at the interface with the electrolyte in order to enable stable long-term cycling.

The products that form as a result of electrolyte decomposition reactions at the electrode interface are known to be extremely important in determining the final cell performance, yet characterizing the organic components of the solid electrolyte interphase (SEI) proves to be challenging with typical techniques. ATR-FTIR is a powerful method for characterizing organic species, but typical materials such as Ge, Si, and ZnSe react with lithium metal during deposition. In this talk, the development of a diamond based in situ ATR-FTIR cell will be discussed and its application to the characterization of organosulfur and fluorinated electrolytes will be discussed. Furthermore, SEI formation with respect to electrochemical potential and time will be described. With this understanding we provide new insights into the formation and chemical nature of SEI components that promote stable cycling of lithium metal electrodes.

2:15 PM EN09.02.03
High Entropy Electrolytes for High-rate Cycling Lithium Metal Batteries Sang Cheol Kim and Yi Cui; Stanford University, United States

Following the demonstration of the Li || TiS_2 battery chemistry in the 1970’s, the Li metal battery has been sought-after for its high energy density, but the reactivity of metallic Li has diverted research efforts to lithium-ion battery chemistries. Recently, the lithium metal battery has been reinvigorated as a viable battery chemistry with the aid of host electrodes, artificial interphases, solid electrolytes, and particularly liquid electrolyte engineering. Through molecular design and the use of highly fluorinated co-solvents, weakly solvating electrolytes with anion-rich Li^+ solvation structures have achieved superior interfacial stability and cycle life. However, despite their high stability, these weakly solvating electrolytes form ion clusters and possess compromised ionic conductivity, implying a trade-off in tuning solvation strength. While many of these strategies have relied on tuning the enthalpic interactions between Li^+ and its surrounding species, entropy as a design knob has largely gone unnoticed for liquid electrolytes. As one of the two descriptors for solvation thermodynamics, which dictates solvation structures and bulk electrolyte properties, entropy can be expected to be an important design parameter.
In this work, we introduce the concept of high entropy electrolytes (HEEs) that achieve improved ionic conductivity while maintaining excellent electrochemical stability. We carefully design experiments to minimize differences in solvation enthalpy by selecting structurally similar solvents, but increase entropy by deploying a large number of solvents. We find that increasing the molecular diversity and concomitantly the mixing entropy of weakly solvating electrolytes can reduce ion clustering while retaining anion-rich solvation structure, which we confirmed through synchrotron-based X-ray scattering and molecular dynamics simulations. Less clustered high entropy electrolyte with higher Li^+ diffusivity exhibit a 2-fold increase in ionic conductivity, enabling stable cycling at high current densities up to 2C (6.2 mA cm^{-2}) in anode-free NMC-Cu pouch cells. We substantiate the generality of the concept by verifying performance improvement in three disparate electrolyte systems. This work highlights a large unexplored design space of HEEs that can improve electrolyte properties for practical lithium metal batteries.

2:30 PM EN09.02.04

Interphase Design by Localized Super-Concentrated Electrolyte for High-Voltage and High-Power Lithium Metal Batteries Youngmin Ko[1], Michael A. Baird[2] and Brett A. Helms[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

Batteries used in electric aircraft must deliver high-power on take-off and landing, providing in stride the ability to recharge at high voltage to make full use of the cathode capacity. Impedance rise associated with electrode–electrolyte interphases remains problematic with conventional electrolytes, resulting in unacceptable power fade. This is exacerbated when recharging cells at high voltage, which is where interphase generation remains poorly controlled. To address these issues, electrolyte design for high-voltage and high-power batteries should emphasize control over the interphase growth contributing to the impedance rise during charge. To this end, we will describe our recent efforts to alter the activity of various electrolyte components at electrode–electrolyte interfaces, granting access to exquisite control over interphase chemistry. Key to our success is the exploitation of ion clustering in locally super-concentrated electrolytes (LSCEs), which produces aggregates with intrinsically different reactivity than solvated species and from which new interphasial chemistries may be produced in-situ. We find in top-performing compositions that interphase stability is most affected by the activity of ethereal solvents in the formulations, particularly at high voltage, and that it is possible to design additives that suppress solvent activity even up to 4.5 V vs. Li/Li$^+$. Li/NMC811 cells cycled with de-novo designed LSCEs maintain 70% of their initial discharge capacity after 1000 cycles with 4 C discharge rate at charge cut-off voltage of 4.35 V, outperforming most reported electrolytes for Li metal batteries. Furthermore, by taking an informatics approach to interphase characterization, we reveal fundamental patterns of reactivity that inform future selection criteria for advanced battery electrolytes.

2:45 PM DISCUSSION TIME

3:00 PM BREAK

3:30 PM EN09.02.07
Self-assembled Protective Layer by Symmetric Ionic Liquid for Long-cycling Lithium-Metal Batteries Jinha Jang[1], Jae-Sun Shin[1], Sunghyun Ko[1], Hyunchang Park[1], Woo-Jin Song[2], Chan Beum Park[1] and Jiheong Kang[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Chungnam National University, Korea (the Democratic People's Republic of)

A lithium (Li) metal is expected to be an ideal anode material for energy-dense storage devices due to its intrinsic high capacities (3,860 mAh g^{-1}). However, its practical implementation was hindered by a dendritic Li deposition, which exacerbates the cycling efficiency of Li-metal batteries. Herein, we present a novel ionic liquid (IL) electrolyte additive modified by symmetric alkyl chains to control the Li deposition. This symmetric design generated a self-assembled lithiophobic shielding layer on Li protuberances, leading to the smooth deposition of Li. In addition, our symmetric ILs stabilized electrode interphase with higher inorganic components by anchoring counter anions near the Li-metal electrode. As a result, our symmetric IL enabled reliable cycling of Li-$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cell (three times excessed Li) with high Coulombic efficiency (~99.8%) over 250 cycles. In this presentation, I will discuss a new design protocol for IL-based electrolytes and provides a promising way to high efficiency, stable-cycling Li-metal batteries.

3:45 PM EN09.02.08
Polymerizable Zwitterionic Molecules and Their Synergism with Commercial Electrolyte Additives for Better Lithium-Ion Batteries Niguse A. Sahalie and Jonas Mindemark; Uppsala University, Sweden

Lithium-ion batteries (LiBs) have achieved great success in the electronics market and are now the industry standard for grid energy storage and the electrification of transportation. The practical achievable capacity of LiBs (for conventional electrodes like layered oxide cathodes and graphite anodes, among others) is rapidly approaching, and there is a strong market demand to develop new batteries with higher energy and power densities than those currently offered by commercially viable materials. To enable electric vehicles with an expanded range of operation, long battery lives, and quick "refueling," such next-generation LiBs must meet certain practical requirements. These include higher energy densities and fast charge-discharge rates, which hinge on new high-voltage, high-capacity, and high-power cathode materials and on stable electrolytes with higher ionic conductivities [1] [2].
In addition, current LiBs with layered oxide cathode material use expensive Cobalt which compromises the green profile and limits the cost reduction needed for their widespread uptake. In this regard, several cathode materials have been developed without cobalt. The LNMO ($LiNi_{0.5}Mn_{1.5}O_4$) cathode is one of the best candidates due to its high voltage and high-power capability features. However, most of the electrolytes undergo oxidative decomposition at such high voltages, preventing their real application. Assembling LNMO with high-capacity anode materials such as Silicon-graphite makes the matter worse, as such anode materials have their own serious issues that cause early cell failure. Different electrolyte formulations using different additives have been tested to mitigate such challenges on both the cathode and anode sides. However, problems with these electrolytes and additives arise from decreasing the conductivity of the electrolyte, the continuous formation of a resistive passivation layer, cost, safety, or sometimes even several of these happening to a single electrolyte.
Herein, in the BetterLiBs project, we have used thermally stable and polymerizable zwitterionic monomers (ZIMONS) blended with commercially available liquid electrolyte additives to improve the performance of high-voltage LiBs in full cell configurations. Zwitterionic monomers have equal numbers of positive and negatively charged functional groups, which can help to easily decouple the two charges of the electrolyte salt. As a result, the ionic conductivity of the electrolyte could be improved. The polymerizable features of ZIMONS are very important in forming a good passivation layer at the electrode/electrolyte interface, leading to stable cycling of the high-voltage cathode material. Therefore, the use of SEI-forming commercial additives together with ZIMONS could be an important approach for stable cycling of full cell LiBs.
The synthesis, screening, and optimization of more than a dozen ZIMONS for their electrochemical performance and their synergism with commercial additives are components of the BetterLiBs initiative. Performing cyclic voltammetry analysis in half cells, synthesized ZIMONS additives are already demonstrating a good stabilizing effect of LP57 electrolytes at both reduction and oxidation voltages. Cycling tests with different ZIMONS additives also show significant improvements in capacity and coulombic efficiency in the high-voltage LNMO configured with a silicon-graphite anode. This improvement in cycling stability is in good agreement with the decrease in cell resistance, which was studied by Intermittent Current Interruption (ICI) measurements. Other cell configurations with graphite anode materials are also being studied.
References
[1] B. Aktekin et al., J. Phys. Chem. C, 122(2018), 11234–11248
[2] S. Park et al., Nature Communications, 12 (2021), 12, 838–849

4:00 PM EN09.02.09
Non-Flammable Liquid Electrolytes for Lithium-Ion Batteries—Performance and Interfaces Florian Gebert; Uppsala University, Sweden

Battery safety, particularly regarding flammability, has come under increasing public and scientific scrutiny as lithium-ion batteries become ubiquitous in everyday life. Much effort is being put into formulating nonflammable electrolytes for lithium-ion batteries (LIBs), as electrolytes are usually the most flammable components of a typical battery cell. Due to the ongoing technical challenges surrounding solid electrolytes, non-flammable liquid electrolytes are an attractive medium-term solution. Two classes of compounds are generally used as nonflammable LIB solvents: fluorinated compounds and organophosphates. Fluorinated solvents generally have good electrochemical properties, but are expensive and come with well-known environmental and toxicity issues. On the other hand, phosphates are cheap, generally nontoxic and more environmentally benign, but currently unviable as they suffer from very poor electrochemical performance.

In this work, the advantages and disadvantages of these two types of non-flammable electrolyte classes are presented using representative compounds from each: difluoromethyl acetate, methyl 2,2,2-trifluoroethyl carbonate and triethyl phosphate. As a starting point, core performance measures such as cycling data, rate capability and cell resistance were collected. The compositions of the passivating films formed by these electrolytes on commercial LIB electrodes were characterized using electron microscopy and photoelectron spectroscopy, and their correlation with electrochemical properties are discussed. Issues specific to each class are explored in detail, such as fluorine dissociation and solvent-cointercalation.

SESSION EN09.03: Poster Session I: Polymeric and Organic Materials for Electrochemical Energy Storage

Session Chairs: Zheng Chen and Jeffrey Lopez
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN09.03.01
Fast-Charging Limitations of Advanced Electrolytes for Lithium Metal Batteries Yuelang Chen; Stanford University, United States

Lithium metal batteries (LMBs) are being actively developed to meet the high-energy-density demand for electric vehicles (EVs). Fast charging is an important requirement for EV applications. While improving lithium metal Coulombic efficiency (CE) has been a focus for LMB electrolyte design, their performance under high current densities is less explored. Here, we evaluate the moderate-to-high-rate cycling stability of three recently developed advanced electrolytes, all of which are weakly solvating electrolytes with anion-derived solid electrolyte interfaces. All three electrolytes showed soft shorting behavior above various threshold current densities. Based on extensive characterizations, we propose a mechanism by which slow ion transport was the main factor that led to poor cycling stability due to concentration polarization, poor Li morphology, and closely packed residual solid electrolyte interphase (rSEI) structure. This work confirms the importance of fast ion transport for LMBs under moderate to fast charging conditions. Therefore, for electrolyte designs, improving CE must be accompanied by efficient ion transport in order to provide a viable solution to practical LMBs.

5:00 PM EN09.03.03
Designing Gel Polymer Electrolyte With Synergetic Properties For Rechargeable Magnesium Batteries Liping Wang[1], Zhenyou Li[1], Zhirong Zhao-Karger[1] and Maximilian Fichtner[1,2]; [1]Helmholtz institute Ulm, Germany; [2]KIT, Germany

The rapid market expansion for consumer electronics and electric vehicles urges the development of electrochemical energy storage devices with high energy density, low cost and high safety. In this regard, the development of multivalent-ion batteries is one feasible solution for such goals. Rechargeable magnesium batteries (RMBs) have emerged as attractive candidates among post-lithium batteries because of the particular features of metallic magnesium (Mg) as a metal anode. However, the realization of practical Mg batteries remains challenging and exploration of suitable electrolyte is imperatively necessary.
Recently developed non-corrosive magnesium tetrakis (hexafluoroisopropyloxy) borate $Mg[B(hfip)_4]_2$ (hfip = $OC(H)(CF_3)_2$) electrolyte exhibits outstanding electrochemical performance and good chemical compatibility in Mg-based systems.[1] The discharge/charge chemistry with this electrolyte has been demonstrated with the sulfur (S) cathode, which is considered as one of the most promising cathode materials, due to its high theoretical capacity (1675 mA h g^{-1}), low toxicity and high abundance. Nevertheless, Mg−S batteries with a liquid electrolyte are still facing critical issues correlated with the dissolution of the sulfur species during the discharging/charging process, so-called polysulfide shuttle effect, which leads to self-discharge and capacity fading.
The development of gel polymer electrolytes (GPEs) may provide a promising solution to alleviate the above issues. A GPE designed by trapping solvent molecules in a polymerized gel network may limit the dissolution and diffusion of soluble electrode materials. For Mg−S batteries, the utility of GPE could be an efficient approach to inhibit the diffusion of the polysulfide. Moreover, GPEs have some additional advantages, including improved safety (less internal short-circuit and less electrolyte leakage) and mechanical durability for electrochemical devices.
Herein, a novel magnesium tetrakis(hexafluoroisopropyloxy)borate ($Mg[B(hfip)_4]_2$)-based non-corrosive gel polymer electrolyte has been developed by an *in situ* polymerization method.[2] Polytetrahydrofuran (PTHF) is chosen as backbone to build the GPE, denoted as $Mg[B(hfip)_4]_2$-PTHF-GPE. This gel polymer electrolyte exhibits unprecedented properties in terms of high ionic conductivity (10^{-3} S cm^{-1}), reversible Mg plating/stripping capability (Coulombic efficiency ~99%, 1000 cycles) and low electrochemical overpotential. Moreover, the gel polymer electrolyte shows good compatibility with sulfur cathode. The stable open circuit potential of the Mg−S cells using $Mg[B(hfip)_4]_2$-PTHF-GPE demonstrates that the GPE can largely suppress the self-discharge of the cell. Furthermore, this GPE can be simply prepared from a liquid electrolyte and easily integrated into devices, which opens a new avenue for the development of magnesium batteries.
References:
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5:00 PM EN09.03.04
A New Class of Intermediate Temperature 1D Anionic Coordination Polymer Proton Electrolytes Albert Epshteyn[1], Brian L. Chaloux[1], Michelle D. Johannes[1], James Ridenour[2], Elias Pomeroy[2] and William Maza[1]; [1]U.S. Naval Research Laboratory, United States; [2]NRC Postdoctoral Associate, US Naval Research Laboratory, United States

Borosulfates and borophosphates are two examples of a recently-discovered new class of intermediate temperature (150 °C-400 °C) solid acid electrolytes that exhibit a 1D anionic coordination polymer structure. We have shown that the borosulfates exhibit extremely high proton conductivities under low humidity environments, while the borophosphates are much more thermally stable, but require significant humidity for proton conduction. We have made significant advances in developing and scaling-up solvothermal synthesis methodologies that can be varied to produce a different solid- state borosulfate and borophosphate structures (verified by SCXRD and PXRD) and exert significant crystallite size control. Examples will be presented of approaches for improving proton conductivities in these materials that include varying mixtures of cations, cation and carrier doping, as well as process optimizations to produce higher quality sintered monoliths.

5:00 PM EN09.03.05

Enhancing Anionic Exchange Membrane Robustness in Vanadium Redox Flow Systems via Multication Side Chain Addition Michael Lee, Sydney Stansberry, Bradley Swan and Chris J. Cornelius; Iowa State University, United States

A more robust energy storage system is needed to provide for increasing energy demands in the world. One highly robust and scalable technology is the vanadium redox flow battery (VRB). Limitations of the standard VRB cell membrane, Nafion, are many. Nafion is too expensive to scale up in numerous cell stacks. A highly acidic and oxidative environment has been shown to foul and degrade the polymer membrane. Also, a primary concern is the vanadium ion crossover through percolation channels which leads to self-discharge reducing the coulombic efficiency. Cheaper and more durable cell membranes have been investigated. Diels-Alder poly(phenylene) (DAPP) materials are very mechanically robust membranes that have the potential to be a cheaper alternative. DAPP with pendant methyl groups on the phenyl rings can be brominated and substituted with quaternary ammonium to create benzyltrimethylammonium groups (QDAPP). Specifically, these cationic groups have been shown to possess lower vanadium ion permeability than Nafion because of the electrostatic repulsion described by the Donna effect. However, higher water uptake at higher IEC values creates swelling and limits crossover prevention. Additionally, ex-situ degradation studies have shown that membranes are prone to oxidation earlier than Nafion. To combat oxidation of the membrane more sterically hindered polymers will be investigated in this work. By incorporating previously reported quaternary ammonium multication side chains with different alkyl spacer lengths it is thought that membrane durability of DAPP will be increased. Additionally, further improvement of the ion conductivity on the previously reported carbonate counter ion form is hoped to be gained with additional cationic groups. Planned studies for this project include cell diffusional studies to determine crossover, ex-situ degradation studies, in-plane and through-plane conductivity measurements, mechanical strength determination, toughness determination, and VRB performance factors such as coulombic and voltage efficiency as well as open current voltage decay and charge discharge behavior. Future studies involve blending QDAPP with varying degrees of IEC.

5:00 PM EN09.03.06
Synthesis and Organic Electrochemical Transistor Characteristics of IDT-based p-type Conjugated Polymers Sang Young Jeong[1], Jung Woo Moon[2], Soonyong Lee[1], Jeong Ho Cho[2] and Han Young Woo[1]; [1]Korea University, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of)

Following the success of organic field effect transistors (OFET), organic electrochemical transistors (OECT), which also belong to a family of 3-terminal devices, was emerged with tremendous attention. Unlike OFET devices' area, the active layer of the electrochemical transistors is volumetric, rendering OECT devices with low operation voltage, high sensitivity and aqueous operability render it with potential as bioelectronics. Based on these contents, we have developed a new vertical OECTs (*v*-OECT) device architecture with polymer active layer vertically sandwiched in between drain and source electrode using two p-type donor-acceptor copolymers.
Two p-type polymers, namely PIDTPEG-BT and PIDTC16-BT was synthesized by applying IDT-BT backbone which had been succeeded in OFET and OPV application. Since the channel length of the vertical transistors is short in contrast to the lateral transistors, *v*-OECTs have the higher conductivity, due to the geometrical advantage of the *v*-OECTs, together with a higher degree of integration. By thermal annealing of active layer films, a different trend in transconductance was observed: increase in PIDTC16-BT and decrease in PIDTC16-BT, which is ascribed to the polymer orientation difference caused by thermal annealing evidenced by grazing-incidence wide-angle x-ray scattering (GIWAXS) measurements. These results provide guidance for further development of material design and device fabrication methods.

5:00 PM EN09.03.07
Cross-linking Chemistry on Solid-State Polymer Electrolytes in Lithium-ion battery Jia-Hua Chen[1], Wen-ya Lee[1], Ru-Jong Jeng[2] and Nae-Lih Wu[2]; [1]National Taipei University of Technology, Taiwan; [2]National Taiwan University, Taiwan

Solid polymer electrolytes, which improve the safety issues in commercial liquid electrolytes, are considered a promising solution for the next generation lithium-ion batteries. Even though sufficient ion conduction capability of solid-state electrolytes has been achieved to date, challenges for electrochemical stability and mechanical properties still remain. Controlling crosslinking chemistry is a promising way to achieve electrochemically stable electrolytes. In this work, we compare various crosslinking chemistry of thermally and photo-induced in-situ polymerization in Polyethylene glycol diacrylate(PEGDA)/butyl acrylate(BA)/succinonitrile(SN) electrolyte, including thiol-ene Michael addition and alkene–azide chemistry. Through comprehensive analysis and clarifying the effect of each crosslinking mechanism on the chemical structures of solid-state polymer electrolytes, we have found that appropriate polymerization is one of the key factors for stable battery performance. The work shows that the manipulation of crosslinking chemistry provides a efficient way to improve the electrochemical performance in lithium-ion batteries.

5:00 PM EN09.03.08
Strategic Usage of Redox Active Material and Sacrificial Zinc Electrode for Spontaneous Hydrogen Evolution Reaction Taeyup Jeong, Chandan C. Gudal, Byeongkyu Kim, Jae Wook Lee, Yong Seok Kim and Chan-Hwa Chung; Sungkyunkwan University, Korea (the Republic of)

Hydrogen is the cleanest and highly efficient source of energy than any of the fossil fuels. The carbon footprint left behind by the incineration of the fossil fuels are causing drastic changes in greenhouse gases which is leading unpredictable global warming and harsh climate changes endangering everyone and everything on the earth. Currently, the generation of hydrogen fuels at industrial level is by conversion of fossil fuel like natural gas, coal, and petroleum, which gives carbon footprint as by-product, here the generated hydrogen is referred as "grey hydrogen." When carbon cauterization process is used in the previous process, the hydrogen is referred as "blue hydrogen." Finally, there is "green hydrogen," which uses renewable energy to create hydrogen without emitting any greenhouse gases. Green hydrogen production does not produce greenhouse gases, which makes it advantageous as a clean energy source independent of the issue caused by global warming. However, the world's green hydrogen production is still significantly smaller than the general hydrogen production that emits greenhouse gases, so it is not attracting attention. Accordingly, research is being actively conducted to produce hydrogen by decomposing water through electrical energy using renewable energy power.
A general electrochemical water decomposition process is performed in a cell that separates both electrodes, anode, and a cathode, using a polymer electrolyte membrane, where oxygen evolution reaction (OER) and a hydrogen evolution reaction (HER) occur, respectively. At this time, a precious metal catalyst is used for an OER, which causes cost problems and has the disadvantage of a relatively slow reaction compared to HER.
In this study, to compensate these shortcomings, the redox reaction using redox active materials (RAM) were used instead of OER. These redox active materials can lower costs by utilizing different methods with metals, organic compounds, and polymers. They can also make up for issues with current oxygen generation process through reversible redox reactions. In addition, beyond compensation for the shortcomings, it was designed so that the HER could occur voluntarily through the low negative potential of the RAM. Since the standard reduction potential of the hydrogen production reaction in a general acid solution (pH 0) is 0 V (vs. SHE), the cell is driven using a cation exchange membrane (CEM) and a bipolar membrane (BPM) according to the pH condition of the redox active substance (RAM) used in the anode. The system can be driven by a spontaneous reaction if the standard reduction potential of the RAM utilized has a negative potential lower than the standard reduction potential of the hydrogen synthesis reaction. After the HER, the oxidation of the zinc sacrificial electrode has a standard reduction potential of -1.23 V (vs. SHE at pH 14) can voluntarily reduce RAM and generate power. As a result, it is possible to voluntarily produce power and green hydrogen by consuming only the Zn sacrificial electrode.
In this study, the spontaneous hydrogen production reaction process was studied using Zn and RAMs. Electricity is generated both during the reduction of the redox active material with Zn and during the reaction that produces hydrogen from the reduced redox active material. This is a benefit of eco-friendly

systems, green hydrogen production, and power generation, and it is implied that it is more energy-efficient than conventional electrochemical systems' hydrogen generation.

5:00 PM EN09.03.09

Phosphine Modulation for Enhanced CO_2 Capture: Quantum Mechanics Predictions of New Materials Charles B. Musgrave[1], Aleksandrs Prokofjevs[2] and Bill Goddard[1]; [1]California Institute of Technology, United States; [2]North Carolina Agricultural and Technical State University, United States

It is imperative to develop efficient CO_2 capture and activation technologies to combat the rising levels of deleterious greenhouse gases in the atmosphere. Using Quantum Mechanics methods (Density Functional Theory), we propose and evaluate several metal-free and metal-containing phosphines that provide strong CO_2 binding under ambient conditions. Depending on the electron donating capacity of the phosphine and the ability of the P-bound ligands to hydrogen bond to the CO_2, we find that the CO_2 binding can be as strong and downhill as -18.6 kcal/mol, which should be quite adequate for ambient conditions. We explore some modifications of the phosphine to improve CO_2 binding, and we elucidate which chemical descriptors correlate directly with CO_2 binding energy. Specifically, we find that charge accumulation on the CO_2 unit of the CO_2-bound adduct has the greatest correlation with CO_2 binding affinity. Finally, we probe the mechanism for CO_2 reduction to CO and methanol in aqueous media.

5:00 PM EN09.03.10

Combining Quinone-Based Cathodes with Non-Corrosive $Mg[B(hfip)_4]_2$-Electrolyte for Magnesium Batteries Sibylle Riedel, Björn Schmidt, Zhirong Zhao-Karger and Maximilian Fichtner; Karlsruhe Institute of Technology, Germany

The increasing demand for high-energy storage systems has led to intensive research into sustainable and low-cost battery technologies. A rechargeable magnesium battery system is considered as a promising approach. Magnesium (Mg) is an abundant element on Earth. Mg metal has a high theoretical capacity and can potentially be used as a metal anode.[1,2] As Mg^{2+} ion is a divalent ion and has a small ionic radius (72 pm vs. 76 pm for Li-ion), it shows strong electrostatic interactions with the classical oxide cathode materials which leads to slow kinetics and strong polarization and consequently poor electrochemical reversibility. Contrariwise, organic materials have more flexible structures, which provide energetically more favorable ion-migration pathways enabling faster ionic diffusion kinetics and improved electrochemical performance.[3] Another key factor that influences the battery performance is the electrolyte. Most of the Mg electrolytes contain chloride, which cause corrosion to the metallic cell components and can generate parasitic reactions in the cells leading to a short cycle-life of the batteries. The $Mg[B(hfip)_4]_2$ electrolyte shows important features for practical applications in terms of the high Mg deposition efficiency, high stability and non-corrosive properties.[4]

Therefore, the combination of organic redox-active cathode materials with $Mg[B(hfip)_4]_2$ electrolytes could be a promising approach for the development of Mg battery technology. On the other hand, the high solubility in electrolyte solutions and low electrical conductivity represent as the main challenges for the use of organic electrode materials. Polymerization and incorporation of a conductive carbon to prepare the organic composites are the common approaches to overcome these problems. However, a low carbon content and homogeneous dispersion of the polymer are required to avoid sacrificing energy density at the cell level and to achieve good electrochemical performance.

One approach we present here is a so-called *in situ* polymerization. The conductive carbon was directly introduced into the polymerization reaction and the polymer chains could grow within the carbon structures. Since this method ensures good contact between polymer and carbon, the carbon content can be reduced. Furthermore, this method is beneficial for preventing the dissolution of the active material in the electrolyte.

The poly-anthraquinone cathode-based Mg batteries in combination with the $Mg[B(hfip)_4]_2$/tetraglyme electrolytes showed a cycling performance for 1200 cycles with a capacity retention of 55%, and coulombic efficiency of 99%.

References
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5:00 PM EN09.03.11

Encapsulation of Pt-based clusters in ZIF-8: Insights from First-Principles Simulations Poonam .[1], Kathrin Kollmannsberger[1], Edoardo Mosconi[2], Roland A. Fischer[1], Alessio Gagliardi[1] and Waldemar Kaiser[2]; [1]Technical University of Munich, Germany; [2]CNR-SCITEC, Italy

The reactivity of a Pt-based nanoparticle catalysts greatly depends on their size and detailed atomic structure. Recently, atom-precise nanoparticles have been generated from molecular ligand-stabilized clusters via encapsulation within a metal organic frameworks.[1,2] In this work, we aim to rationalize the underlying encapsulation mechanism of the ligand-stabilized Pt-based using first-principles simulations. Density functional theory (DFT) calculations and ab initio molecular dynamics simulations (AIMD) were carried out to understand the interaction of the Pt-based clusters with the MOF (ZIF-8) precursors in solution. By DFT, we determine the interaction of ZIF-8 precursors with the CO ligands of the Pt-clusters and reveal chemically distinct sites of all the considered clusters which favor the attraction of Zn^{2+} ions in solution. AIMD simulations of Pt-based clusters in an explicit methanol solvent model shed light on the competition between attraction of Zn^{2+} and the Pt-clusters and desorption of Zn^{2+} by solvation with methanol molecules, revealing an importance of bridging CO ligands to create a Zn-rich environment around the Pt-cluster and to guarantee the successful encapsulation.

5:00 PM EN09.03.13

Effect of Charged Polymers on Electrochemical Performance of Lithium Sulfur Batteries Using Ionic Liquids Jeong Mu Heo, Chae Yoon Lee and Keun Hyung Lee; Inha University, Korea (the Republic of)

Recently a lot of research efforts have been devoted to lithium-sulfur batteries as one of the next-generation energy storage devices because of their exceptional theoretical capacities (1675 mAh/g or 2600 mWh/g). However, migration of soluble polysulfide species through the liquid electrolyte from a positive electrode to a negative electrode, also known as the shuttle effect, often limits the performance of lithium-sulfur batteries, resulting in irreversible cycles and capacity degradation that hinder practical applications. In this study, we employed a positively charged polymer as a binder material that can attract negatively charged polysulfide species generated during the discharge cycle of the device operation to inhibit the shuttle effect and achieve stable electrochemical operation. In the case of using a conventional non-charged polymer binder, the movement and dissolution of ionic polysulfide cannot be prevented and thus stable long-term operation of the lithium-sulfur batteries was not attainable. To further improve the performance of the lithium-sulfur batteries, ionic liquids with low donor numbers compared to organic solvents were utilized to suppress the dissolution of polysulfide. Ionic liquids can also provide other outstanding characteristics such as non-flammability, negligible vapor pressure, high chemical and thermal stability, and wide electrochemical window desirable for developing environmentally stable next generation energy storage devices. The resulting lithium-sulfur batteries using the charged polymer binder and ionic liquids showed superior initial discharge capacity (> 1000 mAh/g) and capacitance retention (> 60% of its initial discharge capacity after 100 charge/discharge cycles).

5:00 PM EN09.03.14
Fast Capture and Stabilize Li-Ions via Physicochemical Dual Effects for Ultra-Stable Self-Supporting Li Metal Anode Xuzi Zhang and Ge Li; University of Alberta, Canada

Lithium (Li) metal is regarded as one of the most promising anode candidates for next-generation batteries, ascribed to its extremely high specific capacity and low redox potential. However, its application is still hindered by the uncontrolled growth of dendritic Li and huge volume fluctuation during cycles. To address these issues, flexible and self-supporting 3D interlaced N-doped carbon nanofibers (NCNF) coated with uniformly distributed 2D ultrathin $NiCo_2S_4$ nanosheets (denoted as CNCS) were designed to eliminate the intrinsic hotspots for Li deposition. Physicochemical dual effects of CNCS come from a limited surface Li diffusivity with a higher Li affinity, leading to uniform Li nucleation and a less random accumulation of Li, as proven by ab initio molecular dynamics simulations. Due to the unique structure, exchange current density is reduced significantly and metallic Li is further contained within the interspace between the NCNF and $NiCo_2S_4$ nanosheets, preventing the formation of dendritic Li. The symmetric cell with Li/CNCS composite anode exhibits a long-running lifespan for almost 1200h with an exceptionally low and stable overpotential under 1 mA cm^{-2}/1 mAh cm^{-2}. The full cell coupled with $LiFePO_4$ cathode at a low N/P ratio of 2.45 shows typical voltage profiles but enhanced performance than that of $LiFePO_4$ coupling with bare Li anode.

5:00 PM EN09.03.15
Solution Casting and Thermal Annealing of Nafion Ionomer for Fuel cell Applications Sylwia A. Sulikowski; Iowa State University of Science and Technology, United States

Fuel cells are a promising technology to produce and develop clean and sustainable energy. Nafion has been regarded as the current benchmark for polymer electrolyte membranes (PEM). The structure of Nafion plays an important role in its unique properties such as excellent thermal stability and high proton conductivity. However, researchers are seeking alternative ways to further develop PEM membranes that can have higher conductivities at higher temperatures and low relative humidity. Pre-treatments are often employed to improve the properties of PEMs by altering their microstructure. In this study, Nafion membranes were created by solution casting in Dimethylformamide (DMF) at 90 ^{O}C followed by annealing at different temperatures (140 ^{O}C and 170 ^{O}C) and rapid cooling. The microstructure of the membranes was investigated using transmission SAXS and was found that the annealing had no effect on the through-plane orientation of the Nafion membranes. However, the water uptake studies showed that when compared to unannealed membranes, membranes annealed at 170 ^{O}C had a reduced water uptake of 65.3%. This can be attributed to large structural modifications with enhanced crosslinking formed due to annealing. Heat treatment at higher temperature induces free volume in the membrane and make the molecular segments more organized. Hence it becomes harder for the water molecules to diffuse into the hydrophobic zone and water uptake and swelling decreases with increase in the annealing temperature. It is postulated that optimizing the annealing and cooling rates would induce more compact chain packing structure which would significantly impact the diffusion and proton conductivity.

SESSION EN09.04: Polymer Binders, Electrolytes and Separators I
Session Chairs: Qi Dong and Minah Lee
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2009

8:30 AM *EN09.04.01
Cellulose Based High Performance Ion Conductors and Energy Devices Liangbing Hu[1] and Qi Dong[2]; [1]University of Maryland, United States; [2]North Carolina State University, United States

I will discuss a general design strategy for achieving one-dimensional (1D), high-performance polymer solid-state ion conductors through molecular channel engineering, which we demonstrate via Cu^{2+}-coordination of cellulose nanofibrils. The cellulose nanofibrils by themselves are not ionic conductive; however, by opening the molecular channels between the cellulose chains through Cu^{2+} coordination we are able to achieve a Li-ion conductivity. This improved conductivity is enabled by a unique Li^+ hopping mechanism that is decoupled from the polymer segmental motion. Also benefitted from such decoupling, the cellulose-based ion conductor demonstrates multiple advantages, including a high transference number (0.78 vs. 0.2–0.5 in other polymers[2]), low activation energy (0.19 eV), and a wide electrochemical stability window (4.5 V) that accommodate both Li metal anode and high-voltage cathodes. Furthermore, we demonstrate this 1D ion conductor not only as a thin, high-conductivity solid-state electrolyte but also as an effective ion-conducting additive for the solid cathode, providing continuous ion transport pathways with a low percolation threshold, which allowed us to utilize the thickest $LiFePO_4$ solid-state cathode ever reported for high energy density (Nature, Oct 22).

9:00 AM EN09.04.02
Effect of Separator Structure on Lithium Metal Batteries Hao Jia, Chao Zeng, Ji-Guang Zhang and Wu Xu; Pacific Northwest National Laboratory, United States

Rechargeable lithium (Li) metal batteries with conventional intercalation cathodes have been considered as the next-generation energy storage systems for transportation and smart grid applications because of their high theoretical energy densities. Although great successes have been reported in recent years, the two major issues related to Li metal anode, dendrite growth and low Coulombic efficiency, still hinder the practical applications of Li metal batteries. Among the components in Li metal batteries, the separator has been considered to be a relatively inert component and its effect on performances of Li metal batteries has seldom been investigated. In our recent studies, we found that the microstructure of the separator has a significant influence over the Li deposition behavior, and consequently, the cycling performance of Li metal batteries. In this talk, the effects of separator structure on Li metal anode and Li metal batteries will be discussed with the combination of experimental and simulation results.

9:15 AM EN09.04.03
Ultra-strong Nanocomposite Separators for Beyond Li-ion Batteries Ahmet Emre, Emine S. Turali-Emre, Ji-Young Kim and Nicholas Kotov; University of Michigan, United States

Multifunctional nanocomposites have been widely investigated to address challenges in next-generation energy storage applications, specifically beyond lithium-ion battery chemistries. The high theoretical specific energy density (2600Wh/kg) and high specific capacity (1675mA/g), along with the natural abundance and low toxicity of sulfur, have been attracting significant attention for the development of an alternative battery system to replace traditional lithium-ion batteries, which suffer from safety and capacity/energy density limitations. However, challenges such as polysulfide dissolution and shuttling prevent the mass commercialization of metal sulfur batteries. Inspired by biological ion transport mechanisms, we show a practical yet comprehensive approach to developing high-performance metal sulfur batteries. Aramid nanofiber (ANF) based composite ion transport membranes prevent dendrite formation and confine polysulfides on the cathode side. ANF composite battery separators provide diverse and opposing properties, including high mechanical properties, high ionic conductivity, and high thermal/chemical stability. Fabrication of such biocompatible, affordable, flexible, structural, and high energy density batteries is quite crucial in powering next-generation electronics, including but not limited to portable, wearable, implantable devices and all kinds of electric vehicles.

9:30 AM EN09.04.04
Polymer Electrolyte with Interconnected MOF Particles along Organic Nanofibers for Solid State Battery Gihwan Kim, Jeung Ku Kang and Jiheong Kang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The demand for lithium-ion batteries is greatly increasing due to the increase in demand for electronic devices including electric vehicles. Lithium-ion batteries mainly use liquid electrolytes including organic solvents, but liquid electrolytes have critical safety problems such as leakage, fire, and explosion. In order to solve this critical problem, it is essential to develop an all-solid-state battery using a solid-state electrolyte. Polymer-based solid-state electrolyte, which is a type of solid-state electrolyte, has excellent characteristics of flexibility, safety, and good interfacial contact with electrodes, but has problems with low ionic conductivity. Herein, we synthesized an enhanced ionic conductivity polymer electrolyte with interconnected Metal-Organic Frameworks(MOFs) along the organic fibers network. It provides a pathway for lithium ions to move rapidly through the interconnected MOFs pore channels. Furthermore, anions sieving effect through controlled pore size to suppress other side reactions and evenly electrodeposition of lithium ions to inhibit lithium metal dendrite formation. As a result, when the all-solid-state battery cell was operated, a lower overpotential was observed than when the conventional polyethylene oxide(PEO) polymer electrolyte was used, and stability was maintained over 1000 hours.

9:45 AM EN09.04.05
A Solvent-Anchored Non-Flammable Electrolyte (SAFE) Zhuojun Huang, Jiancheng Lai, Yi Cui and Zhenan Bao; Stanford University, United States

Lithium-based batteries are ubiquitous in modern-day energy supply systems. However, the volatile and flammable nature of the electrolytes remains a safety challenge. Solvent-free polymer electrolytes are developed to address this, yet they do not have sufficient ionic conductivity for room temperature battery operation. Although gel electrolytes address the ionic conductivity limitation, solvent molecules in them are not anchored and thus the safety feature is compromised. Here, we report that anchoring solvent molecules with salt and polymer can increase the ionic conductivity of the electrolyte without undermining its non-flammability. We name it **S**olvent-**A**nchored non-**F**lammable **E**lectrolyte (SAFE). Specifically, we developed a liquid-state polymer electrolyte composed of LiFSI salts, Dimethoxyethane (DME) solvents, and polysiloxane tethered with ion solvating moieties. DME coordinates with both the salt and the polymer, while together with the salt, they synergistically plasticize the polymer to increase the ionic conductivity. The resulting non-flammable polymer electrolyte has a room temperature ionic conductivity of 1.6 mS/cm and a wide operation window of 25 – 100°C. Benefiting from its liquid nature, SAFE is ready to use without further electrode engineering. When pairing with commercially available electrodes, SAFE demonstrated 400 cycles at room temperature without obvious capacity decay. Different from polymer or gel electrolyte, SAFE addresses the apparent contradiction between non-flammability and ionic conductivity and shows a promising design pathway for next generation safe and manufacturable electrolytes.

10:00 AM *EN09.04.06
Advanced Binder Designs for Emerging Lithium-Ion Batteries Jang Wook Choi; Seoul National University, Korea (the Republic of)

Polymeric binders have turned out to be critical for various properties of many emerging rechargeable batteries. I will summarize my group's efforts in the past ten years in developing uncommon binder designs for silicon and silicon-carbon composite anodes. They are based on supramolecular chemistries involving hydrogen bonding, ion-dipole interaction, molecular machines, etc., with the aim of activating self-healing ability. In the last part of my talk, I will also introduce recent efforts along developing advanced binder designs targeting high-nickel layered cathodes and 5-V class spinel cathodes. Albeit being contained in a small content, all the given cases coherently indicate the critical nature of binders and further opportunities for research.

10:30 AM BREAK

11:00 AM EN09.04.07
Development of a $LiMnFePO_4$ / $Li_4Ti_5O_{12}$ 2Ah Pouch Cell—An Example of the Effective Integration of New Materials Jean-Christophe Daigle[1], Martin Dontigny[1], Alexis Perea[1], Yuichiro Asakawa[2] and Karim Zaghib[3]; [1]Hydro-Québec, Canada; [2]Murata Manufacturing Co., Ltd., Japan; [3]Concordia University, Canada

One of the most promising approaches for limiting climate change is the use of alternative and greener sources of energy (wind, solar, etc.). The electricity generated from these sources fluctuates, however, and a storage solution is needed. The advent of energy storage for wind farms, solar plants, etc., requires a new generation of batteries. It is therefore imperative that a battery with high energy density, a longer life cycle and improved safety be developed.

In this paper, we describe our efforts to develop a safe and long-life cycle $LiMnFePO_4$ (LMFP)/$Li_4Ti_5O_{12}$ (LTO) 2Ah pouch cell. One of the major challenges faced in this pursuit was gas evolution during cycling. Various side reactions with active materials resulted in the generation of gas during cycling. To circumvent this, we implemented several mitigation strategies. To combat electrolyte degradation (1.0 M $LiPF_6$ in carbonate solvents) due to Mn^{2+} dissolution in LMFP, we integrated a new class of polymer as a binder in the cathode preparation, which effectively decreased the degradation during cycling. This polymer also has high voltage stability.[1] At the battery's negative electrode, we developed a new carbon coating method on LTO that minimizes electrolyte degradation and optimizes high C-rate preformances.[2] Although relatively simple, this technology made the pouch cells safer. This unique approach is versatile and can be implemented in pouch cells with any type of chemistry when gas scavenging is required. The 2Ah pouch cells did not experience any inflation during extensive cycling and aging. Cells cycled more then 500 cycles at 45^{o}C with a rate of 1C – 1C before reaching 80% retention capacity.[3]

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11:15 AM EN09.04.08
Self-Healing Binders for Silicon-Based Electrodes Tamara Patranika, Guiomar Hernandez and Kristina Edstrom; Uppsala University, Sweden

Silicon is a promising active material for anodes in lithium-ion batteries owing to its high theoretical capacity (3579 mAh/g)[1]. However, it is well known that the compound contends with large volume changes during cycling, creating cracks in the material and therefore limiting the lifetime and capacity of the cell. To cope with these volume changes, this project aims to develop self-healing binders to improve the cycling stability of lithium-ion batteries.

Both hydrogen bonds and dynamic covalent bonds have been previously used to modify binder systems to get self-healing properties through reversible cross-linking with the binder in the electrode. While the hydrogen bonds have eminent reversibility, the dynamic covalent bonds provide high mechanical stability[2–4]. Both of which is desirable properties to implement in the polymeric binder system.

Specifically, the focus of this work has been on synthesizing borate ester bonds[5], as well as using other commercially available borate groups and coupling them with the polymer binder poly(vinyl alcohol) (PVA). Furthermore, in order to gain more knowledge of the different self-heling groups, other binder systems containing hydrogen bonds have been used for comparison.

The electrochemical performance of the cells with and without the self-healing groups has been investigated, showing an increased capacity with the latter. Besides the performance, understanding the self-healing mechanism of these binders and possible degradation reactions from these functionalities is key to further improve the system and cycle life. Therefore, the effect of the self-heling functional groups on the formation of the solid electrolyte interphase layer has been investigated with X-ray photoelectron spectroscopy. Furthermore, the electrochemical stability of the functional groups was investigated in order to compare the impact of the hydrogen bonding and dynamic covalent bonding, especially at the low operating voltages of silicon.

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11:30 AM EN09.04.09
Recyclable Lithium Battery with Reversible Polymer Binder Chen Fang and Gao Liu; Lawrence Berkeley National Laboratory, United States

The fast growth of lithium battery market generates a strong demand for battery recycling technologies, which are critical for the sustainability of battery industry due to the limited accessibility of battery materials and the high environmental impacts of battery material mining and manufacturing. However, conventional lithium batteries are not specifically designed as recyclable units, where the commonly incorporated polymer binders, the glue-like substances that serve to maintain the mechanical integrity of battery electrode composites, on the other hand, pose significant challenge for electrode disassembly. We developed the Quick-Release Binder technology for construction of recyclable lithium batteries. This novel binder is a two-component polymer system consisting of polyacrylic acid (PAA) and polyethylenimine (PEI) that are compatible with green production and recycling, namely via water processing methods. PAA and PEI can be readily crosslinked via strong carboxy-amino ionic interaction, which is reversible depending on the pH condition of the aqueous solution. Therefore, PAA and PEI can form robust polymer binder system for battery electrode fabrication and can also be readily dissociated under alkaline condition for convenient release and thus recycling of the battery electrode materials. We have demonstrated that the Quick-Release Binder system can be applied to lithium-sulfur battery and lithium-ion battery, illustrating the universal applicability of the Quick-Release Binder system for lithium-based rechargeable batteries.

11:45 AM EN09.04.10
Mixed Conducting Polymer Binders for Rechargeable Batteries Pratyusha Das[1], Rodrigo Elizalde-Segovia[2], Billal Zayat[2], Charlene Z. Salamat[1], Gordon Pace[1], Yunfei Wang[3], Xiaodan Gu[3], Bruce S. Dunn[1], Sarah Tolbert[1,1], Sri Narayan[2], Barry C. Thompson[2] and Rachel A. Segalman[1]; [1]University of California, United States; [2]University of Southern California, United States; [3]The University of Southern Mississippi, United States

Conducting polymers exhibiting mixed electronic and ionic conductivity serve as excellent candidates for electrode binders due to an extension of functionality beyond simple mechanical binding. Here we present our recent work and ongoing developments in the area of mixed conductive cathode binders for Lithium-Ion Batteries (LIBs). In this regard, we have focused on electron-rich 3,4-propylenedioxythiophene-based polymers (PProDOTs), well-known to be stable in their electrochemically doped states. We have shown that dihexyl-substituted PProDOTs (PProDOT-Hx_2) display a substantial increase in electronic conductivity and a more modest increase in ionic conductivity upon electrochemical doping. This behavior has been attributed to their open and partly disordered morphology, facilitating enhanced ion transport compared to the densely packed semi-crystalline poly(3-hexylthiophene) (P3HT). As a result, we observed an improvement in the long-term stability and rate-capability with NCA cathodes relative to PVDF binder. To maximize mixed conduction, further enhancement in ionic conductivity was obtained via structural modification of the PProDOTs to incorporate oligoether side chains ((Hex:OE) PProDOTs). This aligned well with the increasing disorder and electrolyte uptake with increase in oligoether content in the polymers. Additionally, to bestow enhanced mechanical properties to the otherwise brittle conjugated polymer binders, we studied the impact of random incorporation of conjugation break spacers (CBS) to the PProDOT-Hx_2 backbone to induce deformability and ductility (PProDOT-CBS). We notice that solvent-induced swelling in the battery electrolyte results in significant enhancement in mechanical properties, reflected in the long-term cycling studies of these polymers. Our current efforts are focused on augmenting the intrinsic ionic conductivity of these PProDOT-based cathode binders. To this end, we have targeted the attachment of ionic liquid side chains such as imidazolium (Im^+) to the conjugated PProDOT backbone. We expect to gain increased cation mobility, especially Li^+ ion mobility in the resulting PProDOT-Im polymers, thereby gaining application in LIBs and emerging solid-state batteries.

SESSION EN09.05: Polymer Binders, Electrolytes and Separators II
Session Chairs: Daniel Brandell and Minah Lee
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2009

1:30 PM EN09.05.01
Free Energy Sampling to Understand the Effect of Local Ion Coordination in Polymer Electrolytes on Transport Properties Siddharth Sundararaman, Fabrice Roncoroni, Ana Sanz-Matias and David Prendergast; Lawrence Berkeley National Lab, United States

In order to understand the success of polyethylene oxide (PEO) for lithium-ion batteries and explore possible better alternatives for salt-polymer mixtures, we study various ions at different concentrations in poly(ether-acetal) electrolytes [P(nEO-mMO), where EO is ethoxyl and MO is methoxyl]. Free-energy sampling, using metadynamics with tailored interaction potentials, elucidates the various coordination environments of ions and the energetic pathways for ion transport in these systems. Using cleverly chosen collective variables, we gain insight into: (1) the competition between cation-anion pairing and coordination by the different polymers at various concentrations, (2) the relative stabilities of single- vs. multi-chain coordination environments and (3) the impact of multi-chain coordination on the glass transition temperature and associated ion transport. We also use advanced data-mining approaches to classify the diverse set of configuration environments buried in these simulations, gaining a deeper understanding of local coordination environments that might easily have been missed with manual inspection. Armed with this insight we suggest strategies for electrolyte design to improve ion transport in battery applications.

1:45 PM EN09.05.02
Looking Beyond "Segmental Motions": A Deeper Understanding of Ion Transport in Polymer Electrolytes Through a Focus on Ion Coordination Jonas Mindemark; Uppsala University, Sweden

The traditional description of ion transport in solvent-free polymer electrolytes puts an emphasis on how the movement of ions is coupled to the polymer chain dynamics. While this is certainly correct, it neither gives a precise description of the actual mechanism of ion transfer, nor fully encompasses all the different nuances of this process that have been revealed in recent years. Since the typical ion transport process can be imagined as taking place through successive ligand exchanges within the coordination shell of a polymer-coordinated cation, it makes sense to use the coordination as a basis for the mechanistic description. It also makes sense that the coordination chemistry has a major influence on the ion transport characteristics. However, investigating this requires both a diverse set of polymer host materials with variations in coordination properties, and methods to investigate the coordination properties. Recently introduced and functionally diverse host materials, such as carbonyl-coordinating polyesters and polycarbonates, together with newly developed methods to quantify the ion coordination strength, have enabled us to demonstrate a clear link between the strength of ion coordination and the cation transference number of the system, leading to faster cation conduction in weakly coordinating systems. This is relatively straightforward to rationalize in low-salt systems, where ion clustering is minimal, but the effect also seems to be extended to high-salt systems. Through MD simulations, comparisons between the polyether PEO and the polyester PCL reveal differences in ion transport mechanisms related to coordination strength and salt clustering, which ultimately results in high cation transference numbers, thus bringing even further nuance to the mechanisms of ion transport in solvent-free polymer matrices.

2:00 PM EN09.05.03
High Transport Numbers in Solid Polymer Electrolytes Through Novel Lithium Salts Lorena García Maestre, Lixin Qiao, Eduardo Sanchez, Uxue Oteo, María Martínez-Ibañez, Heng Zhang and Michel Armand; CIC EnergiGUNE, Spain

It is well known the increasing demand for energy storage devices in our society. Lithium-ion batteries (LIBs) have been widely investigated over the years, although Li metal (Li^0) batteries (LMBs) are considered now a real alternative due to their lowest electrochemical potential (-3.04V vs. standard hydrogen electrode, SHE) and extremely high theoretical specific capacity (3860 mAh g^{-1}) of the Li^0 electrode.[1] In that field, solid electrolytes present advantages over liquid electrolytes due to their continuous lithium dendrite growth and concerns of flammability. More concretely, solid polymer electrolytes (SPEs) are considered now one alternative to liquid electrolytes due to their cost-effectiveness, high flexibility, ease of processing and safety, being LiTFSI/PEO, the most employed system up to now.[2] LiTFSI/PEO system possesses a very good physical and chemical stability and a very flexible sulfonamide anion center which decrease the crystallinity of the polymer matrix while the ionic conductivity is enhanced. However, although it is nowadays the most widely employed system in SPEs, it stills presents very low Li-ion conductivities (Li-ion transference number; T_{Li^+}, ca. 0.2), poor Li electrode compatibility and poor electrochemical stability against the Al current collector.[3]

The anion chemistry of lithium salts plays an important role in the determination of physicochemical and electrochemical performance of SPEs, affecting the cyclability of SSLMBs. Herein, in this work, we present three novel salt anions with the aim of decreasing the anion mobility and thus, promoting Li-ion conductivity. On the one hand, lithium(difluoromethanesulfonyl)(trifluoromethanesulfonyl)imide (LiDFTFSI), in which replacing one fluorine atom of the -CF_3 moiety by one proton (which will form H-bonds into the anionic structure of the lithium salt) will result in a higher Li-ion conductivity at a low expense of the total ionic conductivity.[4] On the other hand, we present a new *N*-ethyl-*N*-methyl functionalized sulfonimide-based lithium salt (LiTFEMSI), in which one -CF_3 groups has been replaced by a donor character group leading to a high chemical and electrochemical stability and an enhanced T_{Li^+}.[5] Benzene-based lithium salts (LiBTFSI) have been also reported which are based in the π-π stacking interaction between the pair of benzene-based anions leading to a highly selective Li-ion conductive PEs.[6]

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2:15 PM EN09.05.04
Initiated Chemical Vapor Deposition of Anion-Conducting Polymeric Electrolytes for Macroscale All Solid-State 3D Ag–Zn Batteries Hunter Ford, Brian L. Chaloux, Joel B. Miller, Christopher Klug, Youngchan Kim, Battogtokh Jugdersuren, Jeffrey Long, Ryan DeBlock, Michelle D. Johannes, Debra R. Rolison and Megan Sassin; U.S. Naval Research Laboratory, United States

Combining two opposing battery metrics—high energy density **and** power density—in a minimal footprint requires moving away from the ubiquitous, two-century-old 2D planar or jelly-roll battery configurations to a three-dimensional, all solid-state battery (3D SSB). Microscale Li-ion 3D SSBs reported in the literature experimentally confirm the theoretically predicted energy and power enhancements of the 3D SSB configuration.[1] However, lithium-ion batteries pose several challenges including low thermal (cathode and anode) and electrical conductivities (cathode) that restrict them to microscale battery applications, as well as the strategic nature of the active materials. We posit that the demonstrated enhancements of 3D Li-ion SSBs can be extended to the macroscale with a minimal geometric footprint by swapping Li-ion active materials for non-strategic metallic active electrode materials (e.g., Ag and Zn). Three-dimensionally wired, NRL-patented zinc metal sponges serve as anode and scaffold for an interpenetrating, nonperiodic, macroscale 3D SSB.[2]

The remaining roadblock to a macroscale 3D SSB is the incorporation of a submicron-thick solid-state polymeric electrolyte/separator. Initiated chemical vapor deposition (*i*CVD) offers an ideal non-line-of-sight method to generate conformal polymer films onto (and into) complex 3D architectures. For Ag–Zn batteries, we prepare coatings of poly(dimethylaminomethylstyrene) ("pDMAMS") on both planar and complex 3D electrode architectures via *i*CVD. After deposition, the pDMAMS coatings are rendered anion conducting using vapor-phase methylation to introduce quaternary ammonium moieties, followed by solution phase incorporation of the desired anion species (e.g., OH^-, Br^-, or HCO_3^-). Characterization methods, including ATR-IR spectroscopy, X-ray photoelectron spectroscopy, and solid-state NMR spectroscopy compare the structure of the pDMAMS film before and after methylation to bulk, solution-polymerized counterparts, while atomic force microscopy and redox-probe cyclic voltammetry confirm the film is conformal and pinhole-free. Methylated pDMAMS films have an ionic conductivity of ~10^{-6} S cm^{-1} under hydrated conditions. Lastly, we probe the ability of the polymer film to support desirable Ag–Zn redox chemistry in half- and full-cell configurations. Experimental results are compared to molecular dynamics simulations of pDMAMS as a function of anion and film H_2O content.

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2:30 PM BREAK

3:00 PM EN09.05.05
Discerning the Effects of Solid Polymer Electrolyte Properties on Lithium Electrodissolution and Electrodeposition William R. Fullerton and Christopher Y. Li; Drexel University, United States

Solid polymer electrolytes (SPEs) are regarded as a promising solution to enable high energy density lithium metal batteries. While they provide a safer, non-flammable alternative to liquid electrolytes, they still suffer from low ionic conductivity and significant interfacial resistance at the electrode-electrolyte interface. During the electrodissolution process, the accumulation of vacancies can lead to void formation at the lithium-solid electrolyte interface and eventual contact loss between the electrolyte and electrode. This contact loss can increase impedance and induce high local current density upon subsequent plating, and result in dendrite propagation and accelerated impedance growth with cycling. We hypothesize that these processes are strongly dependent on SPE transport properties including ionic conductivity and transference number as well as on mechanical properties such as modulus, toughness and elasticity. To test this hypothesis, we design a series of SPEs which utilize a macromolecular crosslinker to yield a comb-chain network molecular architecture. The comb-chain architecture allows for the design of SPEs with a broad range of mechanical properties through the widely tunable network mesh size and crosslinking density. By modulating molecular structure and chemistry, we can optimize the balance between the aforementioned properties, while elucidating how these properties affect the underlying mechanism of electrodissolution and electrodeposition.

3:15 PM EN09.05.06
Li Deposition Mechanism: A Perspective Gained By Combining Imaging with Theoretical Analysis Tao Gao; The University of Utah, United States

The morphology of the Li deposit governs the performance of lithium metal anode to a large extent. Previous studies have reported many different Li deposit morphologies: hemi-sphere, granular, columnar, whisker (needle-like), Eden cluster, mossy (bush-like), and dendrite (tree-like). To address the challenge of fast-charging LIBs and LMBs, managing Li deposit morphology during battery charging is critical.Nonetheless, the formation mechanism of different Li deposit morphologies remains less studied.
To control the morphology, achieve highly reversible and compact Li deposition and prevent internal short-circuit, significant progresses have been made in engineering electrolyte compositions,SEI chemistry and substrate structures. These efforts have lead to high CE Li deposition/striping (up to 99.5%) at current densities below 1 mA cm^{-2}. To further enhance the performance of Li metal anode, fundamental understanding of the nucleation and growth of Li is necessary. In particular, these questions need to be answered:1) How do deposits develop into different morphologies and how does the morphology correlate with CE and the tendency of internal-short? 2) What governs current heterogeneity and how does it correlate with CE and the risk of internal short-circuit? Understanding these questions will provide valuable insights to guide the rational design of electrolyte and substrates for high-capacity and reversible Li metal anode (> 5 mAh cm^{-2}, > 1000 cycles), high-energy LIB capable of ultra-fast charging (>5 C), and enhanced safety for both technologies.
In this work, we reveal the mechanism of Li deposition on Si and Cu substrates by combing electron imaging, electrochemical tests with theoretical analysis. Specifically, we are interested in these questions: 1) Under what conditions will Li plating happen? 2) Once initiated, how does Li nucleate and grow? 3) How do various factors (particularly current, substrate and temperature) regulate the morphology of the deposited Li? 4) How does the morphology affect the deposition/stripping reversibility?

3:30 PM EN09.05.07
A Salt-Philic Solvent-Phobic (SP2) Interfacial Coating Design for Lithium Metal Electrodes Zhuojun Huang, Jiancheng Lai, Yi Cui and Zhenan Bao; Stanford University, United States

A key challenge to enable lithium (Li) metal batteries as next-generation energy storage devices is to stabilize the interface between Li metal and the electrolyte. A promising strategy is to promote the formation of a salt-derived solid electrolyte interphase (SEI), which has been found more robust and stable than a solvent-derived SEI. Here, we report a Salt-Philic Solvent-Phobic (SP2) polymer coating design concept for Li metal electrode that selectively transports salt over solvent and thus promotes salt-derived SEI formation. This SP2 coating approach resulted in enhanced cycling performance in several types of solvents, such as ether, carbonate, and fluorinated ether and achieved ~400 cycle life (2.5 mAh cm-2, 80% capacity retention) in 50 µm Li|NMC batteries.
My talk will cover the materials design principles for SP2 polymers and characterizations on its unique salt-over-solvent transport property.

3:45 PM EN09.05.08
Overcoming Kinetic Limitations in $LiFePO_4$ Cathodes Using an Electrostatically-Stabilized Polymer Complex Binder Gordon Pace, My Linh Le, Raphaële Clément and Rachel A. Segalman; University of California, Santa Barbara, United States

Polymer binders add critically important structural stability to all lithium ion battery cathodes, but industry standard binders, such as polyvinylidene fluoride (PVDF), are insulating to ions and electrons and therefore are detrimental to the overall charge transport kinetics. We demonstrate electrochemically stable conjugated polymer complexes that enable superior rate performance in $LiFePO_4$ (LFP) cathodes, more than doubling the rate at which the cell can be discharged while maintaining usable capacity, when compared to its PVDF counterpart. While traditional conjugated (conducting) polymer binders enhance conductivity, implementation is limited by electrochemical stability, processability, and solubility. By using electrostatics to stabilize a blend of a charged conjugated polymer with an oppositely charged polyelectrolyte, we form high solids loading, viscous solutions which dramatically improve processability. Further, the ionic crosslinks between the oppositely charged polymers prevent dissolution in the electrolytes, enabling a drop-in alternative to PVDF that dramatically reduces overpotential and increases high-rate performance.

Funding Acknowledgement
This work was supported by the Department of Energy Office of Basic Energy Sciences under Grant No. DE-SC0016390

4:00 PM EN09.05.09
Revisiting the Microstructures of Localized High Concentration Electrolyte Bin Li; Idaho National Laboratory, United States

Liquid electrolytes in batteries are typically treated as macroscopically homogeneous ionic transport media, despite having complex chemical composition and atomistic solvation structures, thus leaving a knowledge gap of microstructural characteristics. A promising electrolyte system design has recently been developed with the title of a localized high-concentration electrolyte (LHCE). These electrolytes are a summation of three components – a charge-carrying salt, a solvent that solvates the salt, and a diluent that is highly immiscible with the salt. This creates the perception of a high-concentration electrolyte (HCE) with high anion-cation interactions that supports a salt-derived, stable solid-electrolyte interphase, while an LHCE improves bulk electrolyte properties, such as ionic conductivity and viscosity, when compared to an HCE. Much trial by error design of this LHCE concept has been supported by simulations to confirm ionic interactions, cycling data to confirm cell stability, and post-mortem analysis to provide evidence of mechanisms. However, a systematic design to extend the capabilities of LHCEs is still to be desired. Here, we analyzed a specific LHCE mixture with the use of a ternary phase diagram to dictate the best viable mixture to extend the localization of solvation structures while maintaining viable cell-level capabilities. It was seen that the electrolyte mixture has complex mechanisms from individual ion solvation up to the solution network scale, both of which are dictated by the interactions between the three electrolyte components. With the support of both experimental and computational analysis of different electrolyte features, we have begun a methodology of formulating the most ideal LHCE mixtures for improving the cyclability of high-capacity battery chemistries.

SESSION EN09.06: Organic Active Materials
Session Chairs: Jeffrey Lopez and Jodie Lutkenhaus
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2009

8:30 AM *EN09.06.01
Imagining Circular Organic Batteries Jodie Lutkenhaus; Texas A&M University, United States

Metals are essential ingredients in today's Li-ion batteries (LIBs), but their continued use presents economic, ethical, and environmental challenges. Projected shortages of cobalt and nickel in the coming decades may cause increased prices, and the global supply chain of these metals, lithium included, is highly localized. The last few years have brought attention to the harsh conditions of and use of child labor in the extraction of some these materials, adding social and ethical concerns. Compounded with the increasing demand for LIBs brought by the expanding electric vehicle market and rapid digitalization of society, there is an imminent need to address these issues. Society must now begin to consider the implications of a LIB's full life cycle, including the carbon footprint, the economic and environmental costs, and material access. These challenges motivate the case for degradable or recyclable batteries sourced from earth-abundant materials whose life cycle bears minimal impact on the environment. This talk imagines how polymers might contribute to the future circular battery economy. We focus first upon our work on radical-contaning polymer batteries, which offers a metal-free battery platform. These concepts are then translated to degradable metal-free organic batteries comprised of redox-active synthetic polypeptide cathodes and anodes. Specifically, the cathode polypeptide was decorated with nitroxide radicals, and the anode polypeptide was decorated with viologen groups. With the addition of an acid, the battery degraded on command, yielding amino acids and other byproducts. Although degradation offers a means to deconstruct batteries, recycling still remains a challenge. This talk closes with current and ongiong recyling approaches for polymer-based batteries and their future prospects. Taken together, polymeric materials offer a path toward the local sourcing, manufacturing, and recycling of batteries to democratize energy storage in global economies.

9:00 AM EN09.06.02
Organic Redox Mediators as Multifunctional Mobile Catalysts for Ambient Air Operational Lithium–air Batteries Sunghyun Ko[1], Yiseul Yoo[2], Jinkwan Choi[2], Hee-Dae Lim[2], Chan Beum Park[1] and Minah Lee[2]; [1]Korea Advanced Institute of Science and Technology (KAIST), Korea (the Republic of); [2]Korea Institute of Science and Technology (KIST), Korea (the Republic of)

Li-air batteries (LABs) have received considerable attention as a potential alternative to conventional lithium-ion batteries due to their exceptional energy density (~3,500 Wh/kg) enabled by the reversible conversion reaction between O_2 and Li_2O_2. However, current development of ambient air operational LABs is hindered by formation of insulating Li_2CO_3 during discharge under CO_2-containing atmosphere. Herein, we provide several p-type redox-active organic molecules that can decompose Li_2O_2 as a new class of redox mediators (RM) for Li_2CO_3 decomposition. Through systematic investigation, we successfully demonstrated that the selected RMs possessing a higher redox potential than 3.7 V (vs. Li/Li^+) can oxidize Li_2CO_3 with significantly lowered overpotential. The in situ gas analysis further supports the reaction mechanism of RM-catalyzed Li_2CO_3 decomposition. Moreover, we firstly report the suppression of highly reactive singlet oxygen ($^1O_2$) generation during RM-catalyzed Li_2CO_3 decomposition. We further showed the enhanced cycle life of RM-containing LABs under air-like atmosphere, confirming the compatibility of employing RMs under practical operating conditions. Collectively, our results provide new possibilities for designing multifunctional catalysts to promote the decomposition of major discharge products (Li_2O_2 and Li_2CO_3) during the ambient air operation of LABs.

9:15 AM EN09.06.03
Investigating the Stability of Organic Electrolytes for Lithium-Air Batteries with High-Throughput Simulations Avni Singhal, Shi Jun Ang, Yang Shao-Horn and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States

Lithium-air batteries have gained significant attention as a solution for applications requiring high gravimetric energy density. Currently, however, electrolyte instability remains a key challenge limiting the practical use of aprotic Li-air batteries. Common organic electrolytes are largely unstable against the oxygen electrode, experiencing degradation due to hydrogen removal, proton removal, nucleophilic attack, oxidations and reductions. Previous works have computationally screened electrolyte candidates for stability based on ground state electrolyte properties. However, the chemical processes that cause electrolyte instability are often kinetically driven and thus thermodynamics and kinetics must both be investigated in order to fully evaluate candidate stability. Computational screening for kinetic stability requires automating the determination of reaction barriers for the numerous potential reaction mechanisms.

High-throughput calculation of reaction barriers is challenging due to the difficulty of locating transition state structures. As such, transition state calculations often rely heavily on user input and chemical intuition and existing automated approaches such as double-ended string methods frequently fail for complex molecules. In this work, we present an automated pipeline for high-throughput determination of reaction free energy barriers for kinetically-controlled electrolyte decomposition processes. By integrating cheminformatics-based reaction encoding, relaxed potential energy scans, and nudged elastic band calculations, our approach enables determination of free-energy barriers for reactions of interest of candidate electrolytes at scale. In particular, cheminformatics tools are used to programmatically generate products from reactants and track reactive atoms, relaxed potential energy scans to obtain initial reaction paths, and climbing-image nudged elastic band calculations to obtain transition state guesses from these starting paths.

We apply this approach to determine reaction barriers for nucleophilic attack by superoxide, which is formed during electrochemical cycling in Li-air batteries. We screen 100+ electrolytes with 400+ potential reactions, validating expected trends in the stability of carbonate and sulfone candidates. We study the effects of chemical functionalization with electron-donating and withdrawing groups and their interplay with steric factors. Finally, we identify functional groups and other chemical modifications that could increase the stability of organic electrolytes in aprotic Li-air batteries.

9:30 AM EN09.06.04
***In-situ* Electropolymerized Metalporphyrin Cathode Materials for High Performance Organic Electrodes** Thomas Smok, Ebrahim Abouzari-Lotf, Thomas Diemant and Maximilian Fichtner; Karlsruhe Institute of Technology, Germany

The interest in organic electrode materials (OEM) for rechargeable batteries has increased tremendously over the last decade.[1] This development is caused by the inherent advantages which OEMs exhibit over commercially leading inorganic materials. Specifically, the accessibility of a broad range of redox potentials due to the molecular engineering of redox-active functionalities allows boosting the storage capacity of organics. Moreover, most materials can be easily synthesized from readily available precursors. This structural diversity leads to the application of organics in different battery cell chemistries including Li-, as well as post-lithium systems like Na-, K-, and Mg- batteries. Challenging aspects of OEM materials are high dissolution in aprotic electrolytes and therefore interlinked rapid decay in capacity.[2] Also low conductivity of OEMs remains an unresolved issue.[1]
One of the most promising representatives for organic electrode materials are π-conjugated heteroatom macrocycles like porphyrins. Using bipolar-type (*b*-type) porphyrins was considered as a conventional strategy to improve the capacity and discharge voltage of OEMs when compared to *p*-and *n*-type materials, respectively.[3] Reported porphyrin materials display good electrochemical performances combined with fast charging kinetics due to a small HOMO-LUMO gap.[4] However, like other organic electrodes, porphyrins often suffer from low conductivity and, consequently, require a significant amount of electrochemically inactive conductive carbon that occupies volume and mass without storing energy. We investigated [5,10,15,25 tetrakis(4-aminophenyl)-porphyrin] (TAPP) and its metal complexes as redox-active cathode materials to address the aforementioned issues. Interestingly, the lithium-ion cells prepared with a high content of CuTAPP active material (70 wt%) demonstrate a stable discharge capacity of ~120 mAh/g over 2000 cycles when cycling with a constant current density of 1000 mA/g. The material also showed a superior rate capability of ~ 60 mAh/g at 8 A/g. The results of DFT calculations and experimental evaluations indicate that the degree of planarity of the metalloporphyrins directly correlates to their cycling stability. On the other hand, the contribution from the central metal redox during the cycling is found to be the reason for the significantly higher performance of the Cu-complex. The findings show a general approach for facing common conductivity challenges of organic electrodes and open up a pathway for practical application in energy storage.

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9:45 AM BREAK

10:15 AM EN09.06.06
Recyclable Organic Radical Batteries Ratul Mitra Thakur, Ting Ma, Grant Shamblin, Suyash Oka, Suvesh M. Lalwani, Alexander Easley and Jodie Lutkenhaus; Texas A&M University, United States

Organic radical batteries are one of the possible routes for transition to a sustainable future and reducing global carbon footprint. However, focusing on the recyclability of these next-generation energy storage devices is important to achieve a circular economy. This work shows the recycling of poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl) (PTMA) and poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl acrylamide) (PTAm) based composite electrodes using solvent extraction technique. The electrochemical performance of the original and recycled electrodes was accessed with cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD). This work identifies the associated challenges of recycling and possible changes in the recycled electrodes. One challenge is the cathode-electrolyte interphase (CEI), which is formed due to the decomposition of organic radical polymer and electrolyte, as identified from time-of-flight secondary ion mass spectrometry (Tof-SIMS). CEI formation consumes some of the active organic radical polymers which results in a decrease in the discharge capacity of the recycled electrodes. This work explores possible routes to address the issue and improve the overall capacity. This work gives valuable insights into challenges and possible solutions for recycling the next-generation electrochemical energy storage devices.

10:30 AM EN09.06.08
Ion-Coupled Electron Transfer of Naphthalene Diimide Derivatives for Non-aqueous Organic Redox Flow Batteries Seongmo Ahn and Hye Ryung Byon; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Organic redox flow batteries (RFBs) have been investigated for future energy storage systems (ESSs). Tailoring organic redox-active molecules tunes solubility, redox potential, and chemical stability, which gives the promise to enhance energy density, cyclability, and calendar life in RFBs. Numerous studies focused on increasing molecular solubility to satisfy Econo-technical levels. In addition, introducing electron-donating and withdrawing groups to the redox-active core modulated redox potentials to negative and positive shifts, respectively. The most effective way to multiply raising energy density is to find a redox-active core undergoing multiple electron-transfer processes. Quinone is the representative one providing a single two electrons transfer in an aqueous electrolyte solution. Fast redox kinetics and chemical stability are achieved by H^+ coupling; The reduced form, hydroquinone, promoted the following electron transfer in the acidic solution. A similar concept is applied for non-aqueous electrolyte solutions and using cations of supporting electrolytes. However, such an ion-coupled electron transfer was rarely studied to date.
Here, we demonstrated naphthalene diimide (NDI) and Li^+ coupled electron transfer in acetonitrile (MeCN). The NDI is an excellent model for the

stepwise two-electron transfer process. Its low solubility by the strong p-stacking interaction was surmounted by introducing ammonium cationic substituents to the NDI via simple condensation and *N*-alkylation. As a result, two ammonium-tethered NDI and bistriflimide ($TFSI^-$) as the counter anion showed 0.9 M solubility in MeCN. Two cathodic events made an anionic radical and dianionic NDI core, respectively. The received electron is delocalized over the NDI core and also stabilized by pairing it with the cation. Cyclic voltammograms showed ~120 mV of potential difference from two cathodic waves with Li^+ of LiTFSI electrolyte in MeCN, which was narrower than ~370 mV with K^+ of KTFSI. It suggested that the Li^+ possessing high charge density was closely coupled with the anionic radical NDI, expediting the second electron-transfer process. The process was also dependent on non-aqueous solvents. High donor-number (DN) solvents widened the potential difference with Li^+ because a thick solvation shell of Li^+ weakened the ion coupling. We applied this system for non-aqueous RFBs. Unlike two distinct galvanostatic plateaus appearing with K^+, the ammonium-introduced NDI with Li^+ showed almost a single overlaid plateau caused by the rapid reduction of the anionic radical. The ammonium-tethered NDI/Li^+ in MeCN cells performed high cyclability and low crossover through an anion exchange membrane, showing a capacity fading rate of 0.0089% for 1000 cycles in RFBs.

SESSION EN09.07: Redox Flow Batteries
Session Chairs: Zheng Chen and Dawei Feng
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2009

1:45 PM *EN09.07.01
Designs of Naphthalene Diimide for Highly Soluble and Stable Negolyte in Aqueous Organic Redox Flow Batteries Vikram Singh[1], Seongyeon Kwon[1], Yunseop Choi[2], Jongcheol Seo[2], Mu-Hyun Baik[1] and Hye Ryung Byon[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Pohang University of Science and Technology, Korea (the Republic of)

Redox flow batteries (RFBs) are intensively researched at the moment, as they are most likely to provide a solution to the global demand for grid-scale energy storage. Given the scale of the intended application, realistic solutions must be scalable, cheap, and safe. Organic molecules are ideal, in principle, and they can be derivatized to optimize their performance. Yet - clear and successful demonstrations of this advantage and rational strategies of how to guide the design of new molecules have rarely been reported.
Herein, I show that starting from naphthalene diimide (NDI) that is highly redox-active, but absolutely insoluble in water. We can rationally design a highly soluble charge carrier by tethering four ammonium functionalities to the NDI core that disrupts the long-order π-stacking that is a key feature leading to precipitation. Notably, the radical intermediate NDI^- form π-stacked dimers and tetramers during the charging process, where the radical character is nullified by antiferromagnetic coupling. It stabilizes radical intermediates without precipitation, and NDI delivers state-of-the-art performance of RFBs at neutral pH. Our approach provides a simple solution to long-standing problems in the field, i.e., solubility, radical reactivity, and operational pH, and the mechanism of stabilizing radical intermediates is generally applied to organic RFB systems.

2:15 PM EN09.07.03
Leveraging Temperature-Dependent (Electro)Chemical Kinetics to Accelerate Aqueous Organic Redox Flow Battery Characterization Eric M. Fell and Michael Aziz; Harvard University, United States

Aqueous Organic Redox Flow Batteries (AORFBs) have emerged as promising and potentially disruptive technologies for the storage of electrical energy from intermittent renewable sources for use over long discharge durations when the sun isn't shining and the wind isn't blowing. AORFBs could become preferred over Li-ion batteries for grid-scale stationary storage due to their potentially low-cost active materials made of earth-abundant elements, their inherent non-flammability, and the intrinsic decoupling of energy and power capacities in the flow battery design. Recent work has demonstrated that calendar life, rather than cycle life, limits molecular lifetimes in AORFBs due to various molecular instabilities that lead to side reactions, thus inhibiting performance [1]. To accurately determine molecular fade rates, we utilize potentiostatic cycling to avoid artifacts caused by drifts in internal resistance and employ volumetrically unbalanced, compositionally symmetric cell configurations to distinguish molecular fade from membrane crossover. Synthetic efforts have continued to improve redox-active organic molecule stability to the point that the most stable chemistries degrade at less than 1% per year [2]. With further lifetime increases, the measurement of lower capacity fade rates necessitates higher precision coulometry methods [3] and thermally accelerated degradation protocols [4] to determine which stabilizing approaches are most effective without waiting for multi-month cycling tests to quantify capacity fade.

We have developed a high-throughput setup for cycling AORFBs at elevated temperatures, providing a new dimension in the flow battery characterization space to explore. Capacity fade rates of previously published redox-active organic molecules, as functions of temperature, are evaluated in the high-throughput setup providing the ability to extrapolate fade rates to lower operating temperatures. The effect of temperature on electrochemical synthesis and recomposition [5,6] of organic molecules is also explored. Collectively, these results highlight the importance of accelerated decomposition protocols to expedite the screening process of candidate molecules for long lifetime AORFBs, which may enable massive grid penetration of intermittent renewable energy.

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electrochemical recomposition of decomposed redox-active species in aqueous organic flow batteries," *Nature Chemistry*, **14**, 1103, (2022).

2:30 PM BREAK

3:30 PM EN09.07.04
Improve the Kinetics of the Ketone-based Aqueous Organic Redox Flow Batteries Ruozhu Feng[1], Ying Chen[1], Xin Zhang[1], Benjamin J. Rousseau[2], Peiyuan Gao[1], Ping Chen[1], Sebastian T. Mergelsberg[1], Lirong Zhong[1], Aaron Hollas[1], Yangang Liang[1], Vijayakumar Murugesan[1], Qian Huang[1], Sharon Hammes-Schiffer[2], Yuyan Shao[1] and Wei Wang[1]; [1]Pacific Northwest National Laboratory, United States; [2]Yale University, United States

Redox flow batteries have a unique architecture that potentially enables cost-effective long-duration energy storage to address the intermittency introduced by increased renewable integration for the decarbonization of the electric power sector. Targeted molecular engineering has demonstrated electrochemical reversibility in natively redox-inactive ketone molecules in aqueous electrolytes. Yet, the kinetics of fluorenone-based flow batteries continue to be limited by slow alcohol oxidation. We show how strategically designed principles can accelerate alcohol oxidation and thus enhance battery kinetics. Rationally designed fluorenone-based flow battery electrolytes demonstrate enhanced rate capability, high battery capacity, and record-breaking long cycling. This study opens a new avenue to improve the kinetics of aqueous organic flow batteries.

3:45 PM EN09.07.05
Polymer Ion-Sieving Membranes Enable High-Performance Aqueous Organic Redox Flow Batteries Anqi Wang[1], Rui Tan[1], Chunchun Ye[2], Neil Mckeown[2] and Qilei Song[1]; [1]Imperial College London, United Kingdom; [2]University of Edinburgh, United Kingdom

Redox flow battery (RFB) technology is promising for grid-scale long-duration energy storage owing to its decoupled power and energy, long discharge duration and long cycle life. In recent years, aqueous organic RFBs based on organic redox-active molecules have attracted significant interest owing to their potential low cost compared to conventional vanadium RFBs. The widespread adoption of aqueous organic RFBs will require low-cost ion-selective membranes that could replace expensive Nafion membranes while achieving high ionic conductivity and selectivity towards redox-active materials. As yet, inexpensive ion-selective membranes are still lacking. Despite the pressing need for high-performance membranes, it remains a significant scientific challenge to develop alternative cost-effective materials and to achieve precise control over their water channels at a sub-nanometre scale for selective ionic and molecular transport.

Here, I will discuss our efforts to develop next-generation ion-selective membranes comprising sub-nanometer pores through modular synthesis of polymers of intrinsic microporosity (PIMs), whose structural diversity is controlled by choice of monomer, polymerization reaction and post-synthetic modification. The interconnected sub-nanometer pores in these functionalized PIMs allow fast, selective transport of ionic and molecular species, overcoming the conventional upper bounds of ion permeability and selectivity found in all existing membrane materials. These PIM membranes enable significant improvements in the efficiency, power density and lifetime of redox flow batteries over several thousand charge-discharge cycles in lab-scale demonstrations.

4:00 PM EN09.07.06
2-Volt All-Iron Aqueous Flow Battery Michael P. Marshak[1] and Elliott B. Hulley[2]; [1]University of Colorado Boulder, United States; [2]University of Wyoming, United States

All-iron flow batteries are attractive for use in large-scale energy storage systems due to the low cost and scalability of iron. However, iron flow batteries often use the $Fe^{2+/0}$ redox couple for the anodic reaction, which plates out iron onto an electrode during the charging process. This plating reaction limits the scalability of the all-iron flow battery for long duration because the amount of iron plated is related to the surface area of the electrode, cell, and stack, and the resulting power-energy ratio of the system cannot be scaled independently to long durations. In adddition, all-iron flow batteries usually operate at low voltages, limiting the power and efficiency of the system.

Here we show how the use of different coordinating organic ligands can modulate the potential of the $Fe^{3+/2+}$ redox couple over 2 volts in water at neutral pH. We further demonstrate the performance and cycling of an all-iron flow battery wherein both anolyte and catholyte solutions comprise iron in the +2 or +3 redox state, with different organic ligands, with an equilibrium cell potetential over 2 volts. The molecular design, bonding, and electronic structure of the organic materials will be discussed highlighting the critical requirments for organic materials to control metal-based redox reactions.

4:15 PM EN09.07.07
Neutral pH Viologen-TEMPO Based Aqueous Organic Redox Flow Battery—The Critical Role of Electrolyte Formulation on Stability and Efficiency Laura Pastor[1,2], Eduardo Sanchez[1], Maddalen Agirre[1] and Nerea Marquínez[1]; [1]CIC energiGUNE, Spain; [2]University of the Basque Country, Spain

The intermittent availably and power of renewable energy sources has become an issue, efficient energy storage systems must be introduced to overcome this obstacle.

Redox-flow batteries stand out as relevant candidates for large-scale stationary energy storage due to their many advantages, including their unique capability to decouple energy storage and power generation.[1]

In recent years, there has been a transition from redox inorganic materials to the development of water-soluble organic redox active materials owing to their low cost, high sustainability, and their structural diversity and tailorability.[2]

Redox flow batteries based on aqueous organic electrolyte have emerged as promising competitors to traditional redox flow batteries. Acidic, alkaline, and neutral AORFBs using different organic molecules/polymers as redox-active materials have been explored lately.

Despite efforts devoted to the development of new active materials, search for stable high redox potential molecules for catholyte remains a challenge, mainly limited to ferrocyanide and TEMPO derivatives which render low cell voltages[3, 4] or present uncertain stability.[5, 6]

As a solution to above mentioned problem, we have contributed to the development of neutral pH Aqueous Organic Redox Flow Batteries employing a novel anolyte-catholyte combination leading to cell voltages >1.2 V and outstanding stability and efficiency. A case of study for Viologen-TEMPO based electrolyte including synthesis, characterization and battery testing is provided.

Considering that the supporting electrolyte and the ion exchange membrane are key components in RFBs and have significant impact on the energy efficiency and power density we perform a study to understand how these factors affect the battery performance.

Several electrolyte formulations were evaluated attending to parameters such as the concentration of active materials and conductive salts. The influence of the cation on the transport phenomena, as well as the role of the anion on the stability of the solution will be discussed. Cell resistance and water transport can be modulated by wise electrolyte formulation. Moreover, different commercial CEM membranes were evaluated aiming at neutral pH systems with high RTE (>80% EE at 60 mA/cm^2) and high power densities.

Finally, with an optimized combination of membrane and supporting electrolyte, cycling test was conducted to reveal the long cycling stability with negligible capacity decay (0,001%/day) over 1000 cycles.

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SESSION EN09.08: Poster Session II: Polymeric and Organic Materials for Electrochemical Energy Storage
Session Chairs: Zheng Chen and Jeffrey Lopez
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN09.08.01
Establishing Structure-Property-Transport Relationship for PBC ionomer blends Andrew White, Thivani Senathiraja and Chris J. Cornelius; Iowa State University, United States

As the world focuses on clean and sustainable power generation without the need for fossil fuels, hydrogen fuel cell technology is becoming a leading choice due to its zero emissions. Proton exchange membranes (PEMs) are a critical part of hydrogen fuel cells, allowing protons to pass between anode and cathode, and improving their durability as well as the structure-transport-property relationship is a key part in furthering this technology. Currently, the industry standard for PEMs in hydrogen fuel cells is Nafion, a perflouronated compound that is used for many applications worldwide. However, the degradation of Nafion leads to the creation of perflourooctanoic acid, a potent environmental hazard when released into the environment, which causes much concern about the future of the compound. To remedy this concern, Nexar, a pentablock copolymer (PBC) has been proposed to serve the same function as Nafion without the environmental risks. In this study, two types of PBC (1.0 and 2.0) were blended in different ratios and solution cast in order to improve the durability and ion conductivity of PEMs created from the blend. SAXS data analysis shows sulfonic acid domain peak shifts from .0154Å to .0176Å, and .0315Å to .0369Å, indicating a change in the microstructure of the PEMs as well as a more ordered structure as a result of blending. Domain spacing between sulfonic acid groups decreases from 400Å to 355Å, resulting in a membrane that can form larger ionic clusters than the parent membrane. To study how the properties of the blended membranes changed, several tests in relation to the operation of fuel cells were undertaken. Titrations were performed on each of the blended membranes in order to observe the ion exchange capacity (IEC) of each, and results showed increasing IEC relative to the amount of PBC(2.0) in the blend. Gas permeation analysis shows a sharp decrease in the permeability of hydrogen and oxygen gasses, while the H2/O2 selectivity of the blended membranes is comparable to that of the parent membrane. Overall, the PBC ionomer blends with different ion exchange capacities shows potential in reducing the fuel cell crossover. Further studies will include thermogravimetric analysis to assess the thermal stability as well as a TEM study in order to observe the morphological changes that have been made.

5:00 PM EN09.08.02
Thermal Annealing of Solution Cast PBC Hybrid Sol-gel Nanocomposites Ionomers Thivani Senathiraja and Chris J. Cornelius; Iowa State University, United States

Tuning the interactions of solid multiblock ionomer is a cost-effective approach to target and advance specific properties for sustainable ion-conducting applications, such as fuel cells, polymer actuators, vanadium flow batteries, water desalination using electrodialysis, and water electrolysis to produce H_2 and O_2 . In this study, polystyrene based sulfonated ionomers called pentablock copolymers (PBC) were employed due to their tailorable morphology. The morphological transitions of PBC ionomer multi blocks was induced using TEOS Sol-gel nanocomposites to understand their structure-property -transport relationship. One of the previous studies portrayed that crosslinking of TEOS-TIP sol-gel network with PBC polymer chains greatly influenced the morphology and properties of multiblock ionomer such as water uptake, proton conductivity, and liquid transport, which are crucial in the fuel cell, lithium-ion battery, or vanadium flow battery applications. However, it was found that the morphology of hybrid membranes transitioned from ordered to random morphology as more TEOS-TIP components were introduced. Hence it was postulated that thermal annealing can be a probable route to further drive the TEOS-TIP network and assemble hybrid PBC membranes into ordered structures as thermal annealing of ionomers leads to the development of interconnectivity between the adjacent ionic channels. The PBC membranes were solution cast using Tetrahydrofuran and were annealed at 80^{o}C and 100^{0}C. The transmission SAXS analysis revealed that the thermal annealing of an unmodified PBC membrane led to the disappearance of their characteristic peaks. This may be attributed to the formation of loose clusters with higher temperature. However, the PBC incorporated with sol-gel shifted towards the lower scattering angle, indicating the formation of large sulfonic acid group clusters. This shows that thermal annealing significantly alters the microstructure of the membranes. Moreover, it was found that thermal annealing and higher TEOS content in the PBC membrane significantly reduced the water uptake by 17% but increased methanol uptake by 22.22%. Due to the enhanced crosslinking between the polymer chains with temperature, it was observed that the gas permeability of the unmodified membranes reduced significantly however the gas selectivity of hydrogen gas and carbon dioxide increased by 30%. While incorporation of sol-gel decreased both permeability and selectivity of the PBC membranes. Future study will incorporate proton conduction, mechanical durability and thermal stability of these PBC hybrid nanocomposite membranes.

5:00 PM EN09.08.03
Protective Interfacial Coating of Polydopamine Layer for Inhibiting Electrolytes Decomposition in Extremely Lean-Electrolytic Lithium Secondary Batteries Myeong Gyun Nam and Pil Jin Yoo; Sungkyunkwan University, Korea (the Republic of)

To meet the rising energy demands, secondary battery systems based on diverse metal ions with a high energy density have been developed. Nevertheless, highly capacitive anode materials, such as Li metal and silicon, typically result in the depletion of the electrolyte and the excessive formation of solid electrolyte interphase (SEI) layers during cell operation. Especially for commercial pouch cells, the amount of electrolyte utilized in cells is significantly less than that used in laboratory-scale coin cells, making the cycle life of pouch cells is significantly more susceptible to electrolyte depletion conditions.

Therefore, to mitigate the issue of electrolytes decomposition, surface passivation strategies involving coating layers are extensively studied. The coatings act as electrolyte-blocking layers to keep the electrolyte away from the surface of the electrode materials, thereby selectively permitting the passage of Li ions. As such, these blocking layers confer the advantageous properties of selective Li-ion conductivity, good insulation, and ample mechanical durability against external stress while simultaneously passivating the surface of the active materials and inhibiting electrolyte decomposition.
Among various candidates for the passivation layer, polymers containing Li-conductive functional groups have also been identified as potential electrolyte-blocking layers. In particular, due to their outstanding coating properties and high Li-ion conductivity on a variety of substrate types, phenolic species could be considered as one of the most promising candidates. Typically, dopamine is the first seeding material in phenolic species to be used as a complexing agent. In the structure of dopamine, the electron-donating amine group has excellent adsorption properties on a variety of surfaces. In addition to other types of interactions, such as hydrogen bonds, van der Waals interactions, and π- π interactions, the indole-transformative nature of amine groups enables the homogeneous adsorption of charges on surfaces, regardless of their type or hydrophilicity.
In this presentation, we introduce polydopamine (PD) as a protective layer to alleviate electrolyte degradation by effectively separating solvent molecules from Li ions. To prove the feasibility, an extremely lean electrolyte testing (ELET) method is proposed as a standard cell testing technique for quantitatively investigating the recyclability of electrolytic species during cell cycling. In this proposed technique, a small coin cell with an extremely small amount of electrolyte (less than 2 μl mAh^{-1}), which is similar to that employed on a commercial scale, is employed to enable the direct and intuitive assessment of cell cycle life taking into account the effect of the relieved electrolyte decomposition. In addition, contour maps to precisely evaluate and estimate the cell performances were successfully constructed using equations derived from the ELET performance and cell configurations, such as electrolyte usage. Consequently, using the ELET technique, we demonstrated that the incorporation of a marginal fraction of the PD layer (~ 4 wt%) significantly reduced the electrolyte consumption of the Si–C composite by 150% relative to that of the parent material. Furthermore, the PD coating inhibited the excessive growth of the SEI, which further confirms the retardation of the electrolyte impregnation. We anticipate that our findings will contribute to the development of high-capacitive materials with superior cycle life and a connection between academic research and practical applications by means of this practical evaluation method that can be applied to a wide range of battery systems.

5:00 PM EN09.08.04
Organic Redox Electrolytes for Continuous Desalination and Li-Recovery System Byeongkyu Kim, Yong Seok Kim, Taeyup Jeong, Doonyapisut Dulyawat and Chan-Hwa Chung; Sungkyunkwan University, Korea (the Republic of)

Capacitive deionization (CDI) has been developed to alternative desalination technology because of its good energy efficiency. In conventional CDI system, ions from the saline are adsorbed on the electrode surface. To improve desalination performance, solid-phase electrode materials with a high specific surface area and electrical conductivity are required for the system. Although recent studies show high specific capacity, these systems require a complex design to scale up due to only the surface of the electrode can contribute to ion removal mechanism. Various approaches, such as membrane CDI, flow-electrode CDI, and desalination batteries, have been tried to solve these issues, but they have not been evaluated to be suitable for designing large-scale and continuous systems.
In the present work, we suggest a system based on the Faradaic reaction of organic redox electrolytes to store the salt in the liquid phase. Considering that a redox flow battery (RFB) generally stores electrical energy as chemical energy in the redox electrolytes via the Faradaic reaction of redox-active materials (RAMs), a hybrid system is designed in which salt removal is performed by CDI, but ion storage occurs in the redox electrolytes rather than the surfaces of electrode materials. In this design, the whole electrolyte volume can be used to store the removed salts. Also, it is believed that the system can maintain its high stability due to electrodes have not participated in the operation.
For continuous desalination system, a desalination- and RFB-cell is fabricated, respectively. An anion- and cation-exchange membrane separates the ion removal region from the anode and cathode in a desalination cell. To maintain charge balance throughout the Faradaic reaction of the redox electrolyte, sodium and chloride ions have been exchanged across each ion-exchange membrane. Therefore, desalination occurs throughout the charging process, in other words. After desalination, the reacted RAMs and salt ion flows continuously into RFB-cell, where the stored energy is discharged. This entire reaction happens repeats with no additional control. Especially, the developed system uses organic material as RAMs (2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, PTIO) and organic solvent for redox electrolyte. The organic state of the electrolyte has various benefits, including the possibility to apply a high voltage of 2.4 V to overcome water splitting limits, scaling of desalination capacity, and sustained desalination performances due to NaCl insolubility in organic solvent. The continuous desalination system based on these designs shows a high desalination capacity value of 80 mg g^{-1} at a desalination rate of 0.11 mg cm^{-2} min^{-1} with the energy consumption value of 109.6 kJ mol^{-1}. Furthermore, the system can be operated continuously over 38 hours without additional control to desalinate a much larger volume of saline.
Moreover, this study suggests an advanced system for collecting Li while desalination. λ-MnO_2 is deployed as an ion-sieve materials in the system to selectively adsorb Li-ion from the solution. The ion-sieve material is installed in the anolyte tank to collect Li-ion while the desalination-cell is operating. Oxidized PTIO aids in the intercalation of Li-ion into the ion-sieve, resulting in the formation of $Li_xMn_2O_4$ in the anolyte tank. The Li recovery process achieves a high selectivity of 57.7 from K^+ and 12.2 from Na^+ while maintaining desalination performances.

5:00 PM EN09.08.05
Molecular Dynamics Simulations of the Polymer Electrolyte-Electrode Interface Aysha Siddika Asha, Justice Nkemakolam Iroegbu, Benjoe Rey B Visayas, Maricris Mayes and Caiwei Shen; University of Massachusetts Dartmouth, United States

Electric double-layer supercapacitors (EDLCs) based on polymer electrolytes are widely studied for flexible, wearable, and multifunctional energy storage applications. However, EDLC electrode materials often present significantly lower capacitances in polymer electrolytes than in liquid electrolytes. This phenomenon has been frequently reported but not systematically studied and understood. Here we present the molecular simulation of a representative polymer electrolyte-based EDLC to reveal the polymer electrolyte-electrode interface at the atomic scale for the first time. The molecule insights combined with experimental verifications provide explanations for the performance disparities between EDLCs using polymer electrolytes and liquid electrolytes.
The simulation model of polymer electrolyte-based EDLC is built with polyethylene oxide (PEO) and lithium perchlorate ($LiClO_4$) between two pieces of single-layer graphene electrodes and compared with an aqueous electrolyte-based EDLC consisting of the same salt except that the PEO molecules were replaced with the water molecules. All simulations were performed using the molecular-dynamics simulation code LAMMPS using the CHARMM force field. We simulated the polymer electrolyte at both melted and solid states under various electrical potentials using the constant charge method. For the experimental part, thin films of PEO-$LiClO_4$ electrolyte were prepared by the solution casting method. Both polymer and aqueous electrolytes (1 M $LiClO_4$ solution) were tested using electrochemical impedance spectroscopy and cyclic voltammetry.
We find from time evolutions of ion concentrations that the polymer systems take longer time than the aqueous system to establish stable EDL structures due to the ionic conductivity discrepancy. After the EDL structures reach equilibrium, the polymer systems show thick inner Helmholtz layers (IHLs) formed by polarized PEO molecules, and similar outer Helmholtz layers (OHLs) and diffuse structures to that seen in liquid electrolytes. Interestingly, unlike ions in typical liquid electrolytes with small solvent molecules, the ClO_4^- ions in polymer electrolytes form OHLs that are inside IHLs near the positive electrodes. The Li^+ ions in polymer electrolytes also form double OHLs that are unseen in other liquid electrolytes. Moreover, the simulation results show that the intrinsic interfacial capacitances of the polymer systems are very close to the values of the aqueous system. Our designed experiments verify that polymer electrolytes can form much better interfaces with electrodes when melted and achieve capacitances approaching that measured with the aqueous electrolyte. The improved interface can be preserved during heating and cooling cycles. These results prove that EDLCs using polymer

electrolytes can potentially achieve capacitances that are comparable to those using liquid electrolytes, which provides guidance for the design and optimization of various flexible, wearable, and multifunctional supercapacitors.

5:00 PM EN09.08.06
Carbon Bio-Waste Eletrocatalyst for Seawater Batteries João P. Ferreira, Tiago Salgueiro, Joao Ventura and Joana Oliveira; University of Porto, Portugal

Humanity is reaching a tipping point where new sustainable energy solutions are needed. Rechargeable sodium seawater battery (SWB), assume the world leadership of high voltage batteries in marine environment. With natural seawater as the active material, the SWB can be supplied infinitely with Na cations. Because of their open structure cathode, the performance of the battery is dependent on the characteristics of the cathode material, such as its specific surface area, porosity, functionalization, and wettability. The redox reactions involved in SWBs are slow electrochemical processes. With increased surface area, a much faster capacitive mechanism arises with an important contribution of the electric double layer (EDL) formed at the cathode interface.
Therefore, in this work, we studied how the performance of a seawater battery cell depends on four different cathode current collectors, commercial, heated and activated carbon felts and a peanut shell derived activated carbon electrode. Their associated performance was evaluated through galvanostic charge and discharge cycles and cyclic voltammetries. Their surfaces were analysed by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and their wettability was measured. The performed electrochemical characterization allowed to observe a gradual improvement of the cathode performance with the increase of the specific surface area due to an enhancement of the capacitive behaviour contribution. Thus, the activated carbon felt showed the highest capacitive behaviour contribution. Nevertheless, the peanut shell derived material (synthesised through a carbonisation and activation using potassium hydroxide method) revealed a voltage gap similar to that of the activated carbon, being even smaller for the highest current. The cyclic voltammetry showed a great capacitive effect and the calculated gravimetric capacitance of the full seawater battery cell employing the peanut shell derived electrode was close to that of the activated carbon. The obtained voltage gaps and gravimetric capacitance demonstrate that the peanut shell derived electrocatalyst coated carbon felt shows good performance. This is caused by highly porous structure of the electrocatalyst with macroporous cores that act as secondary ion-buffering reservoirs, mesoporous walls that provide pathways with low resistance, and micropores that can afford the electric double layer capacitance, and also by a highly functionalized surface where oxygen functional groups. This work opens a new path for the integration of bio-waste in seawater batteries towards a more sustainable future.

5:00 PM EN09.08.07
Forming an Inorganic-Organic Bi-Layered on Li Metal with Reduceable Li Salt@Polymer Layer for High Energy Density Li Metal Batteries
Seungcheol Myeong, Jiseok Kwon, Keemin Park, Yongmin Jung, Taeseup Song and Ungyu Paik; Hanyang University, Korea (the Republic of)

Lithium(Li) metal is considered a promising anode for high energy density batteries. However, lithium dendrite growth during Li plating/striping causes low columbic efficiency and safety issues. The above problems can be controlled by the engineering of an interface between Li metal and electrolytes for better Li-ion kinetics and interface stability. In this study, we form inorganic/organic bi-layer, composed of 200nm thick inorganic (LiF, Li_3N, Li_2S) inner layer (Li metal side) and outside porous PTFE polymer layer (electrolyte side), on Li metal surface. The robust inorganic layer prohibits dendritic Li growth. The flexible and porous polymer layer retains the protection layer structure with high Li-ion flux. In a symmetric cell test, Li metal with the bi-layered protection layer shows stable cycle over 600hours under $1mA*cm^{-2}$ with $5mAh*cm^{-2}$. Full cell cycle test, 20μm lithium metal with bi-layered protection layer anode paired with capacity of $5mAh*cm^{-2}$ high-nickel contents nickel manganese oxide (NCM811) cathode, shows stable cycle performance over 200cycles with the Li anode efficiency of 99.6% calculated by average Coulombic efficiency.

5:00 PM EN09.08.08
3D-Structured Fiber-Mesh Supercapacitors Based on Graphene Oxide/Carbon Nanotube Core and PEDOT:PSS Sheath Fibers Minju Choi[1,2], Il-Young Jo[1], Bon-Cheol Ku[2] and Myung-Han Yoon[1]; [1]Gwangju Institute of Science and Technology, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)

Due to mechanical flexibility, lightweight, and excellent electrochemical performance, conjugated polymer-based pseudocapacitive materials such as poly(3,4 ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) have been regarded as a promising active component for fiber-shaped supercapacitors. However, it has been known that they exhibit several practical issues such as high voltage drop and considerable capacitive degradation for the purpose of relatively long fiber-type supercapacitors. Herein, we developed long-range fiber-type supercapacitors based on graphene oxide-carbon nanotube (GO-CNT; core) and conjugated polymer (PEDOT:PSS; sheath) fibers. The GO-CNT fibers which exhibit very high electrical conductivity over 40,000 s/cm played an important role as a current collector by reducing the voltage drop even in the case of meter-scale long fiber devices. The enlarged volume of PEODOT:PSS sheath was successfully fabricated on the surface of water-wettable GO-CNT core fiber by direct wet spinning of PEDOT:PSS followed by PEDOT:PSS fibers' twisting and self-fusion. The resultant core-sheath fibers showed large length-normalized capacitances of 7.37 and 31.66 F/cm for one and eight strands twisted/self-fused sheath, respectively (volume-normalized capacitance of 120 F/cm^3) while the full cell showed superior energy (2.22 Wh/kg) and power densities (65.5 W/kg). Furthermore, 3-dimensional fiber mesh-type supercapacitors could be fabricated in the form of a hemisphere or cylinder which showed large scalable charge storage capacity under multiple series connections for more practical usage.

5:00 PM EN09.08.09
Preparation of PEDOT:PSS Fibers MXene Based Composite Film for Electrochemical Energy Storage Zuwang Wen, Youngseok Kim and Myung-Han Yoon; Gwangju Institute of Science and Technology, Korea (the Republic of)

Herein, we report on 2D Ti_3C_2Tx MXene and PEDOT:PSS conducting polymer fiber-based composite films with alternating layer structures for electrochemical energy storage application. In the proposed alternating layer structures, the highly-conductive crystallized PEDOT:PSS fibers were self-fused to form porous fibrillar networks to facilitate electrical conduction and enhance mechanical strength. In parallel, PEDOT:PSS fiber layers function as spacers to minimize MXene flakes restacking which shorten electrolyte transport pathway and take advantage of MXene's large electrochemically active surface areas. The resultant composite electrodes were able to deliver large gravimetric capacitances over 400 F/g, and showed minimal capacitance degradation with film thickness. Furthermore, excellent mechanical strength and flexibility of the composite films allowed for folding to arbitrary shapes without apparent electrical/electrochemical damage. We expect this work will pave the way for designing high performance MXene and PEDOT:PSS-based composite materials for their application to energy storage, electrical catalysis, and flexible electronics.

5:00 PM EN09.08.10
Stretchable Gas Barrier Film using Liquid Metal Towards a Highly Deformable Battery Nyamjargal Ochirkhuyag, Yuuki Nishitai, Satoru Mizuguchi, Yuji Isano, Sijie Ni, Koki Murakami, Masaki Shimamura, Hiroki Iida, Kazuhide Ueno and Hiroki Ota; Yokohama National University, Japan

Highly deformable batteries that are flexible and stretchable are important for next-generation wearable devices. Several studies have focused on the stable operation and lifespan of batteries. On the other hand, there has been less focus on the packaging of highly deformable batteries. In wearable devices, solid-state or pouch lithium-ion batteries (LIBs) packaged in aluminum (Al) laminated films, which protect against moisture and gas permeation, are used. Stretchable elastomer materials are used as the packaging films of highly deformable batteries; however, they are extremely permeable to gas and moisture. Therefore, a packaging film that provides high deformability along with gas and moisture barrier functionalities is required for the stable operation of highly deformable batteries used in ambient conditions. In this study, a stretchable packaging film with high gas barrier functionality is developed successfully by coating a thin layer of liquid metal onto a gold (Au) deposited thermoplastic polyurethane film using the layer-by-layer method. The film exhibits excellent oxygen gas impermeability under mechanical strain and extremely low moisture permeability. It shows high impermeability along with high mechanical robustness. Using the proposed stretchable gas barrier film, a highly deformable LIB is assembled, which offers reliable operation in the air. The operation of the highly deformable battery is analyzed by powering LEDs under mechanical deformations in ambient conditions. The proposed stretchable packaging film can potentially be used for the development of packaging films in advanced wearable electronic devices.

5:00 PM EN09.08.11
Design of Carbon-Modified Separators and Current Collectors for Long-Lasting Li Metal-Based Batteries Patrick J. Kim[1], Junghwan Kim[1,2], Kihwan Kwon[1,2], Kwanghyun Kim[1,2] and Junghyun Choi[2]; [1]Kyungpook National University, Korea (the Republic of); [2]Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of)

Metallic lithium (Li) has drawn a huge attention from battery industries and academia investigating next-generation anodes, due to its excellent properties: high specific capacity (3860 mAh g^{-1}), the most negative potential (close to -3.04 V vs. SHE), and low density. Unfortunately, inherent challenges associated with inhomogeneous Li plating/stripping and poor Coulombic efficiency impede the pragmatic use of Li metal anode for conventional batteries. As one of the promising approaches, carbon-based nanomaterials have been widely applied to the modification of battery separator and current collectors. By utilizing carbon-based materials (e.g., graphene powder, carbon nanotubes, carbonized materials and so on), most of the major problems originated from the material properties of polymer separator can be dramatically addressed. In addition, safety problems resulted by the growth of Li dendrites can be significantly improved. Apart from the separator modification, it also has the analogous effects on stabilizing the Li deposition when carbon-based nanomaterials are used for the modification of current collectors. Throughout this talk, we are going to give a talk about our research results and research direction in detail.

5:00 PM EN09.08.13
Unveiling the Microstructure Effect of CNT-Based Current Collector on Li Deposition Behavior Junghwan Kim[1,2], Kihwan Kwon[1,2], Kwanghyun Kim[1,2], Han Seung Min[1], Patrick Joohyun Kim[2] and Junghyun Choi[1]; [1]Korea institude of ceramic engineering and technology, Korea (the Republic of); [2]Kyungpook National University, Korea (the Republic of)

In order to develop a post-modern battery, Li metal batteries (LMBs) has been referred owing to its high specific capacity (3860 mAh g^{-1}) and lowest operating potential (-3.04 V vs SHE). However, LMBs have intrinsic problems related with the poor coulombic efficiency and the formation of dendritic Lithium. These unnecessary phenomena impede the commercialize of Li metal anodes. Among various strategies to overcome these severe challenges of Li metal anodes, the utilization of three-dimensional (3D) current collectors has shown very interesting results in terms of electrochemical performance. In this work, we evaluated two different carbon nanotubes (i.e., double-walled nanotube [DWNT] and multi-walled nanotube [MWNT]) to identify how the microstructure of carbon nanotube current collectors affects the electrochemical performances of LMBs. As MWNT has a more reversible Li$^+$ storage structure than DWNT, it can induce the homogeneous and stable Li deposition over the entire surface of MWNT matrix. This effect suppresses the growth of dendritic Li and directly attributes to the cycle stability of Li metal half-cell at high current density. Moreover, it has proven a possibility in full-cell application when the MWNT current collector was assemble with the LiCoO2 cathode. The MWNT@LiCoO2 cell showed the high coulombic efficiency (99 %) with notable cycle retention (97 % at 50 cycle). This work suggests that application of carbon-based material and structure would be desirable route toward enhancing the cycle stabilities of LMBs.

5:00 PM EN09.08.14
Prussian Blue Coated Separator to Alleviate Transition Metal Cross Over in High Nickel Cathodes Changhyun Park, Min-Ho Kim and Hyun-Wook Lee; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Transition metal layered oxides ($LiNi_xCo_yMn_{1-x-y}O_2$, NCM) have been considered as one of the most promising cathode materials for lithium-ion batteries used in long-mileage electric vehicles and energy storage systems. Despite its potential interests, NCM cathodes are likely to be degraded during the persistent cycling due to the generation of hydrogen fluoride (HF), which is often produced by decomposition of $LiPF_6$, giving rise to severe transition metal (TM) dissolutions into electrolytes. Especially, it was reported that dissolved TM ions tend to cross the separator and deposit on the anode surface with reduction reactions. The TMs can catalyze parasitic reactions such as electrolytic decomposition and dendritic Li growth, ultimately leading to catastrophic safety hazards. In this study, we demonstrate that Prussian Blue nanoparticles (PBNPs) anchored to a commercial polyethylene (PE) separator successfully mitigates such problematic TM crossover toward anode sides. Prussian Blue (PB, $Fe[Fe(CN)_6]$) and its analogues (PBAs) are cubic-type metal-organic frameworks (MOFs) with cyanide ligands around transition metal cations. It is known that its large interstitial sites can host various monovalent ions, divalent ions, and zeolitic water molecules. We found that PB nanolayers embedded in the upper and bottom regions of PE separator improve electrolyte wettability and ion selectivity of separator, effectively reducing cell resistance. In addition, they also significantly suppress TM crossover during cycling, even under harsh conditions (high cutoff potential of 4.6V) that would accelerate TM dissolution. When using a PB coated separator under a harsh condition, NCM||graphite full cells maintain 50.8% of their initial capacity at the 150th cycle. Therefore, we propose that through scalable production of PB-coated PE separator via facile synthesis method, our strategy can help establish and new research direction for the design of high-energy-density batteries in both academic and industrial field.

5:00 PM EN09.08.15
Universal Organic Anodes for Advanced Alkali Ion Batteries Using Halogenated Contorted Hexabenzocoronene Derivatives Seokhoon Ahn; Korea Institute of Science and Technology, Korea (the Republic of)

Contorted hexabenzocoronene (cHBC) derivatives, small organic semiconductors with nanographene were designed and synthesized for alkali-ion batteries such as Li-ion batteris, Na-ion batteries, and K-ion batteries. The aromatic core of cHBC is distorted away from planarity by steric congestion in its proximal carbon atoms. This unique structure of cHBC allows to form self-assembled molecular wires through pi-pi interactions. Lithium ions could be intercalated into the columnar structures of cHBC and stored with facile insertion and desertion advantages compared with graphite anode. Furthermore, when halogen atoms such as fluorine and chlorine are introduced into the outer shell of cHBC, larger alkali ions than lithium ion could be stored in the outer shell through interactions between halogen atoms and alkali ions, supported by simulation. Especially, chlorinated cHBC showed satisfactory cycling performance for NIBs and KIBs owing to the pseudocapacitive behavior with reversible specific capacities of approximately 175 and 260 mAh/g, respectivley.

5:00 PM EN09.08.16
A Prelithiated Silicon-Sulphur High-Capacity Battery with Promising Cycle-Life—A Micelle-Like Electrolyte Additive Suppresses the Polysulfide Dissolution Faiz Ahmed, Defu Li and Gao Liu; Lawrence Berkeley National Laboratory, United States

Prelithiated Si-S batteries are promising storage systems due to their high safety, low cost, and high energy density. However, the practical application of these batteries is limited because of the significant capacity decay as a result of active sulfur loss after charge-discharge cycling, and unstable solid-electrolyte interphase (SEI) on the Si anode [1-3]. Especially the loss of sulfur cathode is caused by the severe shuttle effect of dissolved polysulfide [3]. Several strategies have been reported to suppress the active sulfur loss, but the outcomes are far away from the commercial application of Li-S batteries [4-5]. To simultaneously solve the aforementioned problem, this work report on a novel prelithiated SiOx composite-S/C composite full-cell battery system. Herein, we have used an excellent strategy to suppress polysulfide dissolution using a micelle-like fluorinated ether-based additive with lithium bis(trifluoro-sulfonyl)imide (LiTFSI) electrolyte salts for Li-S battery applications. S/C composite is used as cathode material and prelithiated SiOx composite anode is used as an anode instead of Li-metal in order to avoid side reactions. The LiTFSI imide electrolyte with fluorinated ether-based additive exhibits better electrochemical stability, cycling stability, and a high specific discharge capacity of ca. 1318 mAhg^{-1} with the battery configuration of S/C composite//electrolytes//SiOx composite at 0.1 C. Furthermore, the results demonstrate that the 0.5M LiTFSI electrolyte with fluorinated micelle-based electrolyte additive shows excellent cycling performance by suppressing polysulfide dissolution with excellent capacity retention and coulombic efficiency (99.80%) after 1000 charge-discharge cycles. The newly developed prelithiated SiOx composite-S/C composite full cell achieves a high reversible capacity (924, and 914 mAhg^{-1} at 0.3 and 0.4 C, respectively), and long cycle life (capacity decay only 10% after 500 charge-discharge cycles). Scanning Electron Microscope (SEM) and X-ray photoelectron spectroscopy (XPS) are used to better understand the surface morphology of the cycle electrodes.

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SESSION EN09.09: Polymeric and Organic Materials for Electrochemical Energy Storage
Session Chairs: Zheng Chen and Xiaolei Wang
Friday Morning, April 14, 2023
Moscone West, Level 2, Room 2009

9:00 AM *EN09.09.01
An Ultrafast, Durable, and High-Loading Polymer Anode for Aqueous Zinc-Ion Batteries and Supercapacitors Xiaolei Wang; University of Alberta, Canada

With high theoretical capacities (820 mAh g^{-1} and 5855 mAh cm^{-3}), suitable electrochemical potential (−0.763 V vs standard hydrogen electrode), low cost, and rich abundance of component materials, aqueous zinc-ion batteries (ZIBs) and capacitors (ZICs) have exhibited great promise for grid-level energy storage and other stationary applications. Zn metal as excessive Zn are often used to compensate for the uncontrollable dendritic growth, corrosion behaviour, and low Coulombic efficiency (CE) of the Zn metal. As such, most of the ZIBs and ZICs developed using these electrode materials exhibited actual device energy and power densities that were significantly lower than the corresponding theoretical values. Another key performance metric that needs to be improved in ZIBs is their high-rate charge and discharge. In addition to the dendrite-derived problems commonly experienced in batteries based on other metal anodes, ZIBs are disadvantaged by hydrogen gas evolution from water decomposition especially under high-rate charge/discharge, leading to poor cycle life.
Herein, an ultrafast, stable, and high-loading polymer anode for aqueous Zn-ion batteries and capacitors (ZIBs and ZICs) is developed by engineering both the electrode and electrolyte. The anode polymer is rationally prepared to have a suitable electronic structure and a large π-conjugated structure, whereas the electrolyte is manufactured based on the superiority of triflate anions over sulfate anions, as analyzed and confirmed via experiments and simulations. This dual engineering results in an optimal polymer anode with a low discharge potential, near-theoretical capacity, ultrahigh-loading capability (≈50 mg cm^{-2}), ultrafast rate (100 A g^{-1}), and ultralong lifespan (one million cycles). Its mechanism involves reversible Zn^{2+}/proton co-storage at the carbonyl site. When the polymer anode is coupled with cathodes for both ZIB and ZIC applications, the devices demonstrate ultrahigh power densities and ultralong lifespans, far surpassing those of corresponding Zn-metal-based devices.

9:30 AM EN09.09.04
First Principle and Machine Learning Study to Elucidate the Behavior of Vanillin for Enhancing the Coulombic Efficiency of the Zn Anode in Aqueous Zinc Ion Batteries Yaqiong Li[1], David Hoang[2], Xiulei (David) Ji[2] and Peter A. Greaney[1]; [1]University of California, Riverside, United States; [2]Oregon State University, United States

Zinc metal batteries have been widely researched due to their low-cost, low toxicity, and high theoretical capacity advantages. However, the problem of corrosion of the zinc metal anode (ZMA) has not yet been solved. In this project, we focus on the effect that adding small quantities of vanillin has on improving the Coulombic efficiency of plating Zn from a highly concentrated Water-in-Salt Electrolyte. Specifically, we use molecular dynamics (MD) simulations and ab initio calculations to understand the role that vanillin and its derivatives play in displacing water from the solvation shell of Zn ions at the ZMA surface. To achieve this, we have used Gaussian process regression and Bayesian inference to accelerate our exploration of these solvation structures on the Zn substrate.

9:45 AM BREAK

10:15 AM EN09.09.05
Environmentally Friendly Phytic Acid Additive Enabling Simultaneous Optimization on Electrode Interface and Coordination Environment for Stable Aqueous Zinc-Ion Batteries Yimei Chen and Xiaolei Wang; University of Alberta, Canada

Despite with advantages of water compatibility, low cost, high safety and capacity, aqueous zinc ion batteries (ZIBs) are facing challenges from zinc dendrite, side reactions and low coulombic efficiency, which limits their broad application and mass production. In this paper, phytic acid (PA), an inositol polyphosphate, is introduced as an additive in 1M ZnSO$_4$ electrolyte to suppress zinc dendrite and H$_2$ evolution. The simulation and experimental results show that the phytic acid additive can absorb on the zinc anode surface, covering the active sites for H$_2$ production and guiding the uniform diffusion and deposition of zinc ions. Besides, PA has six phosphate groups, with each phosphorus atom bounding to 4 oxygen atoms. The electronegative oxygen atoms have a strong affinity to Zn^{2+}, and can compete with water molecules in the Zn (H$_2$O)$_6$$^{2+}$, changing the coordination environment of zinc ions. With PA additive, the zinc dendrite and side reactions are suppressed, and a high coulombic efficiency of 99.4% and long cycling stability of more than 1200cycles can be obtained at the current density of 1mA cm^{-2} and capacity of 1mAh cm^{-2}. When coupling with I$_2$/AC cathode, the full cell with PA additive delivers a high capacity of 120mAh g^{-1} at current density of 1A g^{-1}, and can stably cycle for more than 3000cycles, while the battery using 1M ZnSO$_4$ failed at 1300cycles. This work provides a simple but promising approach to the development of high-performance aqueous ZIBs.

10:30 AM EN09.09.06
Modeling to Reveal the Synergistic Effect from Organic Additives that Enhance the Coulombic Efficiency of Zn metal batteries Yanke Fu[1], Heng Jiang[2], Longteng Tang[2], Chong Fang[2], Xiulei (David) Ji[2] and Alex Greaney[1]; [1]University of California, Riverside, United States; [2]Oregon State University, United States

Aqueous zinc metal batteries are a promising technology for safe, cost-effective, and sustainable grid-scale energy storage. However, their commercialization has been stymied by the hydrogen evolution reaction (HER) which parasitically corrodes the active mass of the Zn metal anode during plating/stripping. We have developed a highly concentrated aqueous electrolyte that all but eliminates the HER and enables dendrite-free Zn plating/stripping with 99.9% Coulombic efficiency under the low current density operating conditions where the HER is most problematic. The electrolyte is a highly concentrated "water-in-salt-electrolyte" with two organic additives. This talk will present the results of our *ab initio* molecular dynamics simulations that, when interpreted in conjunction with the results from careful NMR and femtosecond stimulated Raman spectroscopy, reveal the synergistic way in which these organic additives alter the Zn^{2+} solvation structure, and enable formation of a protective organic solid electrolyte interphase (SEI) layer. This electrolyte opens the door to commercially viable rechargeable aqueous zinc metal batteries.

10:45 AM EN09.09.08
Evaluating Li Ion Storage Mechanism In Carbon Nanotube (CNT) Anodes For High Energy Density Li-Ion Batteries: An Atomistic Perspective
Aniruddha M. Dive, Kathleen E. Moyer-Vanderburgh, Francesco Fornasiero and Liwen Wan; Lawrence Livermore National Laboratory, United States

Current Lithium-ion batteries (LIBs) are limited to energy densities of ~150 Wh/kg and pose safety issues associated with dendrite formation and the use of flammable liquid electrolytes that can result in the common battery failure known as thermal runaway and explosion. Lithium metal is an ideal anode for high energy density LIBs due to its high theoretical capacity (3860 mAh/g) but is dangerous due to its propensity to form dendrites. Carbon nanotubes (CNTs) with superior electronic, mechanical, and structural properties provide an exciting alternative as anode for high energy density LIBs. LIBs with vertically aligned CNTs forest help achieve the capacity retention > 80% and superior efficiency over 1000 charging-discharging cycles. However, a fundamental understanding of Li$^+$ ion storage within CNT anodes is largely unexplored and lacking.

Experimental characterization of Li$^+$ ion storage in CNT anodes is expensive and challenging. Previous theoretical studies have evaluated storage mechanism for isolated Li$^+$ ions within small diameter CNTs (< 1.5 nm) forest. In common organic liquid electrolytes, Li$^+$ ions prefer to be solvated and therefore isolated Li$^+$ ions cannot accurately describe the Li$^+$ storage mechanism especially in large diameter CNTs. In the current study, we carefully investigated the de-solvation mechanisms for Li$^+$ ions in EC: EMC (3/7 w/w) 1.2 M LiPF$_6$ liquid electrolytes both inside and outside of pristine CNT. The calculated de-solvation energies for Li$^+$ ion adsorption onto the outside surface (~0.4-0.5 eV) of CNTs show relatively lower energies as compared to inside surface (~ 0.9-1.0 eV) of CNTs. We therefore claim that the Li$^+$ ion storage strongly occurs on the outside surface of pristine defect-free CNTs. We further employ classical molecular dynamics simulations to investigate the Li$^+$ ion storage on the outside of CNTs. The classical molecular dynamics simulations reveal a capacitive-type storage mechanism for pristine CNTs forest. Recent experimental reports suggest a large fraction of storage mechanism in CNT anode to be capacitive type (> 55 %) which supports the findings from atomistic modeling. Introducing structural defects (n-membered C-C rings), functional groups (-OH, =O, -COOH) etc… can lead to intercalation or plating-type Li ion storage in CNT forest which would result in higher capacity as well as energy density. However, for pristine CNTs we report the Li$^+$ ion storage mechanism to be purely capacitive and therefore would serve as potential supercapacitor rather than battery.

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11:00 AM EN09.09.09
Catalysing the Performance of Li-Sulfur Batteries with Two-Dimensional Conductive Metal Organic Frameworks Preeti Bhauriyal and Thomas Heine; Technische Universität Dresden, Germany

At present, the efficiency of high energy density Li-sulfur (Li-S) batteries is being narrowed by the limited strategies to deal with the shuttling effect, sluggish redox kinetics and poor ionic and electron conductivities of the cathode hosts. Recently synthesized triphenylene based two-dimensional conductive metal organic frameworks (2D MOFs) hold the promising characteristics to overcome the limitations with suitable pore and anchoring sites along with the desired electron conductivity.1 In this study, we use density functional theory calculations to investigate 2D honeycomb MOFs with hexa-substituted triphenylene linkers with pairs of varying metal ions (Cu, Ni, and Co) and functional groups (N, O, and S) (M3(2,3,6,7,10,11-hexaiminotriphenylene)2 (M3(HITP)2), M3(2,3,6,7,10,11-hexahydroxytriphenylene)2 (M3(HOTP)2) and M3(triphenylene-2,3,6,7,10,11-hexathiol)2 (M3(THT)2)) to be the potential cathode hosts in Li-S batteries and analyse their structure-activity relationship. The detailed study of structural-electronic characteristics followed by analysis of triangle of catalytic activity conclude that M3(HOTP)2 can deliver higher anchoring efficiency, but it suffers low redox reactivity with high Li diffusion and Li2S decomposition barrier, whereas M3(HITP)2 MOFs appear insubstantial with the possibility of Li polysulfide shuttling resultant of the lower anchoring. Co3(THT)2 not only has superior anchoring efficiency (-1.40 to -2.68 eV) but also shines in facile Li+ diffusion (0.68 eV), small Gibbs free energy requirement of 0.68 eV for Li polysulfide reduction and moderately low Li2S decomposition barrier (1.06 eV) that simultaneously contribute to the performance of Li-S batteries. Our study concludes that the combination of Co and S in Co3(THT)2 make the most suitable cathode host and provides a basis for the designing and screening of new materials having such active components to achieve high performance Li-S batteries.

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11:15 AM EN09.09.10
Different Electrochemical Reaction of Metal Hexacyanometallate According to the Electrode Kinetics Ahreum Choi[1], Taewon Kim[1], Min-Ho Kim[1], Seok Woo Lee[2], Young Hwa Jung[3] and Hyun-Wook Lee[1]; [1]Ulsan National Institute of Science and Technology, Korea (the Republic of); [2]Nanyang Technological University, Singapore; [3]Pohang Accelerator Laboratory, Korea (the Republic of)

Na-ion batteries (SIBs) have received considerable interest owing to the abundance and even distribution of Na compared to those of Li. Metal hexacyanometallates, known as Prussian Blue analogues (PBAs), have been considered as the promising cathode materials for SIBs, because of the inherent advantages of PBAs involving large channel sizes that allow accommodating Na ions. Manganese hexacyanomanganate shows the highest capacity (~200 mAh g^{-1}) among PBAs, accompanying the abnormal insertion of two Na ions in a sub-unit cell. However, the structural distortion by strong Jahn-Teller effect of high-spin Mn(III) aggravates the cyclability of manganese hexacyanomanganate. Herein, we report that manganese hexacyanomanganate shows different electrochemical reaction according to its kinetic properties. Under the sufficiently fast reaction rate, the charge redistribution can be triggered (low-spin Mn^{III} + high-spin Mn^{III} → low-spin Mn^{II} + high-spin Mn^{IV}) instead of Jahn-Teller effect. The relation between kinetic property and the electrochemical reaction of manganese hexacyanomanganate is supported by the analysis through X-ray absorption near-edge spectroscopy (XANES) and X-ray photoelectron spectroscopy (XPS). Moreover, different crystal structures reported by using postmortem synchrotron X-ray diffraction analysis (synchrotron XRD) provide a clue to the mechanism of charge redistribution. The long bonding length between transition metal and ligands in the orthorhombic structure could activate charge redistribution based on the superexchange rule. In this work, we report the charge redistribution mechanism which is the new electrochemical reaction of manganese hexacyanomanganate under the fast kinetics environment. As a result, the unstable redox reaction of high-spin Mn(III) can be stabilized, improving cycle performance of manganese hexacyanomanganate. These results can pave the way for high-performance Na-ion batteries.

SESSION EN09.10: Virtual Session
Session Chairs: Dawei Feng, Minah Lee and Jeffrey Lopez
Wednesday Morning, April 26, 2023
EN09-virtual

10:30 AM EN09.10.01
Melanin and Polypyrrole Coated Nanocellulose Hydrogel Networks for Energy Storage Noah Al-Shamery, Tobias Benselfelt and Pooi See Lee; NTU Singapore, Singapore

Melanins are black-brown pigments of a specific class of poly indolequinones found in nature and inside the human body. [1] They are responsible for processes like photoprotection, radical scavenging, and metal ion chelation. More recently, there has been significant interest in eumelanin as a functional material due to its macromolecular structure and the exploitation of the quinone-hydroquinone redox equilibrium. [1] While eumelanin can be used in many promising applications for environmental, health, energy storage, and sensor devices, melanins are insoluble in most solvents, limiting their processing into homogenous materials and coatings. [2] One avenue that has shown promise for providing a stable network substrate for eumelanin devices is incorporating cellulose nanofibrils (CNFs), a nanoscopic material that originates from plant biomass. [3] In this work, a flexible network consisting of CNFs coupled with conductive polypyrrole (PPy) is utilized to form a functional eumelanin hydrogel material for energy storage applications. The resultant energy densities and conductivity values measured against Zn as the counter electrode in a 0.1M $ZnSO_4$/0.9M Na_2SO_4 aqueous electrolyte surpass those in other synthetic eumelanin composite materials using polyvinylidene fluoride (PVDF) and carbon black. According to scanning electron microscopy and electrochemical impedance spectroscopy, the improved energy densities can be attributed to reduced internal resistance due to the conductive pathways afforded by the conductive PPy vapor-phase polymerized on top of the eumelanin interacting with the CNFs, thus creating a core-shell structure with a PPy concentration gradient decreasing to the inside of the material. A hypothesis for this behaviour is that due to the amphiphilic nature of PPy, this structure has increased hydrophobicity on the outside but is permeable for charges by offering hopping sites to the core where more redox centers are available from the eumelanin. Under atmospheric pressure, this reduces the amount of water from outside conditions penetrating the structure and competing with the electrolyte, thus decreasing the inactive mass in the material significantly. Together with the added redox centers provided by the eumelanin, this could be the reason for the increased energy density. This material was then tested in aqueous electrolyte zinc coin cells, where it was shown to have charge/discharge stability for over 1300 cycles, showcasing this composite material type as a promising eumelanin-based composite energy storage material.

References
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10:35 AM EN09.10.02
Aqueous Organic Redox Flow battery for Grid Energy Storage Dawei Feng; University of Wisconsin--Madison, United States

An increasing amount of renewable energy sources are being integrated into the electric grid in the US and around the world. However, as intermittent wind and solar begin to approach more than a quarter of grid energy production, significant energy storage technology must be employed as well to mitigate the unbalanced energy production and demand in the grid. To meet the emission targets in an economically viable manner, low-cost grid-scale energy storage technology must be developed. This talk will compare different battery technologies and describe our efforts in development of new generation of inexpensive redox active species for redox flow batteries (RFB) that can offer extraordinary energy density and cycling stability. This involves identification of critical needs for redox couple design in RFB and development of simplest yet effective synthetic routes towards redox active molecules with desired performance.

10:50 AM EN09.10.03
High-Donor Electrolyte Additive for Stable Aqueous Zinc Batteries Wenjing Deng and Xiaolei Wang; University of Alberta, Canada

As one of the emerging secondary batteries, rechargeable aqueous zinc-ion batteries (AZIBs) are prevailing over conventional lithium-ion batteries counterparts in terms of low cost, environmental benignity, and intrinsic safety. Metallic zinc anode is highly prized due to its low redox potential, high theoretical capacity, earth-abundance, and water compatibility. Despite these attractive merits, critical issues of unstable Zn chemistry in conventional aqueous electrolytes such as dendrite growth, hydrogen evolution and side reactions would inevitably provoke surface corrosion and damage the anode-electrolyte interface during battery operation. electrolyte engineering *via* introducing additives may become one of the most expedient solutions to achieve anti-side reactions and smooth deposition simultaneously. For parameter, Gutmann donor number (DN) reflects the intrinsic capacity of electron-donating, which can be used to indicate the solubility of intermediate products and the variation of the hydrogen-bonding network in aqueous electrolytes. A unique and facile strategy to improve Zn reversibility in aqueous batteries by tailoring electrolyte solvation structure with high-donor-number N, N-dimethyl acetamide (DMA) solvent additive. it is demonstrated that high-donor DMA additive with strong electron-donating ability can confine free water activity, replace the water in Zn2+ solvation sheath, and reshape hydrogen-bonding network of water, which is highly conducive to reducing the reaction activity. DMA additive is proven capable of replacing coordinated water molecules and participating in the solvated Zn^{2+} sheath, contributing to the restraint of dendrite growth and side reactions. The DMA-modified electrolyte enables remarkable suppression of water-involved hydrogen evolution and severe corrosion, which contributes to preferentially uniform deposition and ultralong cycling life of 4500 h at current density of 1 mA cm^{-2} in symmetric cell, and high Coulombic efficiency of 99.6% in asymmetric cell. Besides, with solvation modulation, full batteries of Zn//VO_2 exhibit long-term cycling performance of 500 cycles and withstand subzero temperature condition. This regulation strategy employing high-donor solvents as additives thereby verifies the effectiveness of aqueous batteries.

11:05 AM EN09.10.04
Abstract Presented (ON-DEMAND ONLY) Low Concentration Sulfolane-based Electrolyte for High Voltage Lithium Metal Batteries Pengcheng Li and Ge Li; University of Alberta, Canada

Electrolyte engineering is crucial for the commercialization of lithium metal batteries. Here, lithium metal is stabilized in highly reactive sulfolane-based electrolyte under low concentration (0.25 M) for the first time. Inorganic-polymer hybrid SEI with high ionic conductivity, low bonding with lithium and high flexibility enables dense chunky lithium deposition and high plating/stripping efficiency. LCE also enables excellent cycling stability of NCM523/Li cells at 1 C (90.7% retention after 500 cycles) and 0.3 C (83.3% retention after 1000 cycles). Even with a low N/P ratio (~2), the capacity retention for NCM523/Li cells can achieve 94.3 % after 100 cycles at 0.3 C. The exploring of the LCE is of paramount significance because it provides more possibilities of the lithium salts selection, especially reviving some lithium salts that are excluded before due to their low solubility. More importantly, LCE has the significant advantage of commercialization due to the cost effectiveness.

11:20 AM EN09.10.05
A Fast, Stable, and Thick Polyimide Anode for Aqueous Zinc Batteries and Capacitors Zhixiao Xu and Xiaolei Wang; University of Alberta, Canada

Zn metal has shown promise as an anode material for grid-level energy storage, yet is challenged by dendritic growth and low Coulombic efficiency. Herein, an ultrafast, stable, and high-loading polymer anode for aqueous Zn-ion batteries and capacitors (ZIBs and ZICs) is developed by engineering both the electrode and electrolyte. The anode polymer is rationally prepared to have a suitable electronic structure and a large π-conjugated structure, whereas the electrolyte is manufactured based on the superiority of triflate anions over sulfate anions, as analyzed and confirmed via experiments and simulations. This dual engineering results in an optimal polymer anode with a low discharge potential, near-theoretical capacity, ultrahigh-loading capability (≈50 mg cm^{-2}), ultrafast rate (100 A g^{-1}), and ultralong lifespan (one million cycles). Its mechanism involves reversible Zn^{2+}/proton co-storage at the carbonyl site. When the polymer anode is coupled with cathodes for both ZIB and ZIC applications, the devices demonstrate ultrahigh power densities and ultralong lifespans, far surpassing those of corresponding Zn-metal-based devices.

SYMPOSIUM

April 13 - April 13, 2023

Symposium Organizers
Katrina Knauer, National Renewable Energy Laboratory
Yeng Ming Lam, Nanyang Technological University
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* Invited Paper
\+ Distinguished Invited

SESSION EN10.01: Decomposing Materials Wastes—Physical, Chemical and Biological Approaches I
Session Chairs: Rose Hernandez and Sierin Lim
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2010

8:30 AM EN10.01.01
From Waste to Energy—Extraction of Mesoporous Nanocomposites from Spent Li-Ion Batteries for High-Performance Supercapacitor Devices with Ultra-High Stability Yasmine I. Mesbah; American University in Cairo, Egypt

Lithium-ion batteries (LIB) are one of the most significant energy storage devices used nowadays. However, a huge number of spent batteries bring harmful resource waste and environmental hazards due to heavy metals and organic electrolytes. Consequently, recycling spent LIB has become a hot topic lately, where researchers are actively working to develop a plethora of methods to extract valuable metals and components. In this study, mesoporous Li-Ni-Mn-Co oxide nanoparticles have been successfully extracted from spent Li-ion batteries using a simple microwave/precipitation method. The extracted Li-Ni-Mn-Co oxides were used to construct functional supercapacitor devices. However, the extracted oxides showed poor stability and low conductivity. To enhance cycling stability and conductivity, fullerene (C76) is used as a carbon additive to form Li-Ni-Mn-Co oxide/C76 nanocomposite material. The morphological, structural, and compositional analyses were performed using FESEM, HRTEM, XRD, and XPS techniques. The Li-Ni-Mn-Co oxide/C76 nanocomposite exhibits high conductivity and high wettability with an enhanced gravimetric capacitance of ~357 Fg-1 at 1.0 Ag-1. The asymmetric supercapacitor devices deliver specific energy as high as ~21.3 Wh/kg at a specific power of ~800 W/kg and a superior retention rate of ~115% after 20,000 cycles with ~100% Coulombic efficiency.

8:45 AM EN10.01.02

Study of Alternative Eco-Friendlier Wood-Plastic Composites of Recycled HDPE Enhanced with Hemp Fibers Iouliana Chrysafi, Eleftheria Xanthopoulou, Alexandra Zampoulis and Dimitrios Bikiaris; Aristotle University of Thessaloniki, Greece

Plastics are the most widely used materials that can be found in almost every human made object and often replace traditional resources such as wood, metal and glass. High-Density Polyethylene (HDPE) replaces many natural resources, due to the low cost and easy processing, but its ever-increasing wastes make it harmful to the environment. Thus, many processes are used to recycle it. On the other hand, the continuous consumption of natural resources that causes a downgrading of the sustainability of the natural environment led the scientific community to study alternative products as a replacement for natural wood. Such alternative materials can derive from agricultural crop residues. Hemp is an ideal replacement for wood due to its lightweight, hydrophobic characteristics, and excellent long-term mechanical stability, with the lowest carbon emissions footprint.

The aim of this research is to use alternative products for the construction of wood-plastic composites (WPCs), as an eco-friendlier solution, that can be used in the construction of floor surfaces, objects, in the interior or exterior spaces, in the construction of frames, and door leaves, but also in the automotive industry in the interior of the car. So, the main goal is the use of recycled HDPE and the replacement of wood with hemp crop residues. In the present work, HDPE was recycled through mechanical and thermal processes (r-HDPE). More specifically, HDPE waste plastics were grinded through a mill and thereafter, extruded through a Haake-Buchler Rheomixer. The thermal and mechanical properties of r-HDPE have been tested compared to HDPE and it was found that after recycling the properties of r-HDPE are not affected so the enhancement with the hemp fibers followed. Composites containing 10, 20, 35 50 and 75% wt. of hemp fibers were prepared also by melt mixing. To improve the adhesion between the fibers and the polymer matrix Joncryl ADR-4400 (JC) and propylene grafted-maleic anhydride (PPgMA) compatibilizers were used.

In this study the chemical, structural, thermal, and mechanical properties of the r-HDPE-hemp fiber composites are examined and the composites with the different compatibilizers are compared. Testing the structural properties of the composites by X-Ray Diffraction (XRD), it is found that the samples are semicrystalline, and their crystallinity decreases with the increase of the hemp fibers content, while there is a shift in the peaks due to the expected disruption of the arrangement of the polymer chains by the addition of the fibers. From the Fourier Transform Infrared Spectroscopy (FTIR) it is concluded that the addition of compatibilizers does not change the chemical structure of the materials. Thereafter, the thermal properties of composites are measured by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). So, it is concluded, that the compatibilizers do not affect the thermal properties of the composites and the decrease on thermal stability will not affect their application in WPCs. Moreover, the decomposition steps were separated dur to the degradation of hemicellulose, cellulose, lignin and rHDPE, respectively. Finally, the mechanical properties are examined by tensile and impact strength experiments. A decrease in tensile and impact strength as the content of the fibers increases due to the higher creation of crack points in the polymeric matrix is observed. However, the enhanced elongation at break is encouraging for their application at WPCs.

All in all, the results of this study are positive and in conjunction with other tests concerning the degradation of the samples, the construction of different WPC-based objects will be feasible in the near future.

Acknowledgments: This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH-CREATE-INNOVATE (project code: T2EΔK – 00008).

9:00 AM EN10.01.03

Editing Degradable Polycarbonates from Waste Resources Fabiana Siragusa, Thomas Habets, Bruno Grignard and Christophe Detrembleur; University of Liege, Belgium

Designing new polymers from wastes while making them intrinsically degradable has become a new challenge to overcome the plastic waste accumulation in the environment and the associated pollutions. Recently, we engineered a novel synthetic pathway to create polycarbonates[1] by the room temperature step-growth copolymerization of highly reactive CO$_2$-sourced exovinylene biscyclic carbonates with various diols derived from biomass[2] or waste commodity plastics. These innovative low carbon footprint polymers are thermally stable, isolable and processable. On the path to circularity, their unique microstructural features offer competitive depolymerization scenarios, enabling the formation of new value-added organic scaffolds that can serve as organic building blocks in medicinal chemistry and organic synthesis, or as monomers for producing new polymeric materials[3,4]. In this talk, we will discuss how these polycarbonates can be easily depolymerized, with a special emphasis to describe the mechanism and the selectivity of the depolymerization process.

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9:15 AM EN10.01.04

Poly(oxazolidone)s as the Next Generation of Non-Isocyanate Polyurethanes—A Facile Access to Recyclable Advanced Materials Thomas Habets, Bruno Grignard and Christophe Detrembleur; University of Liege, Belgium

Polyurethanes (PUs) are world-class relevant materials entering in the conception of multiple daily life applications such as elastomers, foams, adhesives, paints, medical devices… Among them, poly(oxazolidone)s, i.e. polymers characterized by cyclic carbamates repeating linkages, display unique thermal and chemical stabilities making them valuable options for designing the next generation of high performances materials. However, these polymers are commonly prepared by reacting in harsh conditions epoxides with harmful and nasty isocyanates, which utilization is now regulated by REACH legislation. Recently, we engineered a novel sustainable approach toward poly(oxazolidone)s by the valorization of CO_2 and readily available synthons[1–5]. The labile behavior of new discovered bonds was studied at the model molecule level before being implemented to polymeric materials. This novel approach quickly gives access to diversified CANs (covalent adaptable networks) with tunable properties by virtue of monomer design. The so-produced materials can be easily recycled upon thermal reprocessing such as thermoplastic materials while benefiting from the properties of thermosets in working conditions. Besides, chemical recycling of these materials delivers starting building blocks that might re-enter the loop or benefit as valuable building blocks in various fields.

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3 C. N. Tounzoua, B. Grignard and C. Detrembleur, *Angewandte Chemie International Edition*, DOI:https://doi.org/10.1002/anie.202116066.
4 T. Habets, F. Siragusa, B. Grignard and C. Detrembleur, *Macromolecules*, 2020, **53**, 6396–6408.
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9:30 AM EN10.01.05
The Role of Plastic-to-*x* Technologies in a Circular Economy for PET Bottle Resin Taylor Uekert, Tapajyoti Ghosh, Julien Walzberg and Alberta Carpenter; National Renewable Energy Laboratory, United States

The United States generates the most plastic waste of any country and is a top contributor to global plastic pollution. A portfolio of end-of-life strategies must be implemented to minimize environmental impacts and retain valuable plastic material, but it can be challenging to determine how these options compare, especially when they generate products of different values and lifetimes. Here, we use a material flows model equipped with consequential life cycle assessment (LCA) to estimate the circularity, economic cost, and environmental impacts of polyethylene terephthalate (PET) down-cycling by mechanical recycling, closed-loop recycling by glycolysis, up-cycling to fiber-reinforced resin, and conversion to non-plastic products (electricity, oil) on a United States economy-wide basis with annual time resolution. The framework can implement PET end-of-life pathways over time, and uses the resulting trends to predict an optimal sequence of technology phase-in (or phase-out) that maximizes PET circularity while minimizing overall greenhouse gas emissions and cost. This analysis enables consistent comparison of plastic-to-*x* processes on an “apples-to-apples” basis, thereby facilitating prioritization within the ever-growing PET recycling research space.

9:45 AM BREAK

10:15 AM EN10.01.06
Molecular Cages for Automated Chemical Separation in Continuous Flow System Jiratheep Pruchyathamkorn; University of Cambridge, United Kingdom

Chemical separation is essential for several industrial processes, waste water purification, air cleaning, drug synthesis and synthetic research in laboratory. The challenges we are facing now such as global warming and limited oil supplies mean that we must use resources more wisely. To solve these problems, new strategies are required that are more efficient, more environmentally friendly and less energetically costly than those currently employed, as well as economically worth for applying to industry. Metal-organic coordination cages provide new opportunities to address the need for improved separation technologies. Recent work in this field has demonstrated that these containers can encapsulate specific guest species and act as vehicles for targeted molecular transport and separation.

We synthesised $Fe^{II}_4L_4$ water-soluble cage via ‘subcomponent self-assembly’ technique, based on a diamino terphenylene subcomponent, bearing chiral glyceryl groups. The aqueous solution of this cage was used as a liquid membrane in a triphasic U-shaped tube system, separating two organic layers, the feedstock and receiving phases. The cage is able to encapsulate specific guest compounds from a mixture in the feedstock phase and release them in the receiving phase. We could separate naphthalene from larger aromatic compounds such as triisopropylbenzene, as well as ferrocene from its larger derivatives. Within the U-tube system, the transport of compounds was monitored by NMR, GCMS and UV-Vis spectroscopy. To understand the system better, we proposed a kinetic model that can be used to explain the guest transport process, and studied the effect of competing guests on the rate of transport of the selected compounds.

We demonstrated that there is need to improve the bulk liquid membrane separation system to facilitate faster transport, in order to allow it to be used for extraction in industries. It took over 50 days in the U-shaped tube setup for the transport of ferrocene through the cage solution to reach equilibrium. Hence, we designed and optimised a slug flow system to obtain the conditions that offer best extraction efficiency. The continuous flow system gave significantly greater contact areas between phases with better mixing caused by the chaotic internal circulation within the flow, resulting in faster transport (within hours), less amount of solvents needed and less energy required for extraction. The cage could be automatically recycled, and the extraction progress could be monitored in real time by UV-Vis spectroscopy. Further work is being done to precipitate out ferrocene after the guest release, shifting the equilibrium toward the completion of the extraction process in continuous flow system.

This finding is highly industrially relevant, and the main goal is to open up new opportunity for industries requiring novel chemical separation technique.

10:30 AM EN10.01.07
Closed-loop Recycling of Topochemical Polymer Single Crystals Zitang Wei, Xuyi Luo and Letian Dou; Purdue University, United States

Plastics play crucial rules in almost every aspect of life. Unique properties of plastics like chemical and light resistant, strong, moldable, and low cost make plastic materials useful in many aspects of our global society. However, largely relying on feedstock resources like fossil fuels, plastics production is not sustainable. Thus, plastic recycling could be an efficient alternative to save feedstock resources as well as to reduce production cost.
Recently, a series of polymer materials synthesized via topochemical polymerization are considered as strong candidates for next generation recyclable plastics. It is well-known that topochemical polymerization has high efficiency and environment-friendly features, such as solvent-free and catalyst-free reaction conditions, high reaction yield without side reactions, and atom economy. Yet, there exist few studies on depolymerizing and recycling those polymers. In 2014, Dou et al synthesized a topochemically polymerizable polyindenedione derivative [2,2'-Bi-1H-indene]-1,1'-dione-3,3'-diyl dialkylcarboxylate (BIT) system. In this study, high-quality polymer single crystals can be obtained by shining visible light and the polymerization yield is quantitative. Interestingly, in the polymer single crystal structures, a newly formed elongated carbon-carbon bond with length of 1.59Å was discovered, which is longer than normal carbon-carbon single bond (~1.54 Å). Inspired by this discovery, we demonstrate a topochemical approach for creating elongated C–C bonds with a bond length of 1.57~1.63 Å between repeating units in the solid state with decreased bond dissociation energies. 12 distinct polymers from three different classes exhibit rapid depolymerization via breakage of the elongated bond within a desirable temperature range (140~260 °C) while otherwise remaining remarkably stable under harsh conditions. Additionally, one-dimensional polymer single crystals can be processed into two-dimensional thin films and can be melt processed for 3D printing. Processed polymers can maintain a high depolymerization yield with tunable mechanical

properties. This work provides a unique strategy of solving plastic recycle issue by novel molecular design, careful single crystal analysis and innovative material processing.

10:45 AM EN10.01.08
Intrinsic Activity of Silica-Alumina for the Conversion of Polyethylene into Tunable Aromatics Below Pyrolytic Temperatures Makenna Pennel and Matteo Cargnello; Stanford University, United States

Plastic waste is a growing catastrophe that lacks global strategy, largely due to inadequate recycling capabilities. The search for a superior recycling process has spanned decades and disciplines, but recently, low-temperature hydroconversion reactions have gained increasing attention. These reactions typically produce fuel-range alkanes using moderate hydrogen pressures, but questions surround the economics of such conversions given the products are of relatively low monetary value. Other low-temperature reactions that produce value-added products have been proposed. One prominent example is the hydrogen-free tandem hydrogenolysis/aromatization reaction pioneered by Zhang et al., which converts polyethylene into alkylaromatics using a Pt/Al_2O_3 catalyst at 280 °C. These compounds are valuable as lubricants and are currently produced through more energy-intensive routes. A techno-economic assessment for this type of polymer conversion has not been published, but the catalyst will undoubtedly be a cost driver given the low polymer/catalyst ratios and energy-intensive catalyst regeneration procedures detailed in the literature. Lowering catalyst costs and increasing efficiency are paramount to moving the technology forward.

In a preliminary step to address these problems, we examined the intrinsic activity of nominally metal-free, mesoporous silica-alumina mixed oxide materials (SiO_2-Al_2O_3) for the conversion of polyethylene into aromatic compounds. Herein, we demonstrate that SiO_2-Al_2O_3 deconstructs polyethylene into smaller, aromatic molecules under identical conditions as those used by Zhang et al. during reactions with Pt/Al_2O_3. Yields are comparable, the catalyst can be reused without regeneration, and product selectivity can be tuned by altering reaction conditions or the acidity of the SiO_2-Al_2O_3. Notably, the fraction of polyaromatic products increases with the Brønsted acidity of the catalyst, as does the degree of polymer deconstruction. Preliminary work on the mechanism of the reaction suggests that acid sites are responsible for initiating depolymerization and aromatization reactions in analogy to previous work in the literature. This work showcases the intrinsic activity of SiO_2-Al_2O_3 for polyolefin deconstruction/aromatization at sub-pyrolytic temperatures and lays the foundation for future studies involving solid acid and bi-functional catalysts.

11:00 AM EN10.01.09
Consumer Gatekeeping in Sustainable Materials Streams—An Application in Cellulose Nanomaterials Nasreen Khan, D. Cale Reeves and Blair K. Brettmann; Georgia Institute of Technology, United States

U.S. consumers spent 4.5 trillion dollars on goods while generating 292 million tons of municipal solid waste in 2018 – and trends in both spending and waste generation are increasing. Packaging and containers made of paper and paperboard (6.4 million tons) and plastic (10 million tons) are the greatest proportion of landfilled tonnage. Displacing plastic-based materials with bio-sourced materials may be consistent with green chemistry and engineering design principles but does not truly improve the circular economy if the bio-sourced materials travel straight to landfill. Consumers act as gatekeepers in a circular economy, determining which products and materials end up in landfill or are diverted back to post-consumer manufacturers. By understanding consumer behaviors around product acquisition and disposition, products can be manufactured to ensure that the value of materials is retained.
Here we develop a framework for incorporating consumer behavior into circular economy. We advance the green chemistry principle of F-factor by incorporating manufacturing efficiency and consumer behavior into the lifetime functionality of material mass. We demonstrate the framework using cellulose nanomaterials (CNMs) in packaging – a new bio-based material with the dual potential to be a "good citizen" in landfill and to contribute to post-consumer product manufacturing. The framework highlights how increased functionality, and thus the preservation of economic value, arises from the recirculation of material streams that pass through multiple sequential phases: from the manufacturing phase – where green chemistry principles can be applied - to product acquisition - where manufacturing decisions meet consumer decision-making – to product disposition – where consumer behavior dominates – and back to manufacturing. This approach reassesses the impact of sustainable manufacturing practices and showcases new strategic opportunities for high-impact policy interventions – targeting both manufacturers and consumers – to reduce wasted resources and improve the circularity of *function*.

11:15 AM EN10.01.10
Reactive Crystallization via Metal-Organic-Framework Formation Enables Separation of Terephthalic Acid from Textile Impurities Abigail K. Nason, Ronald Jerozal, Phillip Milner and Jin Suntivich; Cornell University, United States

Polyethylene terephthalate (PET) fibers are among the largest plastics in production. Used commonly in textiles, PET fibers are often blended with non-PET components such as cotton, dyes, and additives. As these non-PET components generate impurities during depolymerization, extracting high-purity terephthalic acid (TPA) monomer from the chemical recycling of textiles is challenging. Here, we demonstrate the extraction of high-quality TPA from the impure crude digestion mixtures containing depolymerized PET fibers and non-PET components. Our approach uses reactive crystallization to turn TPA into a metal-organic framework (MOF). As TPA is the only component in the mixture capable of forming an extended, crystalline structure, TPA monomers are separated from impurities as MOF crystallizes. We demonstrate this concept on recycled TPA (rTPA) extracted from a polyester-cotton blend textile through alkaline hydrolysis, where the impure rTPA was used as an organic linker to prepare MOF MIL-53(Ga). This MOF crystallization removed the trapped impurities. After MOF disassembly, colorless TPA, reminiscent of virgin-grade monomer, was obtained. These results demonstrate self-assembly-induced crystallization as a new strategy to selectively recover monomers from complex mixtures.

SESSION EN10.02: Decomposing Materials Wastes—Physical, Chemical and Biological Approaches II
Session Chairs: Katrina Knauer, Yeng Ming Lam, Ann Meyer and Julie Rorrer
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2010

1:45 PM EN10.02.01
Upcycling of Cotton-Based Textile Waste Using Different Recycling Strategies Following the Principles of Circular Economy Varvara Apostolopoulou Kalkavoura, Maria-Ximena Ruiz-Caldas, Natalia Fijol and Aji Mathew; Stockholm University, Sweden

To move from linear towards circular economy model several attempts to close the loop are necessary in every sector. The overconsumption of textiles threatens the environment due to the large land, water and pesticides use for cotton production, the dependance on the fossil-based resources for the production of synthetic fibers, including the release of microplastics during their repeating washing cycles, at the same time as the waste textiles are piling up in landfills or burned in incineration facilities. The challenges in the recycling of textiles are multiscale including the poor sorting, the lower post-consumer fiber quality or the difficulty to separate the pure constituents from blended fabrics.

Here we present and compare few recycling strategies mainly targeting the cotton. By acid hydrolysis using sulfuric or citric acid we are able to obtain cellulose nanocrystals (CNC) and separate them from the synthetic fibers. To identify what impacts the sustainability, we combined our experiments with a life cycle assessment following a cradle-to-cradle approach. One important outcome that increased the sustainability was the recovery of citric acid which had a purity over 90%. Another recycling route that allowed us to further compare the quality of the final products was to perform TEMPO mediated oxidation on cotton and blended fabrics. All processes were then compared to conclude which parameters affect the product yield, the potential for scaling up and the process sustainability.

The efficient recycling of cotton allows us to manufacture waste-based cellulose/nanocellulose materials which have the potential to be used in various applications such as thermal insulation, packaging and water purification. For instance, in our previous work cellulose nanomaterials foams from wood cellulose showed superinsulating properties even at moist conditions, thus recycled nanocellulose has the potential to be used in such applications too, paving the way to upcycle textile waste into high-performance materials.

2:00 PM EN10.02.02

Network Polyesters Enable Circular Uses of Important Petrochemicals and Materials Chen Wang; University of Utah, United States

The life cycle of today's polymer materials is linear. Globally, ~380 million tons/year of plastics are produced, of which only 16% are repurposed, and 67% are discarded in landfill and the environment. Unmanaged waste plastics have become a dire environmental crisis. Innovations are urgently needed to develop tomorrow's materials that are recyclable-by-design. In this presentation, I will discuss redesigning polyester materials for durable goods.

2:15 PM EN10.02.03

X-ray Studies to Elucidate the Effect of Substrate Morphology on Deconstruction Sarah A. Hesse[1,2], Christopher J. Takacs[1,2], Erika Erickson[3,2], Gregg T. Beckham[3,2] and Christopher Tassone[1,2]; [1]SLAC National Accelerator Laboratory, United States; [2]BOTTLE Consortium, United States; [3]National Renewable Energy Laboratory, United States

Plastics are becoming a pollution problem worldwide. Among those plastics is poly(ethylene terephthalate) (PET), one of the five most widely produced and used polymers today. Efforts are underway to create chemical and biological deconstruction pathways for PET, but challenges still remain. While the polymer conformation and morphology appear to play a significant role on the deconstruction of PET, this role is poorly understood. This talk aims to establish how morphology affects the deconstruction of PET, in particular PET deconstruction using PET hydrolases.

PET hydrolases are part of a small number of enzymes that have shown promise in facilitating PET deconstruction, catalyzing hydrolysis of the ester bonds in this ubiquitous synthetic polymer. While one can measure product release resulting from these enzymatic deconstruction reactions, very little is known about the interactions between the enzyme and the polymer during the interfacial biocatalytic reactions.

The current state of the art in characterizing the enzyme-to-substrate interaction relies upon computational chemical modeling and X-ray crystallography, where model PET oligomers (i.e., dimers and trimers) are docked or posed within the enzyme active site. These approaches do not take into consideration the various morphologies of different non-model PET substrates, or how the polymer chain is accessed by the enzyme in the first place. However, it is particularly the morphology and crystallinity of a given PET substrate that dictate the level of deconstruction activity of a particular PET hydrolase. We have used *in-situ* and *ex-situ* X-ray scattering techniques at the Stanford Synchrotron Radiation Lightsource to probe the nano (~1-100 nm) to atomic (<1 nm) length scales of polymers. Understanding the effects of polymer morphology on the enzyme activity will enable expansion to other polymer systems and deconstruction pathways.

2:30 PM BREAK

3:30 PM EN10.02.04

Hydrothermal Liquification of Mixed Food and Plastic Waste from Supermarkets Panagiotis Evangelopoulos; RISE, Sweden

Every year in Sweden, more than 70 000 tonnes of expired food with the packaging from the supermarkets are discarded without passing through proper sorting[1]. Separating plastic packaging and food waste from retailers requires a lot of effort, is time consuming and thus costly. Therefore, in most of the cases the waste is not separated and plastic packaging together with the expired food ends up on the same waste fraction. The hydrothermal liquefaction (HTL) is a promising technology that can be applied into such heterogeneous waste fractions. This mild temperature thermal treatment process can be used for treating food waste together with the plastic packaging without sorting.

The proposed recycling route of HTL is aiming to introduce a new alternative recycling towards the concept of circular economy. Thermochemical processes are the foundation for recirculation of secondary raw materials. Chemical recycling decomposes organic matter into lower molecular weight compounds, leaving no microplastics preventing them from escaping to the aquifer. So, it can stop the occurrence of plastic debris in the environment. The products of HTL are hydrocarbon rich bio-oil that can be used for production of secondary raw materials and combustible gas that can supply the process with the energy needs.

The Hydrothermal Liquification (HTL) has been tested for several applications in the past with positive results. The main advantage of this process is that it can tolerate high moisture content of the feedstock, so no time and energy consuming drying of the feedstock prior to the process is needed[2]. In the case of mixed food waste with plastic packaging, the moisture content of the waste fraction is expected to be high, which makes HTL an attractive option. Another advantage is rather low temperature of the process, which results in lower energy consumption compared to other thermochemical processes. Using these processes, the part of waste that goes to energy recovery can be minimised, leading to lower CO_2 emissions. Moreover, the dependency from virgin raw materials can be reduced since less fossil resources would be needed for production of plastics.

[1] Food waste volumes in Sweden Reports, (n.d.).

[2] A. Dimitriadis, S. Bezergianni, Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review, Renew. Sustain. Energy Rev. 68 (2017) 113–125. https://doi.org/10.1016/j.rser.2016.09.120.

3:45 PM EN10.02.05

Library of Sustainable, Functional Biocomposites Sabrina Shen, Nicolas A. Lee and Markus Buehler; Massachusetts Institute of Technology, United States

Conventional engineering materials often have poor degradation mechanics or recyclability, resulting in accumulation of solid waste that leads to the deterioration of ecological processes. Furthermore, there is significant confusion surrounding recycling infrastructure and concepts of biodegradation and compostability, especially amongst the general population. Rather than improving degradability or recyclability of conventional materials, here we present an alternative approach that uses abundant natural materials to create functional biocomposites that are suitable for conventional or additive manufacturing methods. By combining various organic "binders" and "fillers" with diverse physical,

mechanical, and chemical properties, we create a library of materials that are fully nontoxic and biodegradable in ambient conditions. With sufficient understanding of the behavior of complex biocomposites, functional degradable materials can be tailored toward unique applications.

4:00 PM EN10.02.06
Enabling Circular Polymers Through Computational Design Alexander R. Epstein[1], Xiaoxu Ruan[1], Jeremy Demarteau[2], Eric A. Dailing[2], Rishabh D. Guha[2], Orion Cohen[1], Ryan Kingsbury[2], Brett A. Helms[2,2,2], Stephen J. Cox[3] and Kristin A. Persson[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]University of Cambridge, United Kingdom

Monomer-to-monomer recycling is a promising solution to the global plastic pollution crisis but is not feasible for most conventional plastics due to the difficulty of selectively cleaving a carbon-carbon backbone. One solution is to design polymers to incorporate bonds that can be selectively broken in specific chemical processes. This work demonstrates how computational tools can be used to develop mechanistic insights into how bond chemistry enables monomer-to-monomer recycling. Specifically, we used both classical and quantum methods to simulate the acid-catalyzed hydrolysis mechanism that enables recycling of a new polymer platform, poly(dikeotenamine)s (PDKs), which have been shown to display chemical circularity with >90% monomer yield. We find that the depolymerization rate of PDKs can be greatly varied through heteroatom and functional group substitutions on the monomer and crosslinker. This variance in depolymerization rate arises from unique mechanisms depending on the type and location of chemical substitution; thus, we used simulations across a range of length and time scales in order to examine a range of effects. By understanding how chemical bonding affects PDK recycling, we design the chemistry of PDKs to target specific properties while retaining recyclability. We discuss several cases in which computational and experimental design worked in close collaboration to develop diverse PDK formulations.

4:15 PM EN10.02.07
Illuminating Catalytic Polymer Deconstruction Processes to Understand Effects Beyond the Reaction Center Christopher Tassone[1,2], Gregg T. Beckham[2,3], Nicholas A. Rorrer[3,2], Sarah A. Hesse[1,2], Anjani K. Maurya[1,2], Robert Allen[3,2], Christopher J. Takacs[1,2], Gorugantu Sri Bala[4,2], Linda J. Broadbelt[4,2], David Brandner[3,2], Katrina Knauer[3,2], Kevin Sullivan[3,2] and Bonnie Buss[3,2]; [1]SLAC, United States; [2]BOTTLE, United States; [3]NREL, United States; [4]Northwestern University, United States

Over the last several years the development of catalytic deconstruction approaches has been extremely successful. Homogeneous catalytic approaches have resulted in high selectivity to specific products, with high activity. Thus far development of these chemistries has been focused on achieving chemio-selectivity, as a means of controlling product distributions. However, in general these catalytic reactions occur in solutions in which the polymer is not solubilized, leading to either a solid-liquid phase separated mixture, or an immiscible liquid-liquid phase separated mixture in cases where the reaction temperature is above the melting point of the polymer. In this heterogeneous mixture, the diffusion of catalyst into the bulk of the polymer, as well as the accessibility of catalyst to the desired polymeric bonds of interest become incredibly important in determining the activity of the catalyst, as well as the potential inhibition of the reaction. Here we present detailed structural characterization of the polymer using a combination of x-ray scattering, x-ray spectroscopy, and electron microscopy to understand the molecular and mesoscale structure of the polymer, how this is perturbed by the reaction conditions, and how this evolves over the course of the reaction. We find that the ability of a catalyst to diffuse into the bulk of the polymer, and turn the reaction from a surface limited to a bulk deconstruction process, as well as the interconversion between the amorphous and crystalline fractions facilitated by the production of monomeric products is a crucial design consideration for highly active and selective deconstruction chemistries.

4:30 PM EN10.02.08
Biodegradability Study of Thiol-ene Photopolymers Amelia Heiner, Jeffrey S. Bates and Chen Wang; University of Utah, United States

Polymer materials are used in many commodity single-use applications, including adhesives, over-print varnishes (OPV), packaging materials, and contact lenses. However, these materials are hydrophobic, contain no nutritional value to microorganisms, and include many additives to enhance their performance, making them non-biodegradable. This study examines the synthesis and end-of-life scenarios of thiol-alkene (thiol-ene) films using click photopolymerization. We propose that because of their multifunctionality and the presence of ester groups in their backbones, these polymers may provide nutrients for microorganisms that will enable the biodegradation and disintegration of the material after disposal in non-standard and non-specified environmental conditions. The degradation of the material is investigated through biochemical oxygen demand testing and material characterization. Biodegradability will enable the replacement of non-biodegradable materials in single-use applications.

4:45 PM EN10.02.09
Controlling Polymer Deconstruction to Monomer via Solvation Free Energy Mutian Hua, Jeremy Demarteau, Alexander R. Epstein, Kristin Persson and Brett A. Helms; Lawrence Berkeley National Lab, United States

Polydiketoenamine (PDK) elastomers are circular replacements for difficult-to-recycle polyurethanes used in a wide range of consumer products. The materials, time, and energy efficiency of recycling PDKs back to monomer will be discussed here from two vantage points: the bonds undergoing hydrolysis in strong acid and the solvation of polymer chains in the reaction medium. Specifically, PDKs undergoing depolymerization by hydrolysis in strong acid are insoluble, but swell in the reactive medium, aided by the ionization of diketoenamine bonds. Since both acid and water are required for hydrolysis, solvation emerges as a critical factor governing PDK depolymerization rates at length scales beyond the bond. Understanding the impacts of solvation on depolymerization rates is challenging due to: (1) the high concentration of acid used (~5 M); (2) the collective influences of monomer polarity, MW, crystallinity on the solvation free energy; and (3) the evolution in composition and polymer hierarchies during depolymerization. We will discuss how monomer polarity, crystallinity, and crosslinking density influence the fraction of activated bonds, degree of swelling, and self-diffusion of acid and water, resulting in faster macroscopic rates of chemical depolymerization.

SESSION EN10.03: Poster Session: Decomposing Materials Wastes—Physical, Chemical and Biological Approaches

Session Chairs: Luis Campos and Sierin Lim
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN10.03.01
Molecular Engineering of a Synergistic Photocatalytic and Photothermal Membrane for Highly Efficient and Durable Solar Water Purification
Kun Fang[1], Cui Du[1], Junliang Zhang[1], Shengyang Yang[1] and Chen Zhou[2]; [1]Yangzhou University, China; [2]U of Central Missouri, United States

In recent years, the solar-driven interfacial evaporation system (SIES) has obtained a lot of interest as a potential solution to freshwater scarcity. However, the organic pollutant residues affected the practical application of the distillate generated by SIES. Herein, a solar interfacial membrane (AuNPs@g-C_3N_4/CMF) (AMF) for desalination and removal of multiple water pollutants was prepared by generating Au-doped carbon nitride (AuNPs@g-C_3N_4) directly on the carbonized melamine (CMF) through a co-calcination process. The designed membrane features excellent light absorption, efficient water supply, and low thermal conductivity. All the above advantages of the AMF membrane contributed to an outstanding evaporation rate (1.675 kg m^{-2} h^{-1}) and high photothermal conversion efficiency (94.03%) under 1 sun irradiation. For seawater desalination, the membrane performed well in removing ions from simulated seawater and demonstrated good stability during long-term desalination. Meanwhile, the membrane still exhibits a high evaporation rate (1.24 kg m^{-2} h^{-1}) even in a 10% salt solution environment. Owing to the photocatalysis capability of AuNPs@g-C_3N_4, the AMF membrane also performs effectively in the removal of organic dyes and formaldehyde.

5:00 PM EN10.03.02

Optically Transparent, Mechanically Tough, Spray-Coatable Waterborne Polyurethane Composites Reinforced with Natural Polymer-Derived Nanofibrous Fillers Jungho Jin[1,2]; [1]Univ of Ulsan, Korea (the Republic of); [2]BIOQIT Co., Ltd, Korea (the Republic of)

Waterborne polyurethane (WPU) has emerged as an environmentally benign alternative to conventional PU owing to its low VOC (volatile organic compound) content, low toxicity, non-flammability, and ease of handling. Despite such advantages, WPU in general tends to show inferior mechanical properties compared to conventional PU.

In this work, we introduce an optically transparent, mechanically tough waterborne polyurethane (WPU) nanocomposite incorporating succinylated cellulose nanofibers (SCNF) and chitin nanofibers (SChNF) as the reinforcing fillers. Both a commercially available WPU, as well as, a typical anionic WPU synthesized using poly (tetrahydrofuran) (PTMEG), isophorone diisocyanate (IPDI), and dimethylol propionic acid (DMPA) as the internal emulsifier is used. Aqueous colloidal suspensions of the SC(h)NF nanofillers are prepared via the aqueous counter collision (ACC) method. A simple blending of the two waterborne materials renders homogeneous WPU/SC(h)NF (1–10 wt%) nanocomposite that simultaneously achieves an outstanding mechanical toughness and high optical transparency (>90%). We also demonstrate an environmentally benign aerosol-spray coating of the WPU/SC(h)NF using dimethyl ether (DME) as the aerosol propellant.

5:00 PM EN10.03.04

Raw Biomass Electroreforming to Formic Acid Li Quan Lee[1,2]; [1]Nanyang Technological University, Singapore; [2]Nanyang Environment and Water Research Institute, Singapore

Biomass is widely recognized as a CO_2-neutral, abundant, and renewable resource replacement for fossil fuels. However, the biomass energy extraction still strongly depends on thermal conversion of woody biomass. Without proper carbon capture and storage, this thermal conversion process generates CO_2 emissions. A greener and sustainable method to fully utilise biomass would be much more appealing. At ambient condition, biomass derivatives could be employed into water electrolysis to reform into valuable chemicals. Nevertheless, due to the rigid polymeric structures of biomass, they often require energy-intensive and harsh pre-treatment processes before refining. Herein, we electrooxidized glucose, the monomer from abundant cellulose and achieved high selectively of up to 88% of potassium formate in less than 4h at 1.58V vs. RHE. A simple dilute acid hydrothermal pre-treatment was employed to depolymerize cellulose and hemicellulose of glucose-containing waste sugarcane bagasse without any separation steps. Then, this mixture of sugars with mono- and oligo- saccharides were electro-reformed into organic acid salts dominated by potassium formate. Techno-economic analysis and life cycle assessment was also conducted to evaluate this new process. The coupled carbon-negative green hydrogen generation to raw biomass electroreforming driven by solar renewable energy was also demonstrated, holding great promise to make significant contribution towards a sustainable energy future.

5:00 PM EN10.03.09

Degradation of Organic Molecules by Tribovoltaic Mechano-Chemistry Leqi Lin and Jun Liu; University at Buffalo, The State University of New York, United States

The presence and accumulation of organic pollutants in water systems is a significant threat to the health of humans and aquatic ecosystems. Herein we demonstrate a new pathway for high-efficient degradation of organic molecules based on the tribovoltaic effect. The method does not require photo-irradiation nor electrochemistry, but only use mechanical energy to generate electron-hole (e-h) pairs at dynamic metal-semiconductor contacts. The e-h pairs excited by collision between metal and semiconductor particles in the water are capable of generating highly reactive free radicals and driving dye molecule degradation. Such mechano -catalysis mechanism is proved to be a versatile strategy with a broad range of material selection and mechanical stimuli, which has great implications for cost- and energy-effective water treatment, as well as potential applications in green chemical synthesis.

5:00 PM EN10.03.10

Potential of Polymer Electrolysis for Plastic Materials Takahiro Saida, Kazuma Hisazaki and Takahiro Maruyama; Meijo University, Japan

Plastic waste is conscious of one of the global problems. Most plastic recycling is thermal recycling by incineration; that percentage is 63% of plastic waste in Japan. All know thermal recycling is not sustainable for plastic material and generates greenhouse gas emissions. Material recycling, which is reused by remolding, is 21% in Japan. And thermal recycling also has problems that cannot fully recover the monomer, separate the pigments and dyes, and degrade the quality of plastics. Therefore, we focused on chemical recycling with depolymerization. Chemical recycling is in the minority to the high cost, although it is known that PET can be depolymerization. We aim to develop new chemical recycling by electrolysis with a relatively low cost and small scale.

In general, plastic materials are insulators and are expected to be hard to electrolyze. However, two reports demonstrated the decomposition of polymers. [1, 2] Thus, polymer electrolysis may be possible, but its potential has not been understood correctly. In this study, primary and secondary alcohols with different carbon-chain lengths as the model molecule were electrolyzed to understand the electrochemical behavior of polymer decomposition. In addition, the electrolysis of PVA, PEG, and Nylon 66 was conducted as the first step of depolymerization into monomers.

The electrochemical cell was composed of a working electrode, a carbon counter electrode, a reversible hydrogen electrode (RHE) as a reference electrode, and 0.2 M NaOH. This study employed platinum and iron plate as the working electrode. Cyclic voltammetry (CV) was conducted at room temperature in an inert atmosphere. 1, 3, 5, 7, and 9 carbon atoms (linear) of a primary alcohol and 3, 5, 7, and 9 carbon atoms (linear) of a secondary alcohol were used as the model molecule. Primary and secondary alcohols were added 1mL to the electrolyte to investigate the electrochemical behaviors. PVA and PEG were also added to the electrolyte. Nylon 66 was polymerized on the working electrode directly.

The oxidation currents were observed at addition of primary and secondary alcohols. Their oxidation currents probably meant the decomposition of a model molecules. But their oxidation currents decreased with increasing the carbon-chain length. Therefor polymer, has long carbon chain, was expected to hard to electrooxidation.

The electrooxidation behaviors of PVA and PEG were different. In PVA, the CV shape was almost no change. In contrast, the oxidation current was observed in PEG. The oxidation of polymer may favor the presence of other atoms, such as oxygen, at the main chain rather than the functional group at

the side chain. Nylon 66 oxidation, which had nitrogen atoms at the main chain, also showed oxidation currents. However, the oxidation current of Nylon 66 was only observed in the case of the iron plate as the working electrode. This phenomenon suggests that the suitable catalyst for polymer oxidation likely depends on the presence of elemental species in the carbon chain.
The results of this study demonstrated the realization potential of polymer electrolysis. At the same time, these indicated two issues: all polymers cannot electrolyze, and the electrocatalyst probably depends on the polymer species. Hereafter, it is necessary to develop the electrocatalyst to oxidize or reduce polymers with other atoms in the carbon chain.

[1] O. R. Luca et al. *Molecules*, **25** (2020) 1-9.
[2] T. Jiang et al. *Solar Energy Materials & Solar Cells*, **204** (2020) 1-10.

5:00 PM EN10.03.11
Use of Waste Plastics in the Reduction of Iron Oxides Wenceslao a. Jaimes, Samane Maroufi and Veena Sahajwalla; University of New South Wales, Australia

The unpacking of huge amounts of electronic waste (e-waste) in the world is no longer surprising, since almost 50 million tons were discarded between 2018 and 2019 alone [1]. What is even more surprising is that only 20% of this waste was given a second use other than disposal in open dumps. Within electronic waste, there is a vast variety of plastics, which include polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), and acrylonitrile butadiene styrene (ABS), and it is the latter which it is more commonly found in electronic waste, due to its ease of transformation and low production costs. In order to properly recycle this waste, the purity of the material must be high and of the same material, if it is sought to reuse and produce other by-products; however, this is not necessarily a requirement in the metal and steel industry [2], where the high temperature environment in the process provides a great opportunity to use complex plastic waste, as a reducing agent for recovery of metals (e.g. Iron), and as fuel or as a source of energy in reactions.

The trend to replace natural fuels in the steelmaking process has increased in recent years, following the IPCC waste hierarchy, which says that waste must first be reused, followed by recycling, recovery of energy from it, and finally discarded. In this way, recent works on the implementation of the so-called secondary carbon resource have been reported, one of these is the recycling of 100% end-of-life materials with a high carbon content, such as melamine, or more recently, the potential of using auto-reducible waste toner to recover metallic iron (98% purity) has also been reported. These proposals to partially replace coke as a source of carbon in steel production, has recently been categorized as the new technique of micro recycling, within the alternative sources of carbon include e-waste from printers at the end of life, monitors, discs hard or plastic Although recent studies on tablets based on epoxy resins and their thermal transformation for the manufacture of Fe-Si nanostructures, have broadened the path towards a more sustainable (or colloquially called green) metallurgy. Until now, the extent to which iron oxides are reduced by using e-waste plastics such as ABS or toner has been limitedly explored.

Therefore, at the Centre for Sustainable Materials Research and Technology (SMaRT), the study of the use of non-conventional materials as a replacement for coal in the manufacture of steel is being carried out. Materials such as plastic waste (ABS), and toner residue, have been used to evaluate their effectiveness as fuels and reducing agents in the reactions of iron oxides in the presence of carbon sources. For this, characterisation techniques, such as XRD, XRF, SEM, Gas IR analysis, have been carried out in order to understand materials and interactions at high temperatures, by preparation of different blends of these waste materials and EAF Slag, the degree of reduction was studied by exposing them at 1550 °C under an inert atmosphere in a customised designed furnace. The reduction reactions were confirmed for both waste materials by the detection of CO, CO_2 and H_2 gases. Finally, the observation of the self-reducing toner at high temperatures, i.e., 500-1600 °C, confirmed the reduction of iron oxide via H_2 enabled reactions. Where the studies revealed that ABS-PC and Toner waste materials can act as reducing agents in the reduction of iron oxides from EAF slag and exhibited a degree of reduction of 100% for a Slag/Toner blend, and 99% for a Slag/Plastics blend.

5:00 PM EN10.03.13
Bioplastics From Unprocessed Spirulina Paul Grandgeorge, Hareesh Iyer, Ian Campbell, Kuotian Liao, Mallory Parker, Andrew M. Jimenez and Eleftheria Roumeli; University of Washington, United States

The increasing global materials consumption and the long-lasting detrimental effects of polluting manufacturing industries urgently call for innovative and sustainable new materials. Plastics, in particular, albeit ubiquitous and useful in an enormous range of applications, are associated with un-sustainable sourcing, manufacturing as well as end-of-life fates. During the past decades, various biodegradable plastics with properties comparable to those of commodity plastics have been pioneered. However, despite being biodegradable, these plastics were designed to degrade in aerobic environments, not in general landfills which is the place they usually end up in. As a result, even biodegradable plastics degrade at an unsustainably slow rate.
In this work we discuss the plasticization mechanism, as well as mechanical and thermal properties of bioplastics produced from selected plant and algal biomass. The biomass-based bioplastics are prepared by introducing various amounts (1-40 wt%) of low-carbon sugars as plasticizers and compounding the mixtures. We use a design of experiments to guide the formulations and processing conditions for each mixture. Specifically, we vary heating time, temperature, and shear stress in the extrusion process. The effects of varying the plasticizer amount and altering the processing parameters on the micro-morphology, mechanical and thermal properties of the produced bioplastics are characterized. We study the biomass particle morphology before compounding, through scanning electron microscopy (SEM). After the extrusion process, the bioplastic films are evaluated in terms of micro-morphology again through SEM, and their crystalline features are examined through X-ray diffraction (XRD). Tests are conducted to characterize the mechanical properties of the bioplastics (modulus, strength, elongation to break) and thermal stability is assessed through thermogravimetric analysis (TGA). The processing parameters as well as composition of the prepared bioplastics are correlated to the measured mechanical properties. Finally, a biodegradation assessment of the prepared bioplastics is conducted through characterizing their mass loss profiles during soil burial tests.

SYMPOSIUM

April 11 - April 26, 2023

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SESSION EN11.01: Radiative Cooling I
Session Chairs: Po-Chun Hsu and Chenxi Sui
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2005

10:30 AM *EN11.01.01
All-Day Passive Radiative Cooling for Future Clean Energy Technology Junsuk Rho; Pohang University of Science and Technology, Korea (the Republic of)

With the ever-increasing consciousness of the energy crisis and global warming issues, passive cooling methods that use free and renewable energy sources have been pursued recently. Radiative cooling is an efficient passive cooling strategy that dissipates excessive heat to the universe through thermal radiation. In particular, all-day passive radiative cooling has offered an even larger spectrum of energy-saving applications by suppressing solar absorptivity under solar irradiation. In this talk, we present our recent research progress on all-day passive radiative cooling for practical applications as well as for improved cooling performance. Firstly, we discuss the inverse design of daytime radiative cooling for high performance [1]. The design of a selective multilayer emitter was optimized by a genetic algorithm, and we achieved highly suppressed solar absorption, thereby, high-performance radiative cooling under direct sunlight. We then discuss the efforts to promote the implementation of radiative cooling for real-world applications. We first discuss the realization of all-day radiative cooling devices on a large scale to address practical issues [2-4]. By using silica-coated porous anodic aluminum oxide, we developed a centimeter-scale radiative cooling device demonstrating a maximum cooling of 6.1 °C below ambient during the daytime [2]. We also developed large-scale radiative cooling devices in particle mixture coating format [3]. By further analyzing the effect of each particle on radiative cooling performance, we report a large-scale paint-format radiative cooling device with high performance [4]. Such particle-based devices allow the use of facile one-step and cost-effective fabrication methods, providing the potential for large-scale production and applications. Finally, we present radiative cooling devices with practical functionalities, including transparency [5] and switchability [6]. We discuss a transparent radiative cooling device that transmits visible light reflects near-infrared light and radiates thermal energy to lower the temperature during the daytime while maintaining transparency [5]. Such a transparent can be used for eco-friendly cooling windows in vehicles or buildings. We then discuss a switchable radiative cooling device according to temperature [6]. By exploiting the changeable material properties of vanadium dioxide in response to temperature, we achieved a temperature-adaptive radiative cooling device that radiates thermal energy only when the temperature is above the phase transition temperature.

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11:00 AM EN11.01.02
Hierarchically Patterned Self-Cleaning Polymer Composites for Daytime Radiative Cooling Kai Zhou[1], Xiao Yan[1], Seung Oh[2], Gabriela Padilla-Rivera[2], Hyunjung Kim[2], Donald Cropek[2], Nenad Miljkovic[1] and Lili Cai[1]; [1]University of Illinois at Urbana Champaign, United States; [2]Army Construction Engineering Research Laboratory, United States

Exposure to outdoor heat stress threatens the health of humans taking outdoor physical activities, while the open nature of outdoor activities makes it impractical to use traditional electrical cooling methods. Passive daytime radiative cooling (PDRC), which uses intrinsic optical properties to achieve passive cooling without consuming electricity, has been proposed and developed to tackle outdoor cooling challenges in recent years. PDRC selectively achieves high solar reflectivity and utilizes the fact that the thermal emission can go through the sky window (in the wavelength range of 8—13 µm) into the cold universe (~3 K). However, outdoor PDRC materials are susceptible to environmental contamination, including solid microparticles and water accumulation. Such surface contaminants severely decrease the cooling efficacy, requiring routine cleaning to recover; also, for the PDRC textile worn by humans, aesthetic purposes make the daily dust cleaning necessary. In order to minimize cleaning labor, self-cleaning has been integrated with PDRC. However, commonly used methods to combine self-cleaning with PDRC materials involve adding fluorinating chemicals like polytetrafluoroethylene (PTFE) into the radiative coolers, and their fabrications are usually complex and expensive. A simple, cost-effective strategy to combine self-cleaning with radiative cooling is needed. Here, we develop a hierarchically patterned nanoporous composite (HPNC) using a facile template molding fabrication method to integrate PDRC materials with self-cleaning and antibacterial functions. The HPNC design decouples multifunctional control into different characteristic length scales that can be optimized simultaneously. Using a nanoscale porous polymer matrix and tunable particle fillers to tailor the radiative cooling properties, the HPNC samples enable >7.8°C temperature reduction for outdoor cooling of the human body and 4.4°C sub-ambient cooling for building applications under intense solar irradiance. Meanwhile, a micro-scale pillar array pattern integrated into the HPNC enables superhydrophobicity with self-cleaning and anti-soiling functions to mitigate surface contamination. Moreover, the HPNC design allows for the incorporation of nanoparticles for additional functionality. Here, we embed and coat photocatalytic agents to generate effective photoinduced antibacterial effects. The scalable fabrication and multifunctional capabilities of our HPNC design offer a promising solution for practical daytime radiative cooling applications with minimal maintenance needs.

11:15 AM EN11.01.03
A New Instrument for Angularly and Spectrally Resolved Radiative Emission Measurements of Radiative Cooling Structures Magel Su[1], Gunnar Nelson[2], Himashi Andaraarachchi[2], Parker Wray[1], Uwe Kortshagen[2] and Harry A. Atwater[1]; [1]California Institute of Technology, United States; [2]University of Minnesota, United States

Research on terrestrial radiative cooling has yielded a large volume of theoretical and experimental results for many designs, including thin film multilayer stacks, nanoparticles, and metaphotonic structures, which are capable of passive radiative cooling. However, the most widespread method of characterizing radiative cooling is in an uncontrolled and poorly calibrated outdoor ambient. Direct measurement of the spectral and angular distributions of radiative emission simultaneous with sample surface temperature measurements are thus urgently needed by the community to facilitate inter-comparisons between radiative emission measurements and radiative cooling performance.
Here, we report measurements obtained using a calibrated and extensively modeled custom-designed radiative emission apparatus capable of simultaneous measurements of surface temperature and spectral- and angular-resolved radiative emission. This instrument enables simulation of outdoor ambient environments under well-controlled laboratory conditions. In terrestrial radiative cooling, surfaces are cooled by radiating thermal heat from the terrestrial ambient environment to the cold ambient of space directly through the atmospheric transmission window (8 – 14 µm), while also reflecting sunlight (0.3 – 2 µm) to prevent parasitic solar heat absorption. To simulate an outdoor ambient environment exposed to the clear sky our design utilizes a cryoshroud to simulate the cold ambient of space (2.7 K), a solar simulator, thermoelectric heating elements to control the ambient sample temperature under high vacuum (<1e-9 Bar) as well as ambient conditions, and insulating stage design to reduce convective/conductive heat loss mechanisms. COMSOL thermal and radiation modeling was used to validate our test apparatus design simulating closely outdoor ambient conditions.
We also present thermal and radiative emission results for a nanoparticle-based radiative cooling structure in this instrument, comparing silicon dioxide (SiO_2) and/or silicon nitride (Si_3N_4) nanoparticle films with planar thin film multilayer structures for application in large-scale terrestrial radiative cooling. Nanoparticle films exhibit radiative cooling powers of over 60 W/m^2 at 300 K.

SESSION EN11.02: Radiative Cooling II
Session Chairs: Ting-Hsuan Chen and Yi Long
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2005

1:30 PM *EN11.02.01
Hybrid Evaporative Radiative Cooling for Large Energy Savings Zhengmao Lu[1,2], Arny Leroy[2], Lenan Zhang[2], Jatin J. Patil[2], Evelyn Wang[2] and Jeffrey C. Grossman[2]; [1]EPFL, Switzerland; [2]MIT, United States

Passive cooling technologies can be a game changer for addressing global cooling demand, where standalone evaporative or radiative cooling methods have already shown much promise. However, they often face challenges associated with water consumption, solar absorption, parasitic heating, low cooling power, and humidity constraints. Here, we present a hybrid evaporative-radiative cooling architecture that addresses these previous shortcomings. The structure consists of a solar reflector, a water-rich and IR-emitting evaporative layer, and a vapor-permeable, IR-transparent, and solar-reflecting insulation layer. We showcased this concept with the enhanced specular reflector, the polyacrylamide hydrogel, and the polyethylene aerogel as the three layers, respectively. In Cambridge, MA, USA, we demonstrated 9.3 °C below the ambient under direct sunlight. With minimal water expenditure, our sample consistently stayed below the wet bulb temperature, which is not possible with pure evaporation. Under the same weather condition, we showed 300% enhancement over a state-of-the-art radiative cooler in daytime cooling power. Further, we show that hybrid evaporative radiative cooling offers large energy-saving opportunities in food storage and building thermal management applications for a wide range of climate conditions.

2:00 PM EN11.02.02
Design Transparent Radiative Cooler using Quantum Computing-Assisted Active Learning Seongmin Kim[1], Wenjie Shang[1], Seunghyun Moon[1], Trevor Pastega[1], Eungkyu Lee[2] and Tengfei Luo[1]; [1]University of Notre Dame, United States; [2]Kyung Hee University, Korea (the Republic of)

Passive radiative coolers, which allow emitting radiation through an atmospheric window ($8 < \lambda < 13$ µm), have attracted much attention as a solution to climate change issues, owing to their potential in energy- and refrigerant-free cooling capability. In particular, transparent radiative cooler (TRC) that has high transmission in visible light and high emission in the atmospheric window has been developed for energy-saving windows. However, it is difficult to design a high-performance TRC with high visible transparency along with high ultraviolet and near-infrared reflection and high cooling capability. In this work, we design a visibly transparent radiative cooler using a quantum computing-assisted active learning design scheme that combines machine learning, quantum annealing, optical simulation, and on-the-fly dataset acquisition in one iteration. The optimally designed cooler has high visible light transmission and low ultraviolet and near-infrared light transmission to maximize cooling performance, and high emission in the atmospheric window range. We experimentally demonstrate the optical properties of the designed cooler and demonstrate its passive cooling ability under dynamic environments by field experiments. The field testing results show a temperature reduction of up to 6.1°C when using our fabricated TRC compared with common glass. In addition, we calculate the energy saving for cooling when a standard room uses our designed cooler instead of normal windows, and the results show that the cooler can lead to a potential energy saving of ~86.3 MJ/m^2 annually in hot regions. We believe that the designed TRC can be applied for energy-saving windows and the quantum computing-assisted active learning scheme can be efficiently used for functional material design in general.

2:15 PM EN11.02.03
Superhydrophobic Hierarchical Polymer Film for All-day Passive Radiative Cooling Atmospheric Water Harvesting Zhizhong Cheng[1], Yaerim Lee[1], Ahmet A. Günay[1,2], Jiang Guo[1], Sivasankaran Harish[1] and Junichiro Shiomi[1]; [1]The University of Tokyo, Japan; [2]Middle East Technical University, Turkey

Passive radiative cooling atmospheric water harvesting (PRC-AWH) is a promising alternative to overcome water scarcity issues as an energy-saving technique. However, it is a challenging task to ensure all-day PRC-AWH operation. Here, we report a self-cleaning, scalable, flexible, and optically effective hierarchical polymer film to achieve continuous (all-day) PRC-AWH which exhibits high solar reflectivity, high emissivity, and a high water uptake performance. Owing to its unique hybrid photonic and hierarchical structured surface, the polymer film exhibits high solar reflectivity and ideal infrared emissivity, and achieves superb average subcooling throughout the day. Outdoor tests demonstrate that daytime PRC-AWH is realized in natural weather conditions to collect large amounts of water from the atmosphere. Controlled environment tests further elucidate the droplet capture mechanisms that contribute to the performance enhancement with the use of hierarchical structures at both micro and macro scales. Besides, the hierarchical structures ensure the surfaces to achieve superhydrophobic surfaces where the dust collected on the surface is cleared out by the condensed droplet to keep it clean at all times. Our results demonstrate that such a hierarchical polymer film shows great potential of all-day PRC-AWH that can at least double the yield of water, while removing and collecting water passively and efficiently.

2:30 PM *EN11.02.04
Integration of Radiative Roof Cooling Coating into Buildings as a Zero-Energy Cool Roof Strategy in Hot and Humid Region Lin V. Lu; The Hong Kong Polytechnic University, Hong Kong

Radiative sky cooling has attracted worldwide attention due to its passive cooling potential with zero energy input. Daytime cooling materials with outstanding spectral properties are developing rapidly. Using these new cooling materials as roof coatings can become one of the most prominent radiative cooling methods integrated with buildings. Current existing models and numerical tools are not able to incorporate the spectral selectivity of radiative cooling materials and local precipitable water vapor, thus failing to accurately predict roof thermal performance. Therefore, we newly develops a spectral selectivity-based passive radiative roof cooling model to integrate full spectral properties of emerging cooling materials and consider precipitable water vapor-induced atmospheric radiation for precise evaluation of roof cooling performance. A field experiment was carried out to validate the developed model. The new spectral selectivity-based radiative roof cooling model can be widely employed to accurately evaluate the utilization of daytime radiative coolers as a rooftop strategy in improving building thermal and energy performance. The energy consumption assessment of buildings with radiative roof cooling coating as a zero-energy cool rooftop strategy in hot and humid region, such as Hong Kong, is conducted. Findings can help local policy makers implement cool roof scheme into low-energy building strategy.

3:00 PM EN11.02.05
Radiative Cooling Walls with Asymmetric Emissivity for Building Envelope Qilong Cheng and Yuan Yang; Columbia University, United States

Passive daytime radiative cooling (PDRC) is an attractive electricity-free approach to reducing energy consumption of buildings by reflecting sunlight [wavelengths (λ) ~ 0.3 to 2.5 μm] and emitting infrared radiation (IR) through the atmospheric transparency window (ATW: λ ~ 8 to 13 μm) to the cold sky. Current PDRC research focuses on roofs, but limited attention has been paid to the walls, which occupy a major portion of building envelopes. Unlike the roofs, the walls face both cold sky and hot ground, so either high emissivity or low emissivity is not the best solution. Here we develop a scalable cooling wall with asymmetric emissivity. The wall can simultaneously reflect the thermal radiation from the hot ground and remain emissive to the cold sky, to achieve further building cooling and even sub-ambient cooling, which are demonstrated by simulations and experiments. Such asymmetric emissivity leads to further cooling of ~100 W m^{-2} than conventional walls at a ground temperature > 50 °C, and shows temperature drops of 3.1 °C (peak) / 2.3 °C (daily average) compared to the control wall in the field tests. Taking the United States as an example, the proposed zigzag wall can work effectively over 29% area and benefit 45% population, providing up to 27 MJ m^{-2} year-round saving per wall area for a typical midrise apartment building.

3:15 PM BREAK

SESSION EN11.03: Refrigeration
Session Chairs: Genesis Higueros and Po-Chun Hsu
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2005

3:45 PM EN11.03.02
Moisture Thermal Battery with Autonomous Water Harvesting for Passive Electronics Cooling Jian Zeng[1,2], Renkun Chen[3] and Ravi Prasher[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States; [3]University of California, San Diego, United States

Electronics will consume ~ 20.9% of global electricity by 2030, all of which will end up as heat. Data center alone requires ~ 2.1×10^{11} kWh of cooling load and ~ 1591 billion gallons of water yearly. Passive cooling of high-power electronics with minimum energy and water input is thus critical for the global water-energy nexus but has been challenging due to the large fluctuation in heat loads between the on-/off-peak hours. The thermal fluctuation could be mitigated by latent heat cooling. In this work, we develop a moisture thermal battery (MTB) by coating superabsorbent hydrogel on to a pin fin heat sink with large surface. The MTB leverages large latent heat and high thermal conductance of water evaporation for electronic cooling during on-peak hours and importantly, autonomously harvest atmospheric moisture and store the water during off hours. The MTB provides thermal capacity up to ~ 200 kWh m^{-2} for evaporative cooling with a record-high effective heat transfer coefficient up to ~ 1000 W m^{-2} K^{-1} for a passive device (no external power). The MTB was also demonstrated to suppress temperature fluctuation of a high-power field effect transistor and a computer CPU between the on- and off- peak hours by ~ 15 K, indicating its potential broad applications for autonomous water harvesting and cooling for a wide range of electronic devices with high heat loads.

4:00 PM EN11.03.03
Temperature and Humidity Control Using Lower Critical Solution Temperature (LCST) Mixtures Jordan Kocher and Shannon Yee; Georgia Institute of Technology, United States

Traditional air conditioning systems contribute significant greenhouse gas (GHG) emissions throughout their lifetimes, with roughly one third coming from the refrigerant, one third coming from energy consumption for temperature control, and one third from energy consumption for humidity control. There exists a need to create air conditioning systems that consume less energy and do not use high global warming potential (GWP) refrigerants. Aqueous mixtures that possess lower critical solutions temperatures (LCSTs) will mix with water when below the LCST and separate into a two-phase mixture above the LCST. This allows for the creation of a new air conditioning cycle. The first process in this cycle uses low-grade heat to cause the LCST mixture to separate into a phase that is water-rich and a phase that is water-scarce. Those two phases are then physically separated and cooled back down to ambient temperature. Due to its high chemical potential, the water-rich phase can desorb water into the outdoor air, which produces indirect evaporative cooling that can be provided to a building. Meanwhile, the low chemical potential of the water-scarce phase allows it to absorb moisture from building air, thereby providing dehumidification. After this, the two phases are reheated to once again induce phase separation and repeat the cycle. We have performed a step-wise demonstration of this new cycle with several different LCST mixtures and regeneration temperatures less than 100 C. We rank the LCST mixtures based on their effectiveness in this particular application. However, all of the mixtures fall short of reaching the conditions required for building thermal comfort; namely, the water-scarce phase is unable to dehumidify air to sufficiently low humidities. This demonstrates the need to discover new aqueous LCST mixtures that can provide superior performance when used in this cycle. In particular, we show that more effective LCST mixtures would have more negative enthalpies and entropies of mixing. The discovery of these new mixtures would enable an air conditioning cycle that is driven by inexpensive, low-grade (i.e., solar) heat, consumes no water and very little electricity, and uses no high GWP refrigerants.

4:15 PM EN11.03.04
Passive Freezing Desalination driven by Radiative Cooling Xin Huang and Aaswath Raman; UCLA, United States

With global temperature rises posing fundamental economic, health, and security risks to human civilization, maintaining habitable built environments has emerged as one of our times' most pressing challenge. Passive radiative cooling in particular has emerged as a promising technology, driven by a net radiative heat loss to cold outer space via the atmospheric transmission window in the long-wave infrared (LWIR) wavelengths. However, its potential for generating and remediating water remains an open frontier for research. Indeed, with increasing water scarcity there is now significant interest in finding lower-cost ways to generate fresh water. At the same time, many industrial processes, including oil and gas production, produce high-salinity wastewater that requires remediation.

Conventional desalination processes, including membrane-based and thermal desalination approaches, require large energy inputs which can become prohibitive as salinity increases. Alternatively, the most commonly used passive thermal desalination method is solar desalination which uses the sun as the heat source in an evaporation-condensation cycle. However, weather conditions and solar insolation limit its applicability throughout the year.

Here, we propose a passive approach to a more thermodynamically attractive phase change that can also enable desalination: freezing. In particular, we use radiative cooling to enable passive freezing desalination for the first time. We experimentally demonstrate passive desalination of 37.3 g/L salt water to 1.88 g/L after two radiative cooling-driven freezing desalination stages, with 50% recovery and 17.5 g/L salt water to 0.7 g/L after two radiative cooling-driven freezing desalination stages, with 65% recovery. We develop and validate a thermal model that accurately predicts the performance of the system and extend it to probe the theoretical limits of performance. These results demonstrate that passive freezing desalination driven by radiative cooling could fundamentally enable new technological possibilities for desalination. Further, this could be a complementary method to solar desalination to enable 24-hour, year-round passive thermal desalination.

SESSION EN11.04: Poster Session I
Session Chairs: Sungyeon Heo and Po-Chun Hsu
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN11.04.01
Comprehensive Design Characterization Towards Optimization of Microparticle-Polymer Composite Radiative Cooling Paint Jooyeong Yun[1], Dongwoo Chae[2], Heon Lee[2] and Junsuk Rho[1]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Korea University, Korea (the Republic of)

Passive daytime radiative cooling (PDRC) technology achieves cooling effect by reflecting incoming solar flux and enhancing thermal radiation in the atmospheric transmission window. The trait to operate without any consumption of energy offers great potential as a future energy-saving technology and has attracted substantial interest in many research communities. Among many PDRC structures, random dielectric particles or paint-like coatings have shown powerful radiative cooling performances with excellent scalability and easy fabrication. In this work, we provide a rigorous analysis of the optical properties and radiative cooling performances of PDRC paints comprised of two-material particles, SiO_2 and Al_2O_3 by using 2D FDTD simulation study. We investigate the effects of design variables of particle size parameters, size distribution, binder volume ratio and coating thickness. We then conduct an outdoor cooling measurement of the fabricated PDRC devices to show the radiative cooling potential of our PDRC paint and to analyze and understand its performance based on our numerical investigations. The fabricated PDRC paint exhibited high solar reflectance of 0.958 and strong long wave infrared emission of 0.937 in the atmospheric transparency window achieving maximum temperature drop of 9.1°C. This comprehensive study provides understanding of complex physical relations of materials and structure parameters of the PDRC paint system. This will be an intuitive guidance for researchers to find the optimal design conditions of PDRC paints and to engineer them to be applicable to various environment.

5:00 PM EN11.04.02
Nano-to-Macro Design of Ultra-scalable Hygroscopic Hydrogels for High-Performance Water Capture Carlos D. Diaz, Zhengmao Lu, Kezia Hector, Miles Roper, Xinyue Liu, Gustav Graeber, Leon Gaugler, Evelyn Wang and Jeffrey C. Grossman; Massachusetts Institute of Technology, United States

Hygroscopic hydrogels have recently emerged as low-cost and scalable sorbent materials for a wide range of applications including passive cooling, thermal energy storage, building dehumidification, and atmospheric water harvesting. Despite extensive efforts in the synthesis of novel hydrogels, their performance, as quantified by their a) water uptake and b) sorption kinetics, remains limited. Moreover, the rational engineering of hygroscopic hydrogels has been largely unexplored, hindering their optimization for sorption applications. In this work, we leverage physical models we have developed to enable the hydrogel design across different length scales, ranging from the polymer network scale to the macroscopic material scale, for high-performance water sorption. Specifically, we demonstrate a) high water uptakes of 1.74 g/g at 30% RH, exceeding by 15% previous state-of-the-art hydrogels, achievable by maximizing the salt content during synthesis, and b) the impact of polymer nanostructure on sorption kinetics, providing a path to fast kinetics by adequately engineering the polymer network. By simultaneously improving uptake and kinetics, our results demonstrate superior hygroscopic hydrogels which can enable high-power density thermal energy storage, efficient passive cooling, and large-scale water harvesting.

5:00 PM EN11.04.04
Solar-Thermal Hybrid Concept of Energy Harvesting in Rural Africa Derick C. DeTellem, Sarah Abdallah, Christian Coris, Clayton Baker and Sarath Witanachchi; University of South Florida, United States

In this paper we are reporting the results from an experimental project conducted in Africa to combine the energy harvested with solar cells with energy harvested from waste heat to charge a 12V battery to provide portable electricity for day-to-day use in rural Africa. Communities in rural Africa burn wood for their cooking needs. Most of the heat generated is wasted to the environment. While silicon solar cells have the potential to generate significant currents based on the solar radiation intensity, voltages generated by a single solar cell is limited. On the other hand, thermoelectric modules that convert heat into electricity generates high voltages, but the current is limited by the intrinsic properties of the thermoelectric materials. Under the new hybrid concept, thermoelectric modules generated high voltages from waste-heat while silicon solar cells generated high currents. The hybrid of the combination in a unique configuration has resulted in power outputs that are much higher than the added output of the individual devices. The circuit design, the IV-characteristics, and the conditions for optimum power generation in the hybrid configuration will be presented. The project was supported by an NSF IRES grant.

5:00 PM EN11.04.05
A Unified Multiscale Understanding of Sorption-Based Atmospheric Water Harvesting Yang Zhong, Lenan Zhang, Xiangyu Li, Bachir El Fil, Carlos D. Diaz, Chenyang Li, Xinyue Liu, Alina LaPotin and Evelyn Wang; Massachusetts Institute of Technology, United States

Sorption-based atmospheric water harvesting (SAWH) is the extraction of water vapor in the atmosphere using sorbent materials to deliver point-of-use drinking water directly from the air. With the advances of materials innovations, SAWH devices can operate in a broad spectrum of relative humidity, which opens new avenues to address water scarcity faced by two-thirds of the world's population. Although substantial progress has been made to enable sustainable SAWH, there is still a giant barrier between fundamental studies and real-world applications. Here, we develop a unified multiscale understanding to develop SAWH technologies by bridging the material insights to device optimization. First, we elucidate fundamental water sorption mechanisms, key material properties, and vapor diffusion regimes. To fill the gap between the materials and devices, the physical insights gained at the material level are translated into the optimization principles through heat and mass transfer at the device level. Then, we show the interplay of material and device design can lead to new opportunity space toward the thermodynamic limits of SAWH systems. Finally, we perform a techno-economic analysis to evaluate the economic feasibility of SAWH technologies and envision the impact of large-scale SAWH on the worldwide water economy and environment. Our work provides a unified understanding of SAWH technologies, which can lead the way to the practical development of SAWH at different length scales and its broader global impact.

SESSION EN11.05: Radiative Cooling III
Session Chairs: Sungyeon Heo and Po-Chun Hsu
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2005

8:15 AM *EN11.05.01
Physical Interpretation of Role of Optical Constants in Thermal Insulation and Heat Shielding Coating Hidefumi Odaka; AGC Asia Pacific Pte Ltd, Singapore

Zero Energy Building (ZEB) is a building with net zero energy consumption, meaning the total amount of energy used by the building on an annual basis is equal to the amount of renewable energy created on the site. In this realization, thermal insulation and heat shielding throughout window are considered to be one of the important factors to realize it. Depending on the climate and environment where the buildings are built, appropriate glazing windows are designed to decrease the energy usage. For example, low U value and low Solar Heat Gain Coefficient (SHGC) are required in in the regions with large differences in summer and winter temperature. Low Overall Thermal Transfer Value (OTTV) is necessary in the land of everlasting summer to save the energy consumption by air conditioner. In addition to it, the designing of visible transmittance is attracting much attention to save the lighting energy of building especially in the green building rating of Leadership in Energy and Environmental Design (LEED) and Thai's Rating of Energy and Environmental Sustainability (TREES).

In order to meet the above requirements, many coating technologies have been invented. Atmospheric pressure CVD is used for making transparent conductive film, mainly composed of tin oxide, to make heat shielding window. Sputtering method is applied for making not only Ag-based Low-E with thermal insulation window but also reflective coating for heat shielding, where many stacks are used to control interference of light from visible to infrared region. As a result, optimized window is made, which meet the requirement of customer.

In this presentation, representative products for thermal insulation and heat shielding are reviewed, which is used in business. Then, some physics that determine optical constants, common to Ag, transparent conductive materials and TiN, are discussed from the standpoint of band structure of these materials. It is shown that the inter-band and intra-band transition can explain the origin of optical constants, with the only difference being the contribution of these transition. Finally, optical property of Ag-based Low-E and reflective coating made of TiN are discussed using matrix formalism of electric field intensity of light. In the anti-reflection coating for lens, dielectric materials with large difference in optical constant are stacked to achieve low reflection. On the other hand, both real and imaginary part of the optical constant play an important role to control the light in Ag-based Low-E and reflective coating made of TiN. The meaning of optical constant will be discussed relating to SHGC and OTTV. These phenomena are also discussed using electric field intensity in the multi-layer stack of in Ag-based Low-E and reflective coating made of TiN.

SESSION EN11.06: Dynamic Building Envelopes I
Session Chairs: Sungyeon Heo and Po-Chun Hsu
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2005

9:00 AM *EN11.06.01
Light and Thermal Management by the Kirigami-Based Dynamic Shading Envelopes Heesuk Jung[1,2], Miaomiao Hou[3], Byungsoo Kang[2], Zherui Wang[1], Hyo-jeong Choi[4], Phillip Lee[2], Dorit Aviv[1], Hyeok Kim[4] and Shu Yang[1]; [1]University of Pennsylvania, United States; [2]Korea Institute of Science and Technology (KIST), Korea (the Republic of); [3]Tongji University, China; [4]University of Seoul, Korea (the Republic of)

Conventional heating, ventilation, and air conditioning (HVAC) systems in buildings not only consume substantial energy but increase the heat-trapping gases in the atmosphere, which further aggravates global warming. To improve building energy efficiency and thus reduce negative environmental impacts, we investigate kirigami structures as adaptive building envelopes as a promising alternative to manage building heating and cooling. Numerical simulations are performed to study the mechanisms of light and thermal modulation by the kirigami-based dynamic envelopes by taking into consideration of building locations and occupants needs. We then design outdoor test chambers with thermo- and lux- sensors installed outdoor to demonstrate the effect of kirigami structures with variable cut dimensions on light modulation and temperature inside of chambers. By comparing experimental results and simulation, we gain insights to optimize indoor light and heat management by fine-tuning kirigami designs.

9:30 AM *EN11.06.03
Versatile Electrochromic Platforms for Energy Applications Hong Chul Moon; University of Seoul, Korea (the Republic of)

Multifunctional systems serving simultaneously as two or more devices have attracted significant attention owing to the high integration of electronic devices in cutting-edge technologies. In this work, we introduce the versatile use of electrochromism including thermal management and energy storage. In particular, we are going to describe all-in-one type, single-layer device platforms based on solid-state ionic conductors. It also covers effective strategies to tune electrochromic performance.

10:00 AM BREAK

10:30 AM EN11.06.04
Using Reversible Metal Electrodeposition in Windows to Improve Energy Efficiency and Control Natural Lighting Michael D. McGehee[1], Andrew Yeang[1], Yuchun Cai[1], Gabriel McAndrews[1] and Christopher Barile[2]; [1]University of Colorado, United States; [2]University of Nevada, Reno, United States

Dynamic windows with adjustable tint give users control over the flow of light and heat to decrease the carbon footprint of buildings and improve the well-being of the people inside them. Despite the benefits of dynamic windows, they are deployed in less than 0.004% of commercial building space because the existing technology cannot achieve fast and color-neutral tinting at an agreeable cost. Reversible metal electrodeposition (RME) is a promising approach to solve the problems plaguing the current generation of dynamic glass. Here, we demonstrate the use of polymer inhibitors to reversibly deposit metal films with controlled morphology in dynamic windows. The dynamic windows that employ the polymer inhibitor can readily tint to below 0.001% visible transmittance in less than 3 minutes and exhibit high infrared reflectance (>70%), color-neutral transmittance ($C^* < 5$), and a wider range of optical and solar modulation than any existing technology. The polymer inhibitors also increase efficiency and improve the durability of the windows and enable construction of 1 ft.^{2} dynamic windows with fast response and excellent uniformity.

10:45 AM EN11.06.05
Bioinspired Building Envelop with Lightweight, Unltra Thermal Conductivity, High Energy Dissipation and Fire Resistance Fengyin Du[1,2], Tian Li[2] and Changwen Miao[1]; [1]Southeast University, China; [2]Purdue University, United States

Multiple hazards including impact load, heat damage and fire shock arising from extreme weathers usually bring life-threatening problems to residents. To prevent these threatens, expecially those caused by mechanical-thermal-fire coupled damage, urgently needs the construction of versatile preotective building materials. Herein, we develop an effectvie approach to engineer a bioinspired cement wood with a hierarchical structure through self-assembling cement in polymeric solution. This emerging cement wood demonstrates a unique combination of light weight, high stiffness, superior thermal insulation, remarkable energy dissipation and good fire resistance. When appied as building envelop, the prepared cement-based material can dissipate impact energy and block heat diffusion to block the spread of fire, therefore significantly reducing the risk of property damage or bodily injuries.

11:00 AM EN11.06.06
Dynamically Synergistic Solar and Mid-Infrared All-Season Radiative Thermoregulation Based on Reversible Metal Electrodeposition Chenxi Sui and Po-Chun Hsu; The University of Chicago, United States

The coldness of the deep universe and the hotness of the sun have been considered renewable thermodynamic resources for sustainable thermoregulation. How to utilize both resources showed drastic improvement in the past decade, enabled by the plasmonic and nanophotonic research. Remarkably, the rational photonic and thermal design has pushed forward the power and efficiency of daytime radiative cooling. In this presentation, we will introduce our recent research progress on electrochemical devices that can electrically switch between solar heating and radiative cooling states, by reversibly electrodepositing metal on graphene. Such a non-trivial and opposite spectral tuning requires the fabrication of the ultra-wideband transparent conductive electrode, which is transparent in both solar and mid-IR regimes, and the precise control of the plasmonic nanoparticles' morphology during the reversible metal electrodeposition. With the optimization of every device component, this device can maximize its solar reflectivity at the cooling state and minimize its thermal emissivity at the heating state, and thus can serve as the smart building envelope for year-round HVAC energy saving. Ideally, the device can help buildings save 19.2% of HVAC energy across the United States, based on the building energy simulation results. The durable electrodeposition and broad-band spectral tuning are confirmed by the DFT simulations and effective medium theory. In addition to the synergistic solar and mid-IR dual-band tuning, our electrochromic device can tune the thermal emissivity with 0.85 contrast based on non-volatile and reversible metal electrodeposition, bringing vast opportunities for applications in space heat management, and thermal camouflage.

11:15 AM EN11.06.07
Progress in Energy Saving Thermochromic Smart Window Yi Long; The Chinese University of Hong Kong, Hong Kong

Thermochromic material responds to solar spectrum differently at the stimulus of heat which makes it attractive in the energy saving smart windows application due to its rational response, simple set up and passive response. The most studied inorganic VO_2 has the intrinsic problems of low luminous transmission (T_{lum}) and low solar modulation (ΔT_{sol}) the transmission difference between high and low temperatures). Numerous efforts such as employing dopings, nanoparticle-based composites, and nano-porous structuring have been widely studied. Our group have developed five new approaches to tackle this veritable challenge, namely, biomimetic nanostructuring including photonic structure and moth eye gridded structures tunable plasmonic structures organic and hybrid structures. In addition, new active controls has also been applied to thermochromic material to generate a new electro-thermochromics or mechanical-thermochromic materials. A very recent new liquid window and RC regulation smart windows will be presented.

11:30 AM *EN11.06.08
Infrared Metamaterials from Plasmonic Metal Oxide Nanocrystals Delia Milliron; The University of Texas at Austin, United States

Metal oxide nanocrystals doped with a few percent of aliovalent dopants become electronically conducting and support strong light-matter interactions in the infrared due to localized surface plasmon resonance (LSPR). At the same time, they remain wide bandgap semiconductors, so they are transparent to visible light, offering unique opportunities to selectively control lighting and manage thermal energy. In nanocrystals of the prototypical material tin-doped indium oxide (ITO), for example, the strength and spectrum of light absorption are tunable across the mid- and near-infrared by varying the amount of tin incorporated during synthesis and, secondarily, the nanocrystal size. These nanocrystals are ideal building blocks for optical metamaterials, where the spectra of the components and the nature of the coupling between them determine the effective optical response. Two different assembly strategies illustrate the potential. First, thermoreversible gel networks of nanocrystals are fabricated where LSPR coupling controls the infrared optical spectrum and distribution of near-field hot spots. Second, superlattice films of ITO nanocrystals exhibit tunable epsilon-near-zero (ENZ) spectral windows depending on the mixing ratio between two components with distinct tin doping concentrations. An efficient computational method has been developed to interpret the optical spectra and enable design of metamaterials with targeted optical response.

SESSION EN11.07: Dynamic Building Envelopes II
Session Chairs: Po-Chun Hsu and Yi Long
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2005

1:30 PM *EN11.07.01
Temperature Adaptive Solar and Radiative Coating for Thermal Management of Terrestrial and Space Objects Jiachen Li, Kaichen Dong, Derick Tseng, Kai Xu and Junqiao Wu; University of California, Berkeley, United States

The sky is a natural heat sink that has been extensively used for passive radiative cooling of households. Materials with minimized solar absorption and maximized infrared emission have been realized for daytime radiative cooling. To further improve the overall energy saving of radiative roofs, we developed a mechanically flexible solid film that adapts its thermal emittance to different ambient temperatures at zero energy consumption. Our recent efforts have led to the fabrication of the temperature adaptive radiative coating (TARC) at large scale and low cost. Experiments and simulations show TARC outperforms existing roof coatings for energy saving in most climates. A similar, temperature adaptive solar coating (TASC) could be also envisioned that adapts its solar absorptance to ambient temperature. The TARCs and TASCs may also find broad applications in other markets such as vehicles, spacecraft/spacesuits, textiles, and electronics, the benefits of which have been confirmed by our simulations.

2:00 PM *EN11.07.02
Phase-Changing Copolymers for Thermoresponsive Transmittance Modulation Qibing Pei; University of California, Los Angeles, United States

Thermoresponsive materials exhibiting switchable transmittance via temperature change are useful for smart window applications. We have introduced solid-state thermoresponsive phase-changing copolymer films with large transmittance modulation between room and elevated temperatures. The copolymer films comprise two phase-separated co-monomers. By controlling the domain size and the crystallinity of the phase-changing domain, two distinct transmittance modulation modes are made possible. The first mode undergoes opaque-to-transparent transition from room to elevated temperatures, while the second has the opposite transition. The copolymer films are investigated for either electrically controlled opacity change or autonomous and climate-adaptable solar modulation.

2:30 PM BREAK

SESSION EN11.08: Personal Thermal Management
Session Chairs: Sumanjeet Kaur and Ronghui Wu
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2005

3:00 PM EN11.08.01
Facile Manufacturing of Breathable, Washable and Fabric-Integrated Squid-Inspired Thermoregulatory Composites Sanghoon Lee, Mohsin Ali Badshah, Erica M Leung, Panyiming Liu, Aleksandra A. Strzelecka and Alon Gorodetsky; University of California, Irvine, United States

Effective thermal management is critical for the operation of many modern technologies, such as smart clothing and food packaging. By leveraging the static infrared-reflecting design of the space blanket and drawing inspiration from the dynamic color-changing ability of squid skin, we have developed composite materials with tunable thermoregulatory properties specifically for these applications [1, 2]. Our composites demonstrated an on/off switching ratio of ~25 for the transmittance, regulate a heat flux of ≥ 30 W/m^2 with an estimated mechanical power input of ~ 3 W/m^2, and feature a dynamic environmental setpoint temperature window of ~ 8 °C [1]. Such composites moreover could be sustainably manufactured over large areas of ~ 0.3 m^2 at a low estimated starting material cost of around $ 0.1 m^{-2} [2]. We have now developed washable, breathable, and fabric-integrated variants of our composites that demonstrate the ability to withstand multiple wash cycles, feature air and water permeabilities similar to common fabrics, and maintain their desirable tunable thermoregulatory functionalities, respectively [3]. Due to their state-of-the-art figures of merit, our bioinspired composite materials hold potential as a platform technology for next-generation sustainable and wearable thermal management systems.

[1] E. M. Leung, M. C. Escobar, G. T. Stiubianu, S. R. Jim, A. L. Vyatskikh, Z. Feng, N. Garner, P. Patel, K. L. Naughton, M. Follador, E. Karshalev, M. D. Trexler, A. A. Gorodetsky. A dynamic thermoregulatory material inspired by squid skin. Nat. Commun. 10, 1497 (2019).
[2] M. A. Badshah, E. M. Leung, P. Liu, A. A. Strzelecka, A. A. Gorodetsky. Scalable manufacturing of sustainable packaging materials with tunable thermoregulability. Nat. Sustain. 5, 434 (2022).
[3] S. Lee, M. A. Badshah, E. M. Leung, A. A. Gorodetsky. Manufacturing of breathable, washable, and fabric-integrated thermoregulatory materials inspired by squid skin. In preparation.

3:15 PM EN11.08.02
Visibly Transparent and Infrared Reflective Coatings for Personal Thermal Management and Thermal Camouflage Ho Kun Woo[1], Kai Zhou[1], Su-

Kyung Kim[2], Adrian Manjarrez[1], Muhammad Jahidul Hoque[1], Tae-Yeon Seong[2] and Lili Cai[1]; [1]University of illinois, United States; [2]Korea University, Korea (the Republic of)

Tailoring thermal radiation using low-infrared-emissivity materials has drawn significant attention for diverse applications, such as passive radiative heating and thermal camouflage. However, the previously reported low-infrared-emissivity materials have the bottleneck of lacking independent control over visible optical properties. Here, we report a novel visibly transparent and infrared reflective (VTIR) coating by exploiting a nano-mesh patterning strategy with an oxide/metal/oxide tri-layer structure to realize. The VTIR coating shows simultaneously high transmittance in the visible region (> 80% at 550nm) and low emissivity in the mid-infrared region (< 20% in 7 – 14 µm). Our VTIR coating not only shows a radiative heating effect of 6.6 °C for indoor conditions, but also enables a synergetic effect with photothermal materials to keep human body warm at freezing temperatures for outdoor conditions, which is 10 – 15 °C warmer than normal cotton and Mylar film. Moreover, it demonstrates an excellent thermal camouflage effect at various temperatures (34 °C – 250 °C) and good compatibility with visible camouflage on the same object, making it ideal for both daytime and nighttime cloaking. With its unique and versatile spectral features, this novel VTIR design has great potential to make a significant impact on personal heat management and counter-surveillance applications.

3:30 PM EN11.08.03
Sweat-Responsive Continuous and Wide-Range Infrared Chromism in MXenes for Adaptive Textiles Keqiao Li, Yang Li and Baoling Huang; The Hong Kong University of Science and Technology, China

The dynamic control of infrared (IR) radiation from surfaces is highly desired in a variety of areas. In particular, smart textiles, which can passively cool/warm the human body by regulating the radiative heat exchange with the environment, have aroused significant interest. Unlike air conditioners, such smart textiles can locally regulate the skin temperature without heating/cooling the entire building interior space, which is more efficient and energy-saving. In addition to the modulation of IR emissivity (ε) in a continuous manner over a wide range, adaptive textiles need to satisfy other requirements in flexibility, wearability, and water/air permeability, making it challenging to realize. Here, we report an infrared chromism phenomenon found in stacked $Ti_3C_2T_x$ MXene nanosheets, where the emissivity varies in a wide range of 0.12 to 0.68 as the adsorption/desorption of physisorbed water within the interlayers of stacked nanosheets. This emissivity modulation is a continuous and reversible process without the assistance of any external device and energy input. By intercalating cellulose nanofibers into the $Ti_3C_2T_x$ interlayers, the stability of water adsorption is significantly enhanced, making the dynamic process highly repeatable. Based on this water-induced emissivity modulation, we demonstrate a sweat-responsive adaptive textile that can help the human body adapt to fluctuations in personal heat load. When the human body feels cold and keeps dry, the textile is in low-*ε* modes where thermal radiation of the human body outwards can be suppressed to keep warm; otherwise, the textile can switch to wet states and high-*ε* modes. The radiative heat dissipation is enhanced significantly for cooling the human body. Besides the application in personal thermal management, this strategy may also find opportunities in other scenarios requiring adaptive IR emissivity regulation, including IR camouflage and IR anti-counterfeiting.

3:45 PM EN11.08.04
Noninvasive Measurement of Core Body Temperature from the Human Forearm Gimin Park[1], Seungjai Woo[1], Kyomin Kim[1], Jiyong Kim[1], Sang Kyu Kim[2], Kogsoon Kwon[2], Hotaik Lee[2], Soyoung Lee[2], Sungho Kim[2], Hongsoon Rhee[2] and Woochul Kim[1]; [1]Yonsei University, Korea (the Republic of); [2]Samsung Advanced Institute of Technology, Korea (the Republic of)

The human core body temperature (CBT) is one of the most fundamental indications for determining a subject's health condition [1]. The traditional invasive method of measuring CBT is inserting a temperature probe into specific sites of the human body (*e.g.*, esophagus, rectum, axilla, and tympanic membrane). To overcome the downsides of invasive methods like discomfort and poor standards of hygiene, researchers have developed noninvasive CBT sensors including the zero-heat-flux sensor and the double sensor. The major drawback of these noninvasive CBT sensors is that they hinder the subject's operative capabilities as they must be attached to regions close to the internal organs (*e.g.*, forehead and thorax). In this study, we present a noninvasive method of determining the subject's CBT by gathering certain thermophysical data at the forearm (*i.e.*, the skin temperature, heat flux, and blood perfusion rate). Under a thermoneutral state, experimental data show that the CBT region extends out to the extremities, which includes the large arteries at the forearm. We have measured the surface temperature and heat flux with a resistance temperature detector and a thermopile heat flux sensor, respectively. Also, we have incorporated a way to measure the blood perfusion rate thermally *via* sinusoidal heating. With the measured data, solving the Pennes' bioheat equation in a heterogeneous medium to account for variability in tissue layers allows for the estimation of CBT within a few degrees. The study was performed on human subjects for a period of approximately forty minutes. One subject showed promising results with estimated average range of CBT of 0.73°C. For periods where the subject's actual CBT (axillary temperature) did not fall within the estimated range, the average deviation away from the actual CBT was only 0.24°C. This study leaps towards a more convenient way of gaining the subject's health condition.

[1] G. Park, J. Kim, S. Woo, J. Yu, S. Khan, S.K. Kim, H. Lee, S. Lee, B. Kwon, W. Kim, *Applied Energy* **323**, 119609 (2022)

4:00 PM EN11.08.05
Non-dispersive Production Strategy of Binder-Free Boron Nitride Slurry via Differentiation of Exfoliation, Amorphization and Functionalization Yujin Han, Hanhwi Jang and Yeon Sik Jung; KAIST, Korea (the Republic of)

Miniaturization and high-power consumption of modern electronic devices have led to local heat generation and accumulation issues, and as a result, demand for thermal dissipation technology has increased recently. Hexagonal boron nitride (BN) is recently highlighted as a material for thermal regulation due to excellent thermal conductivity ($750 Wm^{-1}K^{-1}$) with electrical insulation and thermal stability. In spite of the great advantages of superior thermophysical properties, poor interfacial interaction between BN nanosheets often degrades the collective functionality, and conventional approaches inevitably used an additive to compensate for the formability, but this severely diluted the BN's thermophysical properties. In this study, we report a highly effective non-dispersive binder-free BN slurry production method. The method is totally conversive without loss of materials, immediately applicable, and shows wide morphology variability by virtue of excellent dispersity and rheological characteristics. By adjusting hydrodynamic stress regimes and mechanochemical reaction conditions, we strategically differentiate the functionality of BN nanosheets into a physically exfoliated BN (p-BN) as a thermal conductive component and a mechanochemically treated BN (m-BN) as an interfacial adhesive component. Via finding an optimal ratio of p-BN and m-BN that maximize the thermophysical functionality and mechanical stability, the casted BNs exhibit excellent thermal conductivity (> $40 Wm^{-1}K^{-1}$,) with high adhesion energy over $3.8 J/m^2$ without any additive incorporation. Owing to systematically ordered microstructures with rich hydrogen bonding component, the casted BN is well-adhered to the heat exchange unit and successfully reduce working temperatures of the various device modules including high power LED, central processing unit (CPU) and Peltier module. Furthermore, confirmed by high temperature combustion and neutron radiography, the binder-free characteristic with rich boron contents in the casted BN film gives superior flame retardancy (> 900°C) and thermal neutron absorption ($>1.3x10^3 cm^{-1}$).

SESSION EN11.09: Poster Session II
Session Chairs: Sungyeon Heo and Po-Chun Hsu
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM EN11.09.01
Enhanced Thermal Performance of Selenides Compounds Synthesized by Ball Milling or the Pack Cementation Process Evangelia Tarani[1], Dimitrios Stathokostopoulos[1], Dimitris Karfaridis[1], Ioanna Sfampa[2], Fani Stergioudi[1], Nikolaos Michailidis[1], Konstantinos Chrissafis[1] and George Vourlias[1]; [1]Aristotle University of Thessaloniki, Greece; [2]KLEEMANN, Greece

The operation of the elevators inside and/or outside the buildings requires the installation of additional functions in the cabin. However, the use of conventional air conditioners has a detrimental effect on the construction level, energy consumption, noise level in the cabin, and the environment. An innovative method that can be applied alternatively in order to overcome most of these problems is the use of suitable thermoelectric air conditioners. In this direction, thermal storage plays a key role to lower building energy consumption. The thermoelectric materials community has made significant progress on nanostructured and process able materials to improve efficiency and flexibility, reducing manufacturing costs. Selenide compounds, such as Ag_2Se and Cu_2Se, have received a lot of attention because of their promising capabilities in thermoelectric applications. Additionally, Ag, Cu, and Se are less toxic than Bi, Pb, Sb, and Te, while Se is about 10 times more abundant than Te.
Two different methods for the synthesis of Ag_2Se and Cu_2Se compounds have been used. The first one is the high-energy ball milling (HEBM) process, which is a powerful solid-state synthesis/powder mechanical alloying method, using different milling times (1-20 hours). The second one is the simple, cost-effective, and eco-friendly technique of pack cementation. The structural and morphological characterization of the synthesized selenides was studied by Fourier Transform Infrared Spectroscopy, X-ray Diffraction, X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy. The thermal stability of the prepared samples was examined by Thermogravimetric analysis (TGA).
The synthesis of samples with the pack cementation method is the result of a reactive diffusion process due to the reaction of the donor materials with the products of the halide activator.

Acknowledgments:
This research was carried out as part of the project «Design and implementation of innovative lift's air-conditioning systems by using thermoelectric devices» (Project code: KMP6-0074109) under the framework of the Action «Investment Plans of Innovation» of the Operational Program «Central Macedonia 2014 2020», that is co-funded by the European Regional Development Fund and Greece.

5:00 PM EN11.09.02
Real-Time Manipulation of Multiphase Fluids Using Photo-Responsive Surfactants Xichen Liang, Kseniia Karnaukh, Lei Zhao, Serena Seshadri, Sophia J. Bailey, Michael Haggmark, Matthew Helgeson, Michael Gordon, Paolo Luzzatto-Fegiz, Javier Read de Alaniz and Yangying Zhu; University of California, Santa Barbara, United States

The manipulation of multiphase fluids has been identified as a crucial process for a variety of applications, including thermal management of buildings and electronics, power generation, desalination and bio-medical devices. While most previous works rely on passive control of fluid through artificial micro-/nanostructured surfaces, active methods using an electric, magnetic or thermal stimuli to control multiphase fluids offer real-time tunability and multi-functionality. However, existing methods typically rely on a high voltage (10-1000 V), a strong magnetic field (0.1 T), or a high temperature gradient generated by a high power source such as lasers. Here, we demonstrate dynamic control of liquid droplets in a multi-phase fluid system using light-sensitive surfactants that can induce large changes in the interfacial tension thereby exerting a photo-Marangoni force on a droplet. The surfactants are activated by visible light whose intensity is 1-2 orders of magnitude lower than the laser intensities used in thermal-capillary actuation. We characterize the magnitude and rate of change in interfacial tensions of various fluid-fluid systems. We also demonstrate fast and programmable movement of liquid droplet on liquid-infused-surfaces, inside microchannels, and on liquid substrates. Furthermore, we present a theoretical framework underlying the key parameters that contribute to the droplet motion. The results demonstrated in this work opens exciting doors for the use of photo-sensitive surfactants for dynamic manipulation of multiphase fluid systems for energy, building, thermal management and microfluidics applications.

5:00 PM EN11.09.04
Encapsulation and 3D Printing of Salt Hydrates for Thermal Energy Storage Sarah Lak, Patrick Shamberger and Emily Pentzer; Texas A&M University, United States

Thermal energy storage technologies are crucial for the growth of sustainable energies due to the intermittent nature of many renewable energy resources. Salt hydrates, a class of phase change materials (PCMs), are promising as low-cost, high volumetric energy density media for latent heat storage. However, their inherent limitations such as undercooling and incongruent melting render them unstable for extended thermal cyclability. Microencapsulation can mitigate some of these challenges, enhance heat transfer efficiency, and minimize moisture loss/gain from the external environment to improve PCM performance. We demonstrate the use of non-aqueous Pickering-type emulsions, stabilized by alkylated graphene oxide (GO) nanosheets, as templates for subsequent precipitation of commodity polymers to access core-shell microcapsules loaded with salt hydrates. These microcapsules are robust to thermal cycling, exhibit minimal undercooling in comparison with the bulk salt hydrate, and have a high loading (~90 wt%) of pristine core material. Further, this single-step, highly tunable approach is amenable to different salt hydrates as cores and different polymers as shell materials, making it suitable for tailoring capsule properties. Alternatively, we have formulated functional inks containing salt hydrate PCM particles as rheological modifiers in polymer solutions; eliminating the need for prior microencapsulation of the PCM. These inks are then 3D printed into complex hierarchical structures using a direct ink writing technique. This approach affords excellent passive thermoregulation properties to the fabricated composites, representing a significant advancement in developing materials aimed towards energy management and sustainability.

5:00 PM EN11.09.05
Facile Synthesis of High Thermal Conductive h-BN Microspheres/Paraffin Wax Shape-Stabilized Phase Change Materials for Intelligent Heat Storage System Hyung Jin Mun, Ye-Ji Lee, Hyunji Kang, Minseob Lim, Hong-Baek Cho and Yong-Ho Choa; Hanyang University, Korea (the Republic of)

The entire humanity is experiencing a severe energy consumption dilemma. As a result, increasing the efficiency of energy utilization and avoiding its depletion as a critical solution has gained increasing global attention. Thermal energy storage technology plays a significant role in reducing the disparity between energy demand and supply as a highly efficient technique for management of energy [1]. Among all the materials, phase change materials (PCMs) have garnered the most attention in numerous fields such as building and temperature control equipment due to their ability to capture and release a large amount of thermal energy during their melting and freezing processes, with superb advantages of storing or releasing the thermal energy at a constant temperature or within a narrow temperature range. Among a wide spectrum of prospective organic and inorganic PCMs, paraffin wax (PW) is particularly attractive because of their low price, large latent heat, chemical stability, no toxicity, and lack of phase separation. However, one of the main undesirable drawbacks of PW is low thermal conductivity, which decreases the efficiency of heat transfer. Moreover, the leakage of the PCMs when the application temperature exceeds the melting point hinders the direct application to numerous fields. In order to tackle the challenges, a method of encapsulation or shape stabilization of PCMs using supporting materials was considered, which allows the solid state to be maintained during the phase-change process of PCMs.

In this work, we utilized a spray-dry strategy to fabricate thermally conductive hexagonal-boron nitride microspheres (sph-BN) as a shape-stable porous support using the as-synthesized nano-BN (nano-BN) powders. Sph-BN was assembled with polyvinylpyrrolidone (PVP) as an organic binder during the process followed by calcination to form porous structures in sph-BN after elimination of PVP between nano-BN. High thermally conductive sph-BN/PW shape-stabilized PCMs (SSPCMs) composites were successfully obtained by simple solution process that PW is incorporated into the pore sites in sph-BN at above of melting temperature of PW followed by mold-pressing into disk-shaped specimen. The leakage tests by macroscopic photographs of the SSPCMs and pure PW at 25^{o}C and elevated temperature up to 100^{o}C were performed, resulting in pure PW was in a molten state and the primary shape was completely changed while sph-BN/PW composites perfectly kept their primary form even at temperatures much beyond the melting point of PW. The phase change enthalpies and heat storage capacities of sph-BN/paraffin SSPCMs were determined by differential scanning calorimetry. In addition, the latent heats of the SSPCMs increased with increasing contents of paraffin in the composites. The thermal conductivity shows a slight decrease as the ratio of paraffin increases; yet it is still higher than that of pure paraffin, due to the existence of thermally conductive sph-BN in the organic matrix. As mentioned above, SSPCMs we developed represent an important step to develop leakage-protective PCMs with high performance and enhanced thermal conductivity. Therefore, we believe our work can be widely applied to latent heat thermal energy storage.

[1] Dimberu G. Atinafu et al., J. Mater. Chem. A, 6, 8969 (2018)

5:00 PM EN11.09.06

High-Performance Electrodeposited Copper Wicks for Heat-Spreading Vapor Chambers Jui-Cheng Yu[1], Heng-Chieh Chien[2] and Chien-Neng Liao[1]; [1]National Tsing Hua University, Taiwan; [2]Industrial Technology Research Institute, Taiwan

With the increasing heat flux in electronic packages or power electronic devices in the last decade, vapor chambers have been considered a promising solution to this problem due to their excellent thermal performance. A capillary wick structure plays an important role in producing the capillary pressure that drives two-phase circulation in phase-change heat transfer devices such as heat pipes and vapor chambers. In this study, the porous Cu wick structures were fabricated using a new electrodeposition process and examined for their capillary performance. This Cu wick exhibits large channels generated by hydrogen bubbles and small pores in the dendritic Cu deposits produced by high-current electrodeposition. Adjusting the morphology of dendritic copper deposits by using different electrodeposition current densities and copper sulfate concentrations in the electrolyte can effectively enhance the capillary wick performance. The Cu wick is then thermally treated at 700 °C in ambient N_2 for 90 min to improve its structural integrity. The Cu wick shows a superior capillary performance K/R_{eff} of 1.5 ± 0.06 mm and excellent structural stability. Such a high capillary performance can enhance the mass transport rate and effective transport distance of the working liquid in vapor chambers for high-density and long-range heat dissipation applications. Test results demonstrated that a vapor chamber integrated with an electrodeposited Cu wick has excellent heat-spreading characteristics, with an effective thermal conductivity of up to 13500 W/m×K.

5:00 PM EN11.09.07

Shape Stabilized Phase Change Materials Based on Polyethylene Glycol/Carbon Black/Multi-Walled Carbon Nanotubes for Latent Heat Thermal Energy Storage Systems Hyunji Kang, Hyung Jin Mun and Yong-Ho Choa; Hanyang University, Korea (the Republic of)

An impending shortage of fossil fuels, combined with the deterioration of the ecological environment, has sparked widespread interest in environmentally friendly renewable energy sources. Utilization of renewable energy and the development of high-performance energy storage solutions are now essential for scientific and technical progress. Thankfully, thermal energy storage (TES) technologies provide a unified answer to the supply continuity issues of sustainable energy storage systems. TES technologies are often classified as latent heat storage, sensible heat storage, or thermochemical energy storage. In general, latent heat storage is larger than sensible heat storage; as a result, less mass and volume of the material is necessary to achieve a high level of energy efficiency. Furthermore, the phase change occurs at a constant temperature, therefore avoiding corrosion by temperature and other handling issues. The PCM's latent heat property is employed to store energy during phase change. The phase shift includes liquid-vapour transition (latent heat of vaporization) and solid-liquid transition (latent heat of fusion), with the latter being used more often. PCMs are being researched in a wide range of industries, including the construction industry, automotive industry, asphalt industry, food industry, textile industry, and battery thermal management systems[1].

Organic PCMs, such as paraffins, fatty acids, esters, alcohols, polyethylene glycol (PEG), etc., are widely used as TES materials since for their chemical stability, low cost, high phase transition enthalpy, adequate phase change temperature range, and little supercooling. Despite the improvement of latent heat storage technology, liquid phase leaks, poor thermal and electrical conductivity, low photoabsorption capacity, and intrinsic rigidity of pristine PCMs have often hindered the efficient collection and release of energy as needed. Liquid phase leakage and low thermal conductivity of pristine PCMs may cause possibly dangerous conditions and slow thermal charging/discharging rates, respectively. Concerning liquid phase leaks, the most common option is to put nanoporous supporting materials into PCMs to produce shape-stabilized composite PCMs through capillary force and hydrogen bonding interactions. Adding carbonaceous materials, two-dimensional boron nitride nanosheets and MXenes owing to their high electrical conduction, outstanding solar absorption, and high thermal conductivity is a thoughtful approach to achieving highly effective electric to thermal conversion and solar to thermal conversion in materials with poor thermal/electrical conductivity and low photoabsorption capacity[2].

Here, PEG is used as a PCM, and carbon black and CNT are used to construct a supporting material and conductive pathway simultaneously. As a representative linear polymer, PEG is a typical and excellent solid to liquid PCM with the superior properties of nontoxicity, relatively high latent heat storage capacity, broad selectivity of molecular weight, low vapor pressure when melted, and excellent thermal and chemical stability. As a result of the shape-stabilized PCM process, PEG is well attached to the porous structure of carbon, and PEG leakage is prevented above PEG's melting points. Based on the interaction of the synergistic conductive network of CB/MWCNT, the thermal conductivity of composite is improved.

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SESSION EN11.10: Thermal Energy Storage and Utilization I
Session Chairs: Sumanjeet Kaur and Zhengmao Lu
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2005

9:15 AM EN11.10.01
High Density Thermal Energy Storage by Highly Stable Glauber's Salt Composites with Low Supercooling for Building-Scale Application Sung Bum Kang, Youngmun Lee, Daniel Hsieh, Wuchen Fu, Ho Chan Chang, Jay M. Taylor, Mayur S. Prabhudesai, Nenad Miljkovic, Sanjiv Sinha and Paul V. Braun; University of Illinois at Urbana-Champaign, United States

Phase change materials (PCM) are a promising candidate for thermal energy storage in building infrastructure, enabling grid-integrated peak load shaving by utilizing energy production in off-peak hours. Glauber's salt ($Na_2SO_{4.}10H_2O$, Sodium sulfate hydrate) are highly attractive due to their high energy storage capacity and low cost but Glauber's salt suffers from long-standing challenges including high supercooling (> 15^{o}C) and low thermal cyclic stability, which is a major setback for practical building-scale energy storage applications. Here, we developed a unique ionic molecular nucleating agent for Glauber's salt which reduced the supercooling temperature to less than 5^{o}C. By combining this nucleated SSD with a polymer, phase segregation of salt hydrate for over 100 thermal cycles without degradation was achieved. Key was that the polymer confined the SSD crystals, preventing phase separation. In addition, we applied our stable Glauber's salt composite in a miniatured building model and demonstrate that our PCM composite can be utilized for real-world building infrastructure.

9:30 AM EN11.10.02
Interpreting T-History Data on Supercooling and Phase Change Enthalpy of a Salt-Hydrogel Complex for Building Thermal Management Youngmun Lee, Daniel Hsieh, Wuchen Fu, Ho Chan Chang, Sung Bum Kang, Mayur S. Prabhudesai, Jay M. Taylor, Paul V. Braun, Nenad Miljkovic and Sanjiv Sinha; University of Illinois at Urbana Champaign, United States

Phase change materials (PCMs) are promising materials for storing and discharging latent heat in buildings to regulate the thermal environment. Measurement of salt hydrate PCM thermal performance is often challenging because of supercooling and phase segregation. Though differential scanning calorimetry (DSC) has been widely used to measure thermal properties of various phase change materials, DSC uses milligrams of sample and is unrealistic for predicting large-scale materials performance. The T-history method [1], in contrast, handles higher volumes but the analysis typically requires a lumped capacitance assumption. Here, we report and analyze T-History data on a novel salt-hydrogel complex with high viscosity, that renders low Biot number sample preparation extremely challenging. We re-examine the standard T-history method and compared against DSC data in this complex material. We report details of an experimental setup, built with necessary additions to a controlled environmental chamber. We carefully examine the validity of the lumped capacitance assumption and suggest a modified analysis using a computational approach for reliable data. Experimental parameters such as ramp rate and temperature range of the environmental chamber are considered via computational modeling to understand the effect of ramp rate on supercooling [2]. Finally, we report thermal cycling experiments on the salt-hydrogel complex. Our modified approach to measuring supercooling and enthalpy of fusion at large scales is important in better understanding the performance of phase-change materials at scale for building thermal storage.

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9:45 AM EN11.10.03
Thermochemical Heat Pipes for District Heating and Long Distance Thermal Transport Yanan Zhang and Robert Y. Wang; Arizona State University, United States

District heating plays an important sustainability role by delivering waste heat to user-occupied buildings through the use of hot water as an energy carrier. However, one limitation of district heating is the thermal energy losses that occur when heat is transported over long distances. These losses occur because the thermal energy is stored as sensible and latent heat in the water, which is inevitably dissipated to the outdoor ambient environment during long distance transport. In this talk, we explore the combination of thermochemical heat and chemical separation to facilitate a new type of district heating system. This system is capable of transporting waste heat over arbitrarily long distances, and we refer to it as a "thermochemical heat pipe."

In brief, the proposed district heating system transports thermal energy from power plants to user-occupied buildings through reversible liquid-phase endothermic/exothermic reactions. Waste heat from the power plant is used to both (i) drive the endothermic cleavage of an adduct molecule into two small reactant molecules and (ii) chemically separate the reactant molecule via distillation. The separated molecules are then pumped to their destination where they are combined in an exothermic reaction that provides heat to buildings (and chemically reform the adduct molecule). The adduct molecule is then pumped back to the power plant for re-use. Thermodynamic analysis of the system shows that heat transport efficiencies of ~30% are possible when only the thermochemical energy storage component is used. This efficiency can be boosted up to ~70% by incorporating heat exchangers that recover the sensible and latent energy components prior to long distant thermal transport. Pump work analysis shows that thermal transport over thousands of kilometers is feasible when transport is done in the liquid phase.

10:00 AM BREAK

10:30 AM *EN11.10.04
Impact on Energy Use and Load Shifting of Material Properties of Enclosure-Based Phase Change Materials Energy Storage Systems Charles Booten, Ravi Kishore, Marcus Bianchi, Judith Vidal, Ph.D and Roderick Jackson; NREL, United States

Deploying phase change material (PCM) in building envelopes can be effective in reducing space heating/cooling loads and providing load shedding and shifting capacity. However, the full potential of PCM-integrated envelopes can only be harnessed if the PCM undergoes a complete phase change, and the stored energy is effectively transferred to the interior of the building. Thus, there have been proposed dynamic insulation materials and systems (DIMS) to vary the thermal resistance of building envelopes based on the indoor and outdoor conditions to maximize PCM phase change. We also perform a sensitivity analysis of the impact of system and material properties such as latent heat, PCM thickness, transition temperature and range, density, thermal conductivity, and DIMS switch ratio on load shifting. We examine a novel wall design, comprising of a layer of PCM between two layers of DIMS. The PCM-DIMS-integrated wall provides significantly higher energy saving potential than the DIMS-only integrated wall or the PCM-only integrated wall in all climates and wall orientations analyzed in this study. Depending on the climate, the PCM-DIMS-integrated wall could provide 15% to 72% reduction in annual heat gain and 7% to 38% reduction in annual heat loss. We also show that optimized properties can result in a 70% reduction the wall related heat gain during peak hours with only a minor increase in total-daily heat gain. The analysis presented in this study serves to encourage the development of scalable dynamic insulations combined with thermal energy storage systems for buildings.

11:00 AM EN11.10.05
Salt Hydrate Eutectics: Tailored Design of Equilibria, Reversibility, and Stability in Complex Phase Change Material Systems Sophia Ahmed, Anirban Chakraborty, Denali Ibbotson, Sarah Lak, Kartik Rajagopalan, Achutha Tamraparni, Charles Culp, Jonathan Felts, Emily Pentzer, Svetlana A. Sukhishvili, Choongho Yu and Patrick Shamberger; Texas A&M University, United States

A critical aspect of thermal energy storage systems for the built environment is the development of thermal energy storage media that will reversibly store and discharge thermal energy repeatedly within a defined temperature range. For example, to optimize efficiency, some environmental climate control and air conditioning systems require thermal energy storage between 5 to 25 °C. To address this need, eutectic salt hydrates have been identified as promising candidate systems that will allow for the tailoring of bespoke low cost thermal energy storage systems, due to the large number of potential eutectics distributed across a broad temperature range. However, these phase change materials are associated with a number of known limitations (undercooling, phase segregation, low heat transfer rate) which limit their practical use in energy storage systems. Individual strategies have been identified to overcome many of these challenges. For example, nucleation agents are utilized to decrease undercooling, while thickeners or polymers which form salogels are utilized to limit phase segregation. However, the interaction between these different strategies has not been systematically investigated.

Here, we present recent efforts to expand the palette of low cost high energy storage density salt hydrate eutectics developed for building thermal energy storage applications. We compare theoretical predictions against validated eutectic compositions and properties, and highlight some of the advantages and challenges associated with these materials. We specifically address efforts to overcome the known technical limitations of salt hydrates, and their relevance to salt hydrate eutectic systems, including 1) the introduction of specific nucleation agents to promote reversibility in salt hydrate systems, 2) the introduction of polymer salogels to stabilize systems from phase segregating, 3) the introduction of expanded graphite networks to improve heat transfer through these systems, 4) the use of encapsulants to encase PCM particles, and 5) the use of scaled testbeds to evaluate stability of systems under use conditions. Addressing all of these challenges results in a complex multi-phase material system which introduces additional interactions. Here, we will focus on both individual strategies and the resulting interactions, using development of zinc nitrate hexahydrate-based eutectic systems as an example model system. We will demonstrate successful implementation of tailored low-cost PCM systems, and will emphasize ongoing challenges in this area.

11:15 AM EN11.10.06
Thermal Conductivity of a Novel Salt-Hydrogel Complex as a Phase Change Material for Building Thermal Management Daniel Hsieh[1], Youngmun Lee[1], Mayur S. Prabhudesai[1], Sung Bum Kang[1], Ho Chan Chang[1], Wuchen Fu[1], Jay M. Taylor[1], Paul V. Braun[1,2], Nenad Miljkovic[1,1,2] and Sanjiv Sinha[1]; [1]University of Illinois at Urbana-Champaign, United States; [2]Materials Research Laboratory, United States

Use of electricity for space heating, ventilation and air conditioning in buildings may be better managed through temporary energy storage. Compared with electrochemical storage, the levelized cost of thermal energy storage systems can be lower depending on geographical location and thermophysical properties [1]. In any phase change material (PCM), the rate of absorption and release of thermal energy increases with higher thermal conductivity [2]. However, leading PCMs like paraffin waxes have thermal conductivities on the order of 0.1 W/mK. Glauber's salt, a salt hydrate, possesses a relatively high thermal conductivity but suffers from supercooling and phase segregation. Research has shown that polymer-based composites with salt hydrates can prevent phase segregation and limit supercooling over hundreds of cycles [3] though the thermal conductivity of the composite may be reduced leading to low energy storage rates. Here, we report thermal conductivity measurements on polymer hydrogels which are stable in solutions of Glauber's salt. To measure thermal conductivity of soft gels, we use a 3-omega method [4] where heat flows bidirectionally through a substrate below and through a gel placed on top. This suits measurements of both gels and liquids unlike transient plane heat source or transient hot wire methods. We report measurements of thermal conductivity of salt-hydrogel complexes as a function of temperature, cross-linking and salt concentration. In addition, we present modeling of thermal conductivity of sodium sulfate solutions with available theories. We finally employ polarized optical microscopy to observe inside the transparent hydrogel networks, showing that precipitating crystals may influence thermal conductivity measurements for high salt concentrations. Our thermal conductivity results combined with enthalpy of phase change, mass density and specific heat are essential to accurately design thermal storage systems for energy-efficient buildings.

11:30 AM EN11.10.07
Role of Ba-containing Compounds in the Nucleation of Solid Calcium Chloride Hexahydrate Denali Ibbotson, Sophia Ahmed and Patrick Shamberger; Texas A&M University, United States

Currently, heating and cooling of commercial and residential buildings is one of the leading consumers of energy in the country, accounting for 40% of building energy demand and about 75% of all electricity use. One method used to increase HVAC system efficiency and to allow for more efficient load displacement, is to incorporate phase change materials (PCMs) into thermal energy storage systems, as PCMs are able to passively store and release heat, allowing for a pathway to displace peak energy load for buildings to better align with available excess energy generation. However, robust and economical phase change materials that are tailorable to a specific desired energy storage temperature are needed to accomplish this task. Salt hydrates represent one class of PCMs of interest due to their high volumetric energy densities, low cost, and the ability to tailor the energy storage temperature through the design of custom salt hydrate eutectics. However, they can also experience undercooling, a nucleation-limited phenomena which results in the existence of a metastable liquid below the melting point. This phenomena can lead to undesired issues, including incongruent melting and phase segregation. To induce nucleation, and thereby improve the reversibility of the thermal energy storage process, nucleation agents can be added to a PCM system to induce nucleation, and thereby suppress the formation of metastable phases. In many cases, the underlying mechanisms governing which nucleation agents introduce potent nucleation sites and which do not, are not well understood.
In this study, we investigated the dependence of undercooling in calcium chloride hexahydrate ($CaCl_2.6H_2O$), a low-cost salt hydrate that melts at 29°C, on the crystal structure, chemistry, and the solubility of a family of Ba-based compounds. We utilized calorimetric techniques to measure undercooling in small quantities of calcium chloride hexahydrate with different nucleation agents, and differing weight percentages of the nucleation agents. We observed in several cases that the addition of barium-based nucleation agents resulted in at least a 10°C reduction in the undercooling, enabling practical utilization of $CaCl_2.6H_2O$. However, some variability existed between different compounds, as nucleation agents such as barium carbonate and barium hydroxide were observed to be effective nucleators and resulted in a larger reduction of the undercooling, while nucleation agents such as barium iodide or barium chloride dihydrate had minimal effects on the reduction of the undercooling. Additionally, we observed that the presence of insoluble particles of the nucleation agents aided in reducing the undercooling of the system and also resulted in more consistent melting behavior. The structure of the nucleation

agents was also noted to have little effect on the undercooling, however it was observed that a cation substitution reaction can occur while the Ba-based nucleation agent is in solution. Therefore, a resulting phase from the reaction of the Ba-based nucleation agent with calcium chloride hexahydrate could be responsible for the reduction in undercooling, which is an area that will be further investigated. If we can pinpoint the attributes and mechanisms that make Ba-based compounds effective nucleation agents, then it will allow us to design more efficient phase change materials that are better suited for thermal energy storage applications.

SESSION EN11.11: Thermal Energy Storage and Utilization II
Session Chairs: Genesis Higueros and Sumanjeet Kaur
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2005

1:30 PM EN11.11.01
Thermodynamic Analysis of a Smart ThermOREsponsive (STORE) Polymer Desiccant Dehumidification and Cooling Cycle Jordan D. Kocher[1,2], Shannon K. Yee[1] and Robert Y. Wang[2]; [1]Georgia Institute of Technology, United States; [2]Arizona State University, United States

Smart ThermOREsponsive (STORE) polymers represent a new class of desiccant materials that could significantly advance performance in dehumidifiers and air conditioners. STORE polymer desiccants regenerate by undergoing a hygroscopic-to-hydrophobic phase transition at a lower critical solution temperature (LCST). This regeneration mechanism leads to fundamental advantages relative to traditional desiccants. The performance of traditional desiccants is intrinsically tied to psychrometrics because they regenerate by desorbing *gaseous* water into a stream of hot dry air. In contrast, the performance of STORE polymers is intrinsically tied to materials chemistry. STORE polymers instead regenerate by releasing *liquid* water through their LCST phase transition, and this relaxes constraints on entropy generation and minimum regeneration temperature.

In this talk, we present a thermodynamic description of a theoretical air conditioning cycle that uses STORE polymers, which we refer to as the "LCST cycle." We combine the First and Second Law to demonstrate that this cycle has three major advantages relative to the traditional desiccant cycle: (i) regeneration at lower temperatures, (ii) the ability to directly harvest liquid water, and (iii) significantly higher coefficients of performance (COPs). For example, this new cycle can achieve a COP of ~4 when regenerated at 80 °C, whereas traditional desiccant cycles asymptote to a COP of ~ 1. Due to its liquid water harvesting capability, the new cycle potentially eliminates water consumption when used with evaporative cooling, or it can be directly used for atmospheric water harvesting.

This research was performed under an appointment to the Building Technologies Office (BTO) IBUILD- Graduate Research Fellowship administered by the Oak Ridge Institute for Science and Education (ORISE) and managed by Oak Ridge National Laboratory (ORNL) for the U.S. Department of Energy (DOE). ORISE is managed by Oak Ridge Associated Universities (ORAU). All opinions expressed in this paper are the author's and do not necessarily reflect the policies and views of DOE, EERE, BTO, ORISE, ORAU or ORNL.

1:45 PM EN11.11.03
Direct Ink Writing of Three-Dimensional Thermoelectric Microarchitectures Seong Eun Yang, Fredrick Kim, Hyejin Ju, Han Gi Chae and Jae Sung Son; Ulsan National Institute of Science & Technology, Korea (the Republic of)

Micro thermoelectric modules can be used to develop unique components such as energy harvesters, active coolers, and thermal sensors in various integrated systems. However, the fabrication of these modules still relies on expensive traditional microfabrication processes that produce only two-dimensional (2D) thermoelectric films. This limitation severely limits the formation of a temperature gradient across the thermoelectric film, so that sufficient power is not generated to run the integrated system. Here, we present direct ink writing of a micro-scale three-dimensional (3D) thermoelectric architecture for fabricating high-performance micro-thermoelectric generators. We synthesized a Bi_2Te_3-based TE particle ink with extremely viscoelastic properties and applied it to a direct-write process to print microscale 3D TE filaments with high aspect ratios and controlled diameters ranging from 180 µm to 810 µm. Thereby, we could build highly performant 3D TE architectures such as arches and lattices standing on a substrate by computer-aided model design. Our group demonstrated that the addition of a $Sb_2Te_4^{2-}$-based chalcogenidometallate (ChaM) ionic additive ensured the viscoelasticity of the TE particle colloidal ink, enabling 3D layer-by-layer deposition of the TE ink. However, the moderate viscoelasticity observed in these inks was not sufficient for the direct writing process. To overcome this problem, we introduced a new design principle for TE particles in terms of size, size distribution and surface state. First, we demonstrated that the smaller size and narrower size distribution of TE particles results in higher viscoelasticity due to an increase in the effective volume occupied by the particles. Second, the controlled oxidation of the TE particle surface minimizes the screen effect due to the ChaM additive, resulting in a higher viscoelasticity of the ink than that observed with the non-oxidized particle ink. Based on these results, TE inks were optimized to achieve the extremely high viscoelasticity required for 3D direct writing. In addition, the sample dispalyed ZT values of 1.1 for p-type and 0.5 for n-type, similar to the ZT values of typical Bi_2Te_3-based bulk ingots. The direct writability of TE inks allows for microscale TE leg design for optimized thermal management, maximizing temperature gradients and output power in µ-TEGs. We demonstrated the fabrication of µ-TEGs via direct 3D writing of a TE leg with an aspect ratio of 4.1 on a patterned electrode array. Upon heating, the high anisotropy of the TE leg created a large temperature difference of 82.9 °C, resulting in a power output in the order of µW for the unicouple of the TE leg.These results validate the practicability of our 3D direct writing process for fabricating high-performance µ-TE modules that can be integrated into the electronic systems

2:00 PM EN11.11.04
Doped-PbTe Thermoelectric Inks with Viscoelasticity for 3D Printing of Systemically Optimized Power-Generating Tube Jungsoo Lee, SungYoub Kim, Han Gi Chae and Jae Sung Son; Ulsan national institute of science and technology, Korea (the Republic of)

Thermoelectric (TE) technology offers a promising means of improving fossil energy efficiency by generating electricity from waste heat from industrial or automobile exhaust gases. In these applications, thermoelectric modules must be designed in terms of system integration for efficient heat transfer, system simplification and low processing costs. Despite recent advances in material efficiency, the structural designs of TE legs and modules are subject to limited design flexibility within conventional planar structures. For real-world TE power generation applications, the modular structure sometimes needs to be customized for integration with thermal systems or may require geometric or heat-source-structure adjustments. For example, tubular thermoelectric generators (TEGs) have been extensively studied in academia and industry to improve fuel energy efficiency by recovering automotive or industrial waste heat. One significant problem in these applications is the unavoidable temperature drop at the interface between the conventional planar TEG and the exhaust gas pipe due to non-adaptable thermal contact, which significantly reduces the output power. Therefore, post-processing is required by pressing the TEG into the pipe with high force; however, this renders a heavy system. These limitations of modular structures stem from the fundamental challenges of

processing the bulk-scale materials used to fabricate TEGs, such as top-down dicing, metallization, and soldering. This is because precise engineering of the structure for customization of TE legs and modules is not possible.
Three-dimensional (3D) printing technology offers an innovative way to address these challenges through cost-effective direct molding and computer-aided design of 3D bulk-scale TE legs and modules with optimized structures. In this presentation, we report a 3D printing method of PbTe thermoelectric materials for fabrication of systemically optimized high-performance power generation TE tubes. The electronic doping-induced surface charges in PbTe particles were shown to significantly improve the viscoelasticities of inks without additives, thereby enabling 3D printing of PbTe for precise shape and dimension engineering with figures of merit of 1.4 for p-type and 1.2 for n-type materials. The performance of power-generating TE tube fabricated from 3D printed p-type and n-type PbTe tubes has been demonstrated experimentally and computationally as an effective strategy for designing system-adaptive, high-performance thermoelectric generators.

SESSION EN11.12: Virtual Session I
Session Chairs: Ting-Hsuan Chen and Po-Chun Hsu
Wednesday Morning, April 26, 2023
EN11 - virtual

8:00 AM *EN11.12.01
Dynamic Building Envelope Materials for Enhanced Thermal Management and Energy Efficiency Gang Tan[1] and Tengyao Jiang[2]; [1]Zhejiang University, China; [2]Nanjing Tech University, China

Building envelopes, including opaque structures such as roofs and walls as well as transparent structures like windows, account for significant heat losses or heat gains that introduce huge heating and cooling loads, respectively, to the HVAC system. Considering the weather variation with seasons, adaptive building envelopes, through either passive or active approaches, are preferred to achieve high performance in the terms of both thermal management and energy efficiency.
Aimed at enhancing heat gains in winter and heat sheds in summer, roofs and walls can be equipped with solar heating materials and radiatvie cooling materials that could be mechanically switched. Two recent examples are given with one controlled by the electrostatic force and the other fabricated from interwoven surfaces, which produced higher energy savings compared to the solely radiative cooling technology. However, perspectives on weather self-adaptive materials in building applications, especially for opaque structures, are offered to further discuss about the advanced materials with highly responsive feature and broader modulating band from solar to long wavelength infrared spectra.
The thermo-responsive materials, W-doped VO_2 particles and hydrogels, have been utilized to develop dynamic windows in order to optimize the solar light transmission and long wavelength radiation triggered by the change of the ambient temperature. A scalable thermochromic smart window showed independent management over the visual, near-infrared (NIR), and long wavelength infrared (LWIR) radiation (De_{LWIR}=0.4) and presented dynamic heat dissipations while maintaining day lighting capability. When hydrogel material is applied to windows in a commercial building, the interactive effect of the low-e coating has been investigated and the design method has been provided. Numerical energy saving calculations to an as-synthesized hydrogel film combined with an IR-reflective coating have been conducted to evaluate the ultimate solar regulation performance and yielded annual space cooling energy savings of up to 30.6 kWh/yr.m^2 for Tucson, AZ, USA based on the area of window glass.
To incorporate the numerical calculation for the spectra-selective radiative cooling material into the whole-building simulation tool, a systematic strategy of developing a new long-wavelength radiation spectrum integral module (LRSIM) suitable for the state-space model has demonstrated good accuracy (< 3% deviation from measured data) with acceptable computational cost. However, although methods for evaluating the energy savings of the passively-driven dynamically-adaptive materials for building envelopes such as chromic materials have been studied and developed, there lacked of numerical algorithms and engineering-level control profiles to maximize the advantages of harvesting heat or cooling from natural resources (e.g., solar or outer space). Additional research work is needed to bridge this gap and therefore motivate the wide utilization of actively-enforced dynamic materials in buildings. As an example, a new electro-chromic window is used to present the different energy performances under the three pre-defined operation schedules, based on occupancy schedule, cooling/heating demand schedule, and the day lighting dominated schedule, for a single-room building in various climates.

8:30 AM EN11.12.02
Large-scale Fabrication and In-operando Crystallization Study of Expanded Graphite/Zinc Nitrate Hexahydrate-Potassium Nitrate Eutectic Composites with Robust Thermal Properties. Anirban Chakraborty, Choongho Yu, Patrick Shamberger and Sophia Ahmed; Texas A&M University, United States

High enthalpy of fusion (ΔH_{Fusion}) and suitable melting point (M.P.) makes zinc nitrate hexahydrate (ZNH) and its eutectics popular as phase change materials (PCM) for low temperature thermal energy storage (TES). Primary challenges in salt hydrates are their low thermal conductivity (k) and stability after thermal cycling. Past studies have attempted to enhance k by adding loose carbonaceous fillers like expanded graphite (EG). However, infiltrating salt hydrates within binder incorporated, hydrophilic-treated, robust EG matrices that are reliable up to ~1000 thermal cycles is yet unexplored. For practical application of PCM composites like electronics, solar plants, green buildings, etc. reliable thermal performance throughout its operational lifetime is essential. Nevertheless, the reliability of thermal conductivity in EG/salt hydrate composites over relevant numbers (~10^3) of melt/freeze cycles has barely been studied. Here we propose, a methodology for large-scale fabrication of PDMS-bonded, ZNH/KNO_3 composites, tailoring enhanced k and ΔH_{Fusion}, with reduced supercooling (ΔT_{Sup}), M.P. and endothermic range. The binder imparts strong connections between the EG to improve thermal conductivity and stability of TES properties up to 1,000 melt/freeze cycles. The thermal conductivity increased with EG content, although its initial magnitude and long-term retention were observed to be tradeoffs. In-operando crystallization studies to further understand the variation of thermal conductivity, revealed the influence of carboxymethyl cellulose (CMC) thickener in attenuating k fading over prolonged melt/freeze cycling. The thickener prevented the formation of large PCM crystals that could potentially impair thermal connections between EG. We believe the outcome of this study introduces a new dataset to the scientific community regarding robust ZNH eutectic composites for low temperature TES applications.

8:45 AM EN11.12.03
Sticky Thermoelectric Materials with Ultra-thin High Performance Foam for Hierarchically Designed Flexible Peltier Sheets Norifusa Satoh[1], Masaji Otsuka[1], Jin Kawakita[1], Junnosuke Murakami[2], Junichi Nakadate[2] and Takayuki Nakanishi[2]; [1]National Institute for Materials Science, Japan; [2]Sekisui Chemical Company, Limited, Japan

To improve energy efficiency of temperature conditioning for human body and to also prepare for extreme heat with climate change, Peltier human coolers have been developed and commercialized [Ref. 1]. However, its usage has been limited, such as a neck cooler, because the commercial Peltier devices are heavy and solid, constraining the size of contacting area for heat transfer. To slim their thickness and weight and to also meet the multiple complex requirements for mass production of flexible Peltier sheets, we have designed and developed sticky thermoelectric (TE) materials with a strategy adopting from other organic devices like organic light-emitting diodes and dye-sensitized solar cells: hierarchically hybridizing the multiple components to meet each requirement [Ref. 2-4]. At the microscale hybridizing inorganic TE particles with low-thermal-conductive organic solvents, the sticky TE materials suppresses the thermal conduction, which enable to keep the temperature difference based on the Peltier effect even on the thin sheet structure for flexibility. At the nanoscale, the surface/interface modification reduces the electrical resistance between TE particles. At the atomic scale, the Seebeck coefficient of TE particles is optimized. Instead of the organic sheet sealant surrounding the sticky TE materials, in this study, we employ an ultra-thin foam sheet because of its high sealing ability, low thermal conductivity, and shock absorption capacity. We observed that the low thermal conductivity contributes to keeping larger temperature difference between the upper and lower sides, and also confirmed that the shock absorption capacity relaxes the tension on the upper and bottom electrode sheets during the bending. We discuss details in this presentation.

Ref. 1: Itao et al. J Jpn Soc Precis Eng 2016;82:919-924 (in Japanese).
Ref. 2: Satoh et al. Sci Technol Adv Mater 2018;19:517-25.
Ref. 3: Satoh et al. MRS Advances 2020;5:481-7.
Ref. 4: Satoh et al. Soft Sci 2022;2:15.

8:50 AM MOVED TO EN11.13.03

9:20 AM *EN11.12.05
Smart Materials for Sustainable Energy Storage in Refrigerated Spaces Nastaran Barhemmati; Viking Cold Solutions Inc, United States

The sustainability and high performance of refrigerated space used for the preservation of perishable products capitalize on conservation techniques that reduce environmental impact. The concept encompasses a variety of strategies including the exchange or improvement of mechanical refrigeration systems by Thermal Energy Storage (TES) that incorporate Phase Change Materials (PCM), and advanced refrigeration controls powered by cloud-based optimized algorithms. TES as a part of an integrated system improves overall efficiency resulting in lower energy costs while improving the shelf life and quality of perishable foods and other products. The system employs Thermal Energy Storage cells installed in refrigerated rooms in combination with intelligent controls. The smart PCM in TES is highly efficient at capturing thermal energy while the PCM is undergoing a phase change from solid to liquid, and collectively the PCM has a large latent heat compared to sensible heat. The Phase Change Material in the TES system provides latent heat capacity to the refrigerated environment, allowing the TES to absorb a large amount of thermal energy from the surrounding environment while remaining at the same temperature. This function allows the refrigerated environment to maintain an optimal targeted operating temperature for an extended period of time without running the mechanical refrigeration equipment, thus saving a substantial amount of electricity.

SESSION EN11.13: Virtual Session II
Session Chairs: Po-Chun Hsu and Ronghui Wu
Wednesday Afternoon, April 26, 2023
EN11 - virtual

9:00 PM *EN11.13.01
Nanostructured Passive Cooling Based on Evaporation and Radiation Jia Zhu; Nanjing University, China

Nanostructures with carefully tailored properties can be used to manipulate the flow of light, heat and water, to enable high performing passive cooling through evaporation and radiation. I will present our recent progress.

The first example is cooling photovoltaic device through evaporative cooling. We demonstrate a monolithic tandem solar electricity-water generator that synergistically produces electricity and clean water by utilizing the full spectrum of solar irradiance. This design posseses two components: a top infrared-transparent photovoltaic device using above-band-gap photons, and a bottom solar water purifier using the below-band-gap photons. A well-designed water-proof thermal interconnecting layer (WTIL) makes these two components work synergistically: the bottom purifier serves as an evaporative cooler of the top solar cell to increase its efficiency, whereas the thermalization energy of the top cell is reutilized by the bottom purifier for producing more clean water. We experimentally demonstrate that this prototype hybrid tandem design can be applied to various solar cells such as silicon and perovskite.

The second example is about passive cooling. Radiative cooling which sends heat to space through atmospheric transparency window without any energy consumption, is attracting significant attention. For radiative cooling to achieve high cooling performance, it is ideal to have a selective emitter, with an emissivity dominant in the atmospheric transparency window. Here we will present a hierarchical design for a selective thermal emitter to achieve high performing all-day radiative cooling. Moreover, it is revealed that nano-processed silk possesses excellent performance of radiative cooling. Eco-friendly radiative cooling materials demonstrate excellent potential for protecting ice from melting under sunlight.

9:30 PM EN11.13.02
Germanium-Sensitized Cell Using Glycerol Electrolyte Haruki Kohata, Mone Hemmi and Sachiko Matsushita; Tokyo Institute of Technology, Japan

1. Introduction
There's an increasing demand for novel energy production technology to achieve environmental sustainability. As "heat" is ubiquitous, thus a probable candidate for energy source, our group has been investigating semiconductor-sensitized thermal cells (STCs)[1],[2]. Unlike conventional systems, STC can convert heat into electricity without the emission of CO_2 or temperature difference, enabling the production of clean energy in various conditions.
STCs' mechanism originates in that of the dye-sensitized solar cell (DSSC). However, instead of photoexcited charges, STC uses thermally excited charges of the semiconductors to facilitate redox reaction in the electrolyte until it reaches an equilibrium at the electrodes' surface. By disconnecting the circuit, ions in the electrolyte diffuse and go back to their original equilibrium[3]. This charging and recovering phenomenon has been reported with STC comprised of Ge as a semiconductor and Cu ion-dissolved polyethylene glycol (PEG) as an electrolyte at 80°C[4]. However, its long-term stability remains a challenge, due to volatility and poor heat resistance. In this work, we propose STC using glycerol (Gly) as a solvent to enhance the long-term stability of STCs.

2. Experimental

The STC was manufactured in a glove box under Ar atmosphere. The electrolyte was prepared by mixing CuCl, CuCl2, LiCl, Gly or PEG on the hotplate for 2 h. The concentrations were: LiCl (0.30 mmol /PEG or Gly(g)) and Cu ion (1.0 mmol / PEG or Gly(g), Cu^+:Cu^{2+} = 1:1). An *n*-Si substrate (1.5 cm × 2.5 cm) on which Ge was deposited was used as the working electrode. An FTO glass substrate was used as the counter electrode, on which the double-sided insulating tape (114 µm thickness) with a hole of 6 mm diameter was attached. The electrolyte was dropped into the hole and *n*-Si/Ge substrate was used to cover the hole to form a cell (with the Ge side touching the electrolyte). For fabricated cells, cycliv voltammetry (CV) and long-term operations were performed.

3. Discussions
Open circuit voltage (V_{OC}) and short-circuit current (J_{SC}) of fabricated cells were obtained using CV at the scan rate of 10 mV/s. The V_{OC} and J_{SC} were 250 mV, 7.9 µA /cm^2 using Gly, compared to those of 350 mV, 4.8 µA /cm^2 using PEG. The larger J_{SC} by the replacement of PEG by Gly is probably attributed to the larger dielectric constant of Gly, causing larger diffusion of Cu ions. The use of Gly increased the power by more than 3 times, from 1.29 µW/cm^2 with conventional PEG solvent, to 5.50 µW/cm^2.
The long-term operation was performed at 80^{o}C. After 200 nA discharging, the V_{OC} measurement was immediately initiated for 5 h at 80^{o}C. As a result, stable V_{OC} and J_{SC} were obtained even after the second cycle. Moreover, the charge transfer resistance at Ge/electrolyte surface did not show a significant difference before and after charging.

4. Conclusion
In this study, we investigated the battery performance of STCs using glycerol as a solvent. It was discovered that glycerol's high dielectric constant enabled remarkably stable discharge cycles of STCs for the first time. This discovery brought us one step further toward the utilization of heat, a potential energy source.
This work was technically and financially supported by Tohnic Co., Japan, Sanoh Co., Japan, and the Open Facility Center, Tokyo Tech., Japan; and financially supported by JST START University Ecosystem Promotion Type, Grant Number JPMJST2182, Japan, and JSPS KAKENHI Grant Number 21H02041.

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[2] Y. Inagawa, et al., J. Phys Chem C, 123, 19, 12145, 2019.
[3] Kohata et al., Energy Fuels, 36, 19, 11619, 2022.
[4] S. Matsushita, et al., J. Mater. Chem. A, 7, 18249, 2019.
[5] Proc. SPIE 11722, Energy Harvesting and Storage: Materials, Devices, and Applications XI, 1172206 (12 April 2021).

9:45 PM *EN11.12.04
Thermo-/Electrochromic and Passive Radiative Materials for Thermal Management of Buildings and Human Body Yanfeng Gao; Shanghai University, China

Thermochromic energy efficient windows represent an important protocol technology for advanced architectural windows with energy-saving capabilities through the intelligent regulation of indoor solar irradiation and the modulation of window optical properties in response to real-time temperature stimuli. In this presentation, recent progress in some promising thermochromic systems is summarized from the aspects of structures, the miro/mesoscale regulation of thermochromic properties, and integration with other emerging energy techniques. Furthermore, the challenges and opportunities in thermochromic energy-efficient windows are outlined to promote future scientific investigations and practical applications in building energy conservation. The presentation also talks about our recent progress in electrochromic materials. Besides the scope of buildings, the development of a textile that cools skin both in sunshine and in room can not only protect the human body from a severely hot working environment but also save energy by lowering air conditioner load. We have developed several concepts that combine solar energy reflection and "passive radiative cooling" for strengthening both solar energy blocking and heat dissipation through long-wave infrared (LWIR) radiation at wavelengths of 8–13 µm. For example, a technique is achieved by coating a textile with an Al_2O_3 dispersed-cellulose acetate. Cellulose acetate possesses high emissivity in the LWIR region, which can promote effective LWIR radiation (2.5–25 µm). Al_2O_3 has a high thermal conductivity (30–40 W m^{-1} K^{-1}) and can enhance solar energy reflectivity. By coating Al_2O_3-cellulose acetate, solar energy reflectivity of the textile significantly increases from 62.6% to 80.1% (0.3–2.6 µm). A cooling performance experiment reveals that this modified textile can reduce the temperature of simulated skin by 2.3–8 °C compared to that of an unmodified reference. Furthermore, in a real-life cooling performance experiment, a modified T-shirt can avoid the overheating of actual human skin by 0.6–1.0 °C, corresponding to a temperature decrease by 1.9–3.3 °C for the internal surface of the textile.

SYMPOSIUM

April 10 - April 25, 2023

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SESSION MD01.01: Machine Learning I
Session Chairs: Mathieu Bauchy and Pratibha Dev
Monday Morning, April 10, 2023
Moscone West, Level 3, Room 3010

9:00 AM *MD01.01.01
Machine Learning in the Quantum Regime Through Physical-Principle-Informed Representations Qimin Yan; Northeastern University, United States

Materials design in the quantum regime call for the integration of multi-tier materials information that goes beyond atomic structures. Especially, many quantum behaviors are greatly controlled by local bonding environments and physical constraints related to symmetry. In this talk, I will give several examples of how domain knowledge and physical principles for quantum material systems can be incorporated into machine learning frameworks through representation learning to greatly improve the performance of machine learning models for property predictions. Motivated by Pauling's rules, I will show that local bonding environments (structure motifs) can be incorporated into a graph-based machine-learning architecture to make reliable property predictions for solid-state quantum materials including complex metal oxides. The proposed atom-motif dual network model demonstrates the feasibility to incorporate beyond-atom materials information in a graph network framework and achieves state-of-the-art performance in predicting the electronic structure properties of complex metal oxides. Through unsupervised learning, abstracted material information such as chemical formulas and motif connections can be combined with national language processing technologies to effectively represent fundamental elements in materials and use them in downstream learning tasks. I will demonstrate how contrastive representation learning can be used to incorporate physical constraints that control the collective behavior of electron densities into neural-network-based density functional design. At the end of the talk, I will discuss the continued development of machine learning models for quantum materials that embrace local/global symmetries and symmetry-based interactions.

9:30 AM MD01.01.02
High-throughput Virtual Screening of Existing Organic Chromophores for Materials Discovery Omer Omar[1], Daniele Padula[2], Tahereh Nematiaram[1] and Alessandro Troisi[1]; [1]University of Liverpool, United Kingdom; [2]Universitá di Siena, Italy

High-throughput virtual screening (HTVS) has, in recent years, become an extremely powerful tool in the discovery of novel organic optoelectronics due to advances in hardware and architecture, facile access to both experimental and high-level theoretical datasets and vast improvements to quantum chemical methods. We have already taken advantage of HTVS[1] by considering the Cambridge Structural Database,[2] where we have successfully predicted candidates for singlet fission,[3,4] thermally activated delayed fluorescence,[5] non-fullerene electron acceptors[6] and luminescent crystals which show superradiance or near-infrared emission.[7] The main advantage of searching a database with known experimental structures, along with low bias, is the potential to source candidates and test them experimentally with no worry regarding synthetic feasibility; a serious downfall of any *de novo* study.

Our latest HTVS study considers the much larger ZINC database;[8] a set of many millions of small-to-moderate organic compounds. With a quote of approximately 13 million structures that are 'commercially available' this unfeasibly large set forms the library of our study. With innovation in the form of conjugated core clustering, conformational analysis, accurate experimental calibration and rigorous protocol benchmarking, we are able to accurately assess, with TD-DFT, the electronic structures for the entire set of 13 million with the computation of approximately 150 thousand unique structures. This forms one of the largest quantum chemical datasets to date.

The ZINC database of commercially available compounds was chosen specifically for easy access to real compounds which can be ordered and tested in our own in-house laboratories. From of our wealthy database, we have verified our protocol experimentally and identified promising materials for both near-infrared and anti-Kasha dual emission by testing over thirty unique compounds using absorption and fluorescence-lifetime spectroscopy. These properties are extremely rare and coveted and have applications in a wide range of photonic devices.

An additional, extremely rare phenomenon that has been sought recently within our optoelectronic database is the violation of Hund's rule in some molecules, or in other words, compounds that exhibit an inverted singlet-triplet gap[9] due to atom-localised intramolecular charge transfer (*i.e.* lowering the exchange energy to degeneracy between S_1 and T_1 state) coupled with spin polarisation in the S_1 state due to large contributions from double excitations. This becomes invaluable for devices (e.g. OLEDs) which seek to harvest triplet excitons by making the reverse intersystem crossing energetically favourable. Promising theoretical results using high-level multireference wavefunction methods suggest totally new design rules beyond the known heptazine case due to the low bias in our datasets.

References

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9:45 AM MD01.01.03
Machine-Learning Potentials for Molecular Dynamics Simulations of CO_2 Chemisorption and Diffusion in Mg-MOF-74 Bowen Zheng[1,2], Felipe Lopes Oliveira[3], Rodrigo F. Neumann[3], Mathias Steiner[3], Hendrik Hamann[1], Grace Gu[2] and Binquan Luan[1]; [1]IBM T. J. Watson Research, United States;

[2]Univerisity of California at Berkeley, United States; [3]IBM Research-Brazil, Brazil

For curbing the global temperature increase, effective approaches for carbon capture are needed. By utilizing amine-based liquid sorbents, current methods suffer from a high-energy cost for the thermal desorption step that is responsible for 60-80% of the total operating costs. The use of solid sorbent materials for carbon capture has been proposed as an alternative to amine-based liquid sorbents due to their lower desorption energy requirement, which can potentially boost the commercial viability of point-source carbon capture.

Among various porous solids for gas separation and purification, metal organic frameworks (MOFs) are promising materials that potentially combine high CO_2 uptake and CO_2/N_2 selectivity. So far, within the hundreds of thousands of MOF structures known today, it remains a challenge to computationally identify the best suited species. First principle-based simulations of CO_2 adsorption in MOFs (particularly, the ones with open metal sites) would provide the necessary accuracy, however, they are impractical due to the high computational cost. Classical force field-based simulations would be computationally feasible but they do not provide sufficient accuracy. Thus, the entropy contribution that requires both accurate force fields and sufficiently long computing time for sampling is difficult to obtain in simulation. The effect of chemisorption on an open metal site manifests itself more prominently at lower pressures, precisely where the desorption step happens and, therefore, is of utmost importance for the regeneration cost.

Here, we report the quantum-informed machine-learning force fields (QMLFF) for atomistic simulations of CO_2 in MOFs. We demonstrate that the method has a much higher computational efficiency (~1000x) than the first-principle one while maintaining quantum-level accuracy. As a proof of concept, we show that the QMLFF-based molecular dynamics simulations of CO_2 in Mg-MOF-74 can predict the binding free energy landscape and the diffusion coefficient similar to experimental values. The combination of machine learning and atomistic simulation paves the way for more accurat

10:00 AM BREAK

10:30 AM MD01.01.05
A Generalized Model for Charge Transfer Integral Predictions Using Graphs and Transfer Learning Michael Rinderle, Neel Misciasci, Ioannis Kouroudis and Alessio Gagliardi; Technical University Munich, Germany

In recent years, many machine learning models were developed to predict charge transfer integrals in organic semiconductor materials [1, 2]. While reporting good prediction accuracy for one specific molecule or a small number of closely related molecules, the transferability of the trained models to other molecules is limited. Typically, tens of thousands of configurations are needed to train a model with sufficient accuracy. The large amount of required training data is a limiting factor for the development of generalized machine learning models to predict charge transfer integrals.
To address this issue, we applied transfer learning techniques to obtain a more generalized model. This led to improved predictions of unseen molecules. Furthermore, adding a few configurations of a new molecule significantly increased the accuracy. In order to predict molecules of various sizes, we use graph structures to encode molecule information and implement message-passing and pooling layers to extract a fixed-size feature vector for further prediction in a deep neural network.
We present an extendable framework to predict charge transfer integrals in organic semiconductor materials and reduce the number of training configurations needed to generate a model that can be applied to new molecules.

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10:45 AM MD01.01.06
Rationalizing Space Charge Layer Formation in Li^+ Solid State Electrolytes—Data Driven Surrogate and Bayesian Optimized Inverse Problem
Ioannis Kouroudis, Manuel Gößwein and Alessio Gagliardi; Technical University Munich, Germany

Ion conducting solids find uses in energy storage and conversion, with a prominent application being all-solid-state batteries. However, despite significant research into interface reactions, passivation layer formation and electrochemical stability still remain fundamentally not understood. To this end, a range of simulation tools have been developed to model experimental observations and shed light to the underlying physical mechanism. Most ab-initio simulations however require significant computational resources and an irreducibly large amount of time. Therein lie two fundamental bottlenecks of any simulation based investigation. Firstly, solving the inverse problem of determining the necessary for the simulation but unmeasurable physical parameters of the system, often requires multiple trial and error runs, a process which is typically arduous. Secondly, a full investigation of the parameter space is simply infeasible both time and resource -wise.

In this study we propose a solution to both these bottlenecks and apply it to the formation of the space charge layer (SCL) in Li^+ ion conducting solid state electrolytes (SSE). A kinetic Monte Carlo (kMC) model is constructed and compared with an experimental setup, where the SCL thickness is measured [1]. However, the kMC model inputs, namely permittivity concentration of Li^+ in the SSE bulk and maximum concentration of Li^+ , cant be directly measured.

To this end, we have constructed a Gaussian Processes surrogate model and used it in conjunction with Bayesian Optimization [2] to solve the inverse problem and generate parameter suggestions that fit the kMC simulations to the experimental observations. To test the effectiveness of this method beyond the fitting of one experimental setup, we additionally created synthetic experiments and tasked our pipeline with reclaiming their physical parameters. Our results showed that the inverse problem is solved in a data efficient and highly accurate way. To test the limits of this claim, we constructed a synthetic experiment with more particles which caused simulation time to increase tenfold, in comparison to the simulations used for training the surrogate. However, our algorithm has managed to extrapolate, fitting the parameters with accuracy higher than 90% from the very first parameter suggestion. This is vitally important as it shows that training the model on relatively inexpensive configurations we can extract information for exponentially more expensive areas of the parameter space at a fraction of the time.

To exploit the predictive capabilities of the surrogate model, a full parameter space investigation was performed. This allowed for a deeper insight in the dependence of the SCL to the parameter combinations, shedding light to the potential underlying mechanisms.
Additionally, the model allows to identify regions of high uncertainty, which may be refined by targeted kMC simulations for improved accuracy.
Hereby, highly accurate parameter screening is achieved at low computational cost, up to five orders of magnitude lower than a direct kMC simulation.

[1] Leon Katzenmeier, Manuel Goßwein, Alessio Gagliardi, and Aliaksandr S Bandarenka.
Modeling of space-charge layers in solid-state electrolytes: A kinetic monte carlo approach
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11:00 AM MD01.01.07

***Ab Initio* Thermodynamics and Atomistic Modeling of NiTi SMA with Machine Learning Interatomic Potentials** Prashanth Srinivasan and Blazej Grabowski; Universität Stuttgart, Germany

Equi-atomic Nickel-Titanium (NiTi) shape memory alloy (SMA) possesses interesting properties such as pseudo/super-elasticity and shape memory effect. They arise from the ability of the alloy to exist in two different phases and undergo a stress- or a temperature-induced reversible phase transformation. Austenite is the high-temperature parent phase which has a B2 cubic crystal structure, and it transforms into the low- temperature martensite, which has a B19' monoclinic structure. Modeling the behavior of NiTi is challenging, since there are other competing phases (orthorhombic B19 or the base-centered orthorhombic B33). The thermodynamic phase stability still remains ambiguous and one needs to resort to *ab initio*-based methods such as density functional theory (DFT). DFT predicts the B33 phase as the lowest energy structure at 0 K (Huang et. al., 2003), although it has never been experimentally observed. Ab initio molecular dynamics (AIMD) calculations have shown that the B19' and B2 phases are entropically stabilized at temperatures above ≈100 K (Haskins et. al., 2016), but the calculations were restricted to a single exchange correlational functional (XC). Additionally, studying kinetic effects during the phase transformation using only DFT is also severely expensive.

In this work, we try to address both the above issues. Using a recently developed thermodynamic integration (TI) technique (direct upsampling, Jung et. al., 2022) aided with machine-learning based moment tensor potentials (MTPs, Shapeev 2016), it is possible to efficiently calculate high-temperature thermodynamic properties and phase stability to DFT accuracy. We perform such calculations to analyze the prediction of three different XCs (GGA, LDA and SCAN) in the phase stability of NiTi in order to find the most accurate representation. We also perform large-scale molecular dynamics (MD) simulations using the MTPs fitted to high-temperature AIMD data from the different XCs, in order to study the kinetically-driven phase transformation behavior in each of these cases. Preliminary results show that the B2 and B19' phases do get en- tropically stabilized with temperature for all XCs. The MTPs are extremely accurate in predicting the energies and forces of various phases in comparison to previously existing conventional interatomic models such as the EAM and the MEAM. Only the MTP fitted to the SCAN XC data predicts a reversible B2-B19' transformation. In the case of GGA and LDA, the B2 phase transforms into a B19 phase on cooling, suggesting that there might be an energy barrier in the B2-B19' transformation path.

References

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11:15 AM MD01.01.08

Direct Inverse Design of Molecules in Graph Space Felix Therrien, Alexander Davis, Edward H. Sargent and Oleksandr Voznyy; University of Toronto, Canada

True inverse design of materials--providing properties and obtaining candidate materials with these properties--is the holy grail of computational materials discovery. To achieve this goal, typical materials discovery pipelines generate material structures, predict their properties and repeat these two steps in an iterative fashion. In recent years a number of graph neural networks (GNNs) have been developed in order to accelerate this process that had previously relied first principles methods such as density functional theory. Here, we exploit the intrinsically invertible nature of these neural networks to directly generate molecular structures with desired input properties. Starting from a random graph, we perform a gradient ascent through the fixed weights of the GNN in order to optimize its output towards the desired property. Basic chemistry rules are enforced through an additional objective function and simple constraints on the graphs construction. We demonstrate how this method can generate realistic molecules with specific properties (e.g., a HUMO-LUMO gap of 3 eV) using widely adopted GNNs trained on the QM9 database.

11:30 AM MD01.01.09

Structure-Property Relationship of Dynamically Crosslinked Polymer Networks via 3D Convolutional and Graph Convolutional Neural Networks Alexandra Filiatraut and Mehdi Zanjani; Miami University, United States

In recent years, Machine Learning techniques have evolved to address many complex issues across different disciplines, including unique materials science applications. Two such Machine Learning techniques, Convolutional Neural Networks (CNNs) and Graph Convolutional Neural Networks (GCNNs) provide algorithms that process data networks for learning and prediction of various system features and properties. The ability of such Machine Learning techniques to process architecturally-structured data makes them ideal for processing 3D representations of polymer networks to predict material properties. Our study considers polymer composites synthesized from dynamically crosslinked networks. Such polymer networks consist of multiple components that can interact with each other in complex ways. The polymer backbone and the crosslinking agents may be designed in a variety of architectures with the potential to deliver a wide range of physical properties. Understanding the effect of polymer network architecture on the resulting properties of the material is an important and challenging task. CNN and GCNN techniques can provide a useful platform to investigate structure-property relations of crosslinked polymer networks.

In this study, we compare the two aforementioned Machine Learning techniques to determine their efficacy in predicting mechanical properties of dynamically-crosslinked polymer materials. We investigate the relationship between polymer network configuration and the resulting mechanical properties of crosslinked polymer composites. Molecular Dynamics (MD) simulations are employed to generate stress-strain curves for a variety of crosslinker and backbone polymer configurations. The results of the MD simulations are gathered as the reference dataset to be utilized within both Machine Learning (ML) frameworks. We establish "3D images" of the polymer network configurations obtained from MD simulations to build a CNN model, and develop "particle connectivity maps" to set up a GCNN framework, in order to investigate the relationship between the architecture of the network and the mechanical behavior of the material. We discuss the efficiency and accuracy of both methods in evaluating the mechanical properties of each system and study the impact of the configurational details of each network on its properties. The results of this work provide an insight into the use of CNN and GCNN techniques to predict mechanical properties using 3D representations of polymer systems. Additionally, this work helps identify crosslinked polymer network architectures that can deliver desired mechanical properties for future experimental implementation.

11:45 AM MD01.01.10

Physics-integrated Neural Differentiable (PiNDiff) Model for Isothermal Chemical Vapor Infiltration Process Deepak Akhare, Tengfei Luo and Jian-Xun Wang; University of Notre Dame, United States

Composites are a class of materials actively considered for various applications in today's aerospace, automotive, and civil industries owing to their high strength and lightweight. The performance, quality, and repeatability of the composite materials are greatly influenced by the manufacturing process. The mechanical properties of the composites depend on various variables and parameters of the manufacturing process, which are challenging, if not impossible, to determine and optimize experimentally. Traditional first-principle modeling approaches are not accessible due to the complex physics involved. Moreover, the functional form of the consultative relations used in the numerical model needs to be approximated with the help of experimental studies, thereby limiting its applicability. On the other hand, purely data-based DNN models, although showing great promise, heavily rely on "big data" and often suffer from the generalizability issue in out-of-training regimes, impeding their effective applications in modeling complex composite manufacturing processes. A hybrid model that combines incomplete physics knowledge with available measurement data within a differentiable programming framework opens new avenues to tackle the challenges. In this work, a physics-integrated neural differentiable (PiNDiff) model is developed, where the partially known physics is integrated into the recurrent network architecture to enable effective learning and generalization. The merit and potential of the proposed method have been demonstrated in modeling the densification behavior of composite during the isothermal chemical vapor infiltration (ICVI) process. The ICVI process, one of the chemical vapor infiltration (CVI) processes, is widely used to manufacture carbon-carbon (C/C) and C/SiC composites. Modeling the ICVI process using the traditional first-principle approach will be a near-to-impossible task owing to the number of species produced due to pyrolysis and the complex reaction occurring in the ICVI process. The proposed PiNDiff model handles these complexities using a homogenization approach and learns the unknown physics brought out by the homogenization assumption. The PiNDiff model learns unknown physics from limited, indirect data and, meanwhile, can be used to infer unobserved variables and parameters. The demonstrated PiNDiff strategy may provide a general strategy to model phenomena where physics is only partially known and sparse, indirect data are available.

SESSION MD01.02: Machine Learning II
Session Chairs: N M Anoop Krishnan and Qimin Yan
Monday Afternoon, April 10, 2023
Moscone West, Level 3, Room 3010

1:30 PM *MD01.02.01
Combining High-Throughput Calculations with Machine Learning to Predict Phase Preferences of Transition Metal Dichalcogenides Pratibha Dev[1], Pankaj Kumar[1,2], Vinit Sharma[3] and Sharmila N. Shirodkar[1]; [1]Howard University, United States; [2]Present address: University of Tennessee, Knoxville, United States; [3]Oak Ridge National Laboratory, United States

Layered transition metal dichalcogenides (TMDs) are a chemically distinct and technologically important family of materials, which can adopt one of the several known crystal structures. A question that naturally arises is: *What dictates the observed phase preference of TMDs?* An answer to this important question can help to understand and hence, manipulate composition-structure-property relationships, paving the way for engineering properties of TMDs. In fact, this is an old problem, which was actively debated in the 1960s to1980s. It has once again become an important and relevant question with the emergence of 2D quantum materials. By combining high-throughput density functional theory-based calculations with machine learning techniques, we address this six-decade old question about TMDs for a much larger chemical phase-space than what was considered in the earlier works. Our analysis not only rediscovered known physicochemical attributes considered by earlier researchers, but also discovered other factors that were not previously known to influence the structural preferences displayed by TMDs. This work [Phys. Rev. Materials **6**, 094007 (2022)] demonstrates how machine learning can be used to tackle old problems in Condensed Matter Physics.

Funding: This work is supported by the National Science Foundation (DMR-1752840). The computational support is provided by XSEDE under Project PHY180014.

2:00 PM MD01.02.02
Predicting the Mechanical Response Profile of Porous Materials via their Microstructures Winston Lindqwister and Jacob Peloquin; Duke University, United States

Porous media represent a wide range of materials that have yet to be fully understood and present a challenge in being harnessed to their full ability. From rocks to bone to cement, the ubiquity of porous materials across engineering disciplines cannot be overstated. However, due to the non-uniformity of their structures, it has been challenging to accurately assess performance of these materials across a wide variety of stimuli, such as mechanical response or diffusivity. Recent work has shown that this complexity may boil down to the great heterogeneity and stochasticity of a porous material's microstructure. Unfortunately, due to the multiscale effects and Multiphysics inherent to these systems, an exact relationship between a porous material's microstructure and its structural performance remains elusive. Although destructive testing and finite element analysis are proven methods for calculating a porous material's properties, the former is costly, wasteful, and impractical at larger scales, and the latter is computationally intensive and time-consuming. Machine learning has proven itself over the past few decades as a method of expediting the discovery of correlations within data and creating powerful predictive models. However, common obstacles for creating an effective machine learning model include having a lack of data for training the model and having an overcomplicated set or unnecessary number of input features. In order to overcome the challenges and drawbacks of using these various methods, we have developed a methodology for analyzing porous material structure-property relationships that includes generating realistic synthetic structures, extracting relevant and useful geometric descriptors for defining the structures, and using these descriptors of reduced complexity to train a machine learning model that predicts the mechanical response of the structure from its descriptors. Through this work we aim to accelerate the analysis of porous material structure-property relationships via a machine learning model trained on microstructural features.

2:15 PM MD01.02.03
Harnessing Neural Network for Predicting X-Ray Spectroscopy of Amorphous Carbon Materials Hyuna Kwon[1,2], Wenyu Sun[2], Yu-Ting Hsu[2], Wonseok Jeong[2], Shubham Sharma[2], Matthew Carbone[3], Fikret Aydin[2], Xiao Chen[2], Deyu Lu[3], Liwen Wan[2], Michael Nielsen[2] and Tuan Anh Pham[2]; [1]University of California, Riverside, United States; [2]Lawrence Livermore National Laboratory, United States; [3]Brookhaven National Laboratory, United States

X-ray absorption spectroscopy (XAS) provides a wealth of information about the local structure of materials. Recently, significant advancement has been made in the development of machine learning models for predicting local environments of absorbing atoms from XAS. However, existing studies have primarily focused on crystalline systems, while less has been paid to more complex and disordered systems. In this work, we develop a neural network model for predicting XAS spectra of amorphous carbon (a-C) using the local structural descriptor as a sole input. In addition, we compared the performance of different structural descriptors, including the Local Many-Body Tensor Representation (LMBTR), Atom-Center Symmetry Function

(ACSF), and Smooth Overlap of Atomic Positions (SOAP). We find that the use of LMBTR yields the highest accuracy, and the inclusion of both bond length and bond angle information is necessary for accurate XAS prediction. Furthermore, among the three representations, LMBTR offers a unique advantage in interpretability as the input components can be easily associated with specific structural features. We also extend our model to predict not only local structure features of a-C, such as bond lengths and angles but also its global chemical composition from XAS spectra.

2:30 PM MD01.02.04
Asking Graph Neural Networks the Right Questions for Material Discovery. Jason B. Gibson, Ajinkya Hire and Richard Hennig; University of Florida, United States

The ability of machine learning to extract structure-property relationships from density functional theory calculation has enabled the acceleration of material discovery and characterization. Recent publications continue to bolster ever-increasingly accurate models. However, when these models are used in practice, the model's performance is often quite different than the test scenario suggests. This performance discrepancy can often be attributed to the subtleties of how we pose the question that we train the model to answer. In this talk, I will first describe a data augmentation technique we developed to screen for thermodynamic stability [1]. This data augmentation technique yielded a 3-fold reduction in formation energy prediction error compared to previously published models. The model was designed to change the question we ask during training from "what is the formation energy of this structure?" to "what is the formation energy of this structure once relaxed?". I will then describe a new graph neural network architecture and the subtle changes we made during training that profoundly affected the model's performance. The network uses a novel graph embedding and two disconnected graph neural networks to predict the probability of experimental synthesizability of a structure generated by substitution from a prototype structure. Preliminary results show that this method boasts a significant performance boost compared to compositional-based models.

[1] Gibson, J., *et al. npj Comput Mater* **8**, 211 (2022).

2:45 PM MD01.02.05
Developing Single Deep Neural Network for Predicting Complete Phonon Properties of Inorganic Crystals Spanning 63 Elements Ming Hu; University of South Carolina, United States

Existing machine learning potentials for predicting phonon properties of crystals are limited to either small amount of training data or a material-to-material basis, primarily due to the exponential scaling of model parameters with the number of atomic species or elements. This renders high-throughput infeasible when facing large-scale new materials. Unlike previous machine learning models with inherently limited training on small data and global properties, we develop Elemental Spatial Density Neural Network Force Field (Elemental-SDNNFF) with abundant atomic level environments as training data. Benefited from this innovation, we integrate >30 million atomic data to train a single deep neural network without increased expensive ab initio simulations. The effectiveness and precision of the Elemental-SDNNFF approach is demonstrated on a set of >100,000 inorganic crystalline structures spanning 63 elements in the periodic table by prediction of complete phonon properties. Our algorithm achieved a competitive force root mean square error of less than 10 meV/Å and a speed-up of 3 orders of magnitude in comparison to first principles. Self-improvement schemes such as active learning and data augmentation techniques are also incorporated allowing human-free refinement of the force accuracy on arbitrary combinations of chemistries. As case studies of our predicted phonon properties, deep insight into the ultralow lattice thermal conductivity (<1 W/mK) of 774 predicted Heusler structures are gained by p-d orbital hybridization analysis and charting the data in the bonding-antibonding map, which offers a quick approach for future screening of crystals with strong intrinsic phonon anharmonicity. We also searched Weyl points with predicted phonon band structures of 1,662 half and 1,550 quaternary Heuslers. Topological Weyl points were found in more than 68% and 87% of half and quaternary Heuslers, respectively, with identification of a new class of two-band charge-2 WPs referred to as "double Weyl points". Our algorithm is promising for accelerating discovery of novel phononic crystals for emerging applications, such as heat dissipation in electronics, thermoelectrics, and coherent phonons for quantum information technology.

3:00 PM BREAK

3:30 PM MD01.02.08
TEM Image based MXene 3D Structure Construction using a Minimum Energy Based Deep Learning Algorithm Congjie Wei[1], Jiaxin Zhang[2] and Chenglin Wu[1]; [1]Missouri University of Science and Technology, United States; [2]Oak Ridge National Lab, United States

With the significant improvements and developments in transmission electron microscopes (TEM) techniques, accurate observation and identification is now more commonly adopted in angstrom-level precision, which reveals as sequential images about the real-space information. However, it still has difficulties to analyze the spatial defect distribution, phase transformation and dynamic phenomena since the TEM images can only record the appearances of the surface atoms while the out-of-plane information is severely missing. In this work, a first principle based deep learning algorithm is proposed and adopted to reconstruct the 3D transition states of a MXene healing process experimentally observed. Starting from the TEM image, all related Ti and C atoms around or within the laser-made hole could be categized into 3 groups based on the confidence of the information obtained from the TEM images. Around hole atoms are assumed to have crystalline structure and set as the input along with the in-plane information of atoms that can be observed directly within the hole. Out-of-plane information of the latter group of atoms are then treated as the output of the algorithm along with the spatial distribution of all underlying atoms. The input and output information are reformed into graphical representations and treated as a graph reference problem. The trunk of this algorithm is set as a deep convolutional neural network incorporated with attention-based and non-attention-based components. To conform to the distance prediction, smooth potentials are constructed for Ti-Ti, Ti-C and C-C interactions based on first principle calculation. The minimum potential energy accumulation of all atoms within the hole is set as one of the convergence conditions of the algorithm along with the fitting of the training data sets. Our models are trained on defected MXene structures optimized with DFT, where different sizes and number of atoms are considered. The predictions of this algorithm fit well with the TEM images and help with the understanding of the healing processes observed in MXene materials.

SESSION MD01.03: Machine Learning III
Session Chairs: Grace Gu and Adri Van Duin
Tuesday Morning, April 11, 2023
Marriott Marquis, Second Level, Foothill C

10:30 AM *MD01.03.01
Microscopy is All You Need Sergei Kalinin and Kevin Roccapriore; University of Tennessee, United States

Machine learning and artificial intelligence (ML/AI) are rapidly becoming an indispensable part of physics research, with domain applications ranging from theory and materials prediction to high-throughput data analysis. Over the last several years, increasing attention is attracted to the use of AI interacting with physical system as a part of active learning – including materials discovery and optimization, chemical synthesis, and physical measurements. For these active learning problems, microscopy arguably represents an ideal model application combining aspects of materials discovery via observation and spectroscopy, physical learning with relatively shallow priors and small number of exogenous variables, and synthesis via controlled interventions. In this presentation, I will discuss recent progress in automated experiment in electron and scanning probe microscopy, ranging from feature to physics discovery via active learning. The applications of classical deep learning methods in streaming image analysis are strongly affected by the out of distribution drift effects, and the approaches to minimize though are discussed. I will further illustrate transition from post-experiment data analysis to active learning process, including learning structure-property relationships and materials discovery in composition spread libraries. Here, the strategies based on simple Gaussian Processes often tend to produce sub-optimal results due to the lack of prior knowledge and very simplified (via learned kernel function) representation of spatial complexity of the system. Comparatively, deep kernel learning (DKL) and structured Gaussian Processes methods allow to realize both the exploration of complex systems towards the discovery of structure-property relationship, and enable automated experiment targeting physics (rather than simple spatial feature) discovery. The latter is illustrated via experimental discovery of ferroelectric domain dynamics in piezoresponse force microscopy. For probing physical mechanisms of tip-induced modifications, I will demonstrate the combination of the structured Gaussian process and reinforcement learning, the approach we refer to as hypothesis learning. Here, this approach is used to learn the domain growth laws on a fully autonomous microscope. The future potential of Bayesian active learning for autonomous microscopes is discussed. These concepts and methods can be extended from microscopy to other areas of automated experiment.

11:00 AM MD01.03.02
Explainable Machine Learning for Hydrogen Diffusion in Metals and Random Binary Alloys Grace M. Lu[1], Matthew Witman[2], Sapan Agarwal[2], Vitalie Stavila[2] and Dallas Trinkle[1]; [1]University of Illinois Urbana Champaign, United States; [2]Sandia National Laboratories, United States

Hydrogen diffusion in metals and alloys plays an important role in the discovery of new materials for fuel cell and energy storage technology. While analytic models use hand-selected features that have clear physical ties to hydrogen diffusion, they often lack accuracy when making quantitative predictions. Machine learning models are capable of making accurate predictions, but their inner workings are obscured, rendering it unclear which physical features are truly important. To develop interpretable machine learning models to predict the activation energies of hydrogen diffusion in metals and random binary alloys, we create a database for physical and chemical properties of the species and use it to fit six machine learning models that achieve root-mean-squared-errors between 105-124 meV on the testing data. By analyzing the feature importances of these fitted models, we identify relevant physical properties for predicting hydrogen diffusivity. While metrics for measuring the individual feature importances for machine learning models exist, correlations between the features lead to disagreement between models and limit the conclusions that can be drawn. Instead grouped feature importances, formed by combining the features via their correlations, agree across the six models and reveal that the two groups containing the packing factor and electronic specific heat are particularly significant for predicting hydrogen diffusion in metals and random binary alloys. This framework allows us to interpret machine learning models and enables rapid screening of new materials with the desired rates of hydrogen diffusion.

11:15 AM MD01.03.03
Overcoming Time Step Limitations in Molecular Dynamics Simulation with Machine Learning Fei Zhou; Lawrence Livermore National Lab, United States

Molecular dynamics simulations are usually limited to small time steps of about 1 fs, a major limitation on the capability of atomistic simulations to reach large time scales. We present a machine-learning method to accelerate molecular dynamics simulations by taking very large time steps. The data-driven approach, built with equivariant graph neural networks, is trained from MD trajectories to faithfully reproduce the same dynamics. The method was demonstrated on a few representative case studies, including single-particle in a 1D double-well potential, and solvated butane dihedral angle dynamics. We show that quantitative agreement on these barrier-crossing events can be achieved with our approach.

11:30 AM MD01.03.04
Modeling Ring-Opening Polymerization with Machine-Learned Committors Jacob Gissinger and Kristopher E. Wise; NASA Langley Research Center, United States

Many important industrial and biological processes depend on ring-opening polymerization (ROP), including large-scale production polymers, such as nylon 6, and a variety of biodegradable polymers and high-performance resins. Large-scale simulations (>200K atoms) of ROP were performed using a deep neural network-based method that captured the effect of the local chemical environment of the reactive sites using training data from quantum chemical methods. The utility of this method was demonstrated by modeling the cationic ROP of bis-benzoxazine, a promising resin for use in advanced high-temperature application composites (>200°C). Density functional theory calculations were used to map out the various ring opening and polymerization reaction paths that occur during the thermal processing of bis-benzoxazine. The probabilities of these reactions, as a function of local atomic configurations, were used to construct committor functions using a neural network approach. The learned committor functions were then used to determine when a particular reaction occurred within the REACTER framework for reactive molecular dynamics simulations. The experimentally observed exotherm that occurs during bis-benzoxazine ROP was captured in an effective manner in the simulations by imposing a local heating of the system that corresponds to the enthalpy of reaction for each reaction. The dependence of the final polymer morphology on the ROP reaction temperature was analyzed at the molecular scale. The results presented in this work indicate that machine-learned committor functions are a promising approach for incorporating high-fidelity reactivity criteria that capture the effect of local chemical environments into large-scale polymerization simulations.

11:45 AM MD01.03.05
Deepfaking Low-Energy Interface Structures Using a Generative Adversarial Network Adrian Xiao Bin Yong and Elif Ertekin; University of Illinois Urbana-Champaign, United States

Understanding the properties of solid-solid interfaces is important to a wide range of applications, from energy-storage devices to electronic devices to surface coatings. However, interfaces are challenging to model explicitly because the interface structure is not limited to a single possible configuration, unlike the unit cell of a single phase which often has only one ground-state configuration. Certain interfaces can exhibit significant disorder due to atomic rearrangement, chemical mixing, variable composition, etc., where there is likely an entire distribution of structures that reflect the real interface. In such cases, an interface structure search, that extends beyond simply pressing two slabs of materials together, would be necessary to identify energetically favorable interface structures. A random search of low-energy structures by generating atoms randomly at the interface is computationally expensive and inefficient, leading to the need for a more intelligent search scheme. We will demonstrate that the interface structure search problem can harness the power of machine learning not only through machine learning interatomic potentials to accelerate relaxations, but also through generative modeling. By training a generative model on a dataset of low-energy interface structures, the generative model can learn the underlying distribution and generate new low-energy structures. The generative model we have developed is a generative adversarial network (GAN), applied to lithium halide solid electrolyte/cathode interfaces for all-solid-state battery application. We will show that the GAN is capable of learning from the low-energy structures to generate a large number of atoms (> 250 atoms), and outperforms random search.

SESSION MD01.04: Machine Learning IV
Session Chairs: Ekin Dogus Cubuk and Sergei Kalinin
Tuesday Afternoon, April 11, 2023
Marriott Marquis, Second Level, Foothill C

1:45 PM MD01.04.01
Semi-Supervised Prediction of Double Transition Metal MXene Stability Kat Nykiel and Alejandro Strachan; Purdue University, United States

MXenes are a recently discovered class of 2D materials with important electronic, optical, and magnetic applications. Double transition metal (DTM) MXenes are particularly of interest due to the tunability of their properties and the top-down synthesis approach of MXenes. Experimentalists have synthesized more than 46 DTM MXenes that have been published in open literature. Each DTM MXene is etched from a bulk M'M"AX phase, where each M', M", A, and X indicate a different element resulting in a large domain of possible combinations and relative lack of synthesized examples. We apply semi-supervised learning methods that leverage the unlabeled data to better predict synthesizable materials and guide experiments. In this work, we compare several pseudo-label semi-supervised learning approaches to predict stable DTM MXenes. The previously published experimental DTM MXenes are used as labels and unlabeled data is collected using a high-throughput density-functional theory workflow for 8712 MAX phases and their 726 MXenes. From these results, several DTM MXenes were predicted to be stable in ambient conditions, potentially expanding the family of DTM MXenes and providing a framework for predicting synthesizability of new material candidates.

2:00 PM MD01.04.02
Machine Learning to Describe Structure-Property Relationships Within a Large Cluster Expansion Approach Cindy Wong and Andre Schleife; University of Illinois at Urbana-Champaign, United States

The cluster expansion (CE) approach is used to describe and model the configurational site disorder of alloy materials systems and how changes in the local arrangement can affect materials' properties. When increasing the cell size used in the expansion, the number of non-degenerate configurations exponentially increases thus manually sampling the resulting configurational space becomes expensive when using first-principles density functional theory (DFT). In this work, we demonstrate the use of machine learning to model the structure-property relationship of 36-atom $Be_{(1-x)}Zn_xO$ clusters by uniformly selecting 5% of all configurations and their dielectric functions from DFT as the training set. The model is used to predict the remaining 95% of total configurations and its accuracy is demonstrated by using thermodynamic averages compared to results from smaller supercells. We then discuss the best practices and considerations when applying this approach to other multicomponent systems like dataset size and curation followed by descriptor quality when making predictions.

2:15 PM MD01.04.03
Deep Learning Prediction and Optimization of Photon Upconversion in Lanthanide-Doped Nanoparticles Eric Sivonxay, Xiaojing Xia, Emory Chan and Samuel M. Blau; Lawrence Berkeley National Laboratory, United States

Deep learning prediction and optimization of photon upconversion in Lanthanide-doped nanoparticles
Eric Sivonxay, Samuel M. Blau

Lanthanide-doped upconverting nanoparticles (UCNPs) have unique optical properties, capable of near-infrared excitation to yield visible and ultraviolet emissions. UCNPs have broad applications ranging from biosensing and drug delivery to super-resolution microscopy. Factors affecting the nonlinear photophysical properties of UCNPs include size, shape, doping, shell thickness, and surface ligands, defining a vast chemical design space. Due to the complexity of the energy transfer networks formed by the 4f electron shells of the lanthanide dopants, rationally designing UCNPs with high upconverting efficiency for tailored applications remains unfeasible. While Monte Carlo simulations allow for reasonably accurate in silico prediction of optical properties, calculations scale poorly with particle size and dopant loading, constraining the search for UCNPs with desirable properties to be fundamentally Edisonian. Here, we report efforts to overcome these challenges by combining high-throughput data generation with nanoparticle representation learning. We combine a high-performance implementation of lanthanide energy transfer Monte Carlo with automated workflows and HPC resources to generate the first large dataset of over 5,000 simulated spectra for UCNPs. We then develop a novel representation of nanoparticle features, enabling deep learning of spectra. Finally, we apply these models to optimize UCNP heterostructure, targeting high UV emission for 3D printing, and present preliminary results.

2:30 PM BREAK

3:00 PM *MD01.04.05
Atomistic-Scale Simulations of Realistic, Complex, Reactive Materials—The ReaxFF Method, its Applications and Recent Developments Adri Van Duin, Yun Kyung Shin and Benjamin Evangelisti; Pennsylvania State Univ, United States

The ReaxFF method provides a highly transferable simulation method for atomistic scale simulations on chemical reactions at the nanosecond and nanometer scale. It combines concepts of bond-order based potentials with a polarizable charge distribution.
Since its initial development for hydrocarbons in 2001[1], we have found that this concept is transferable to applications to elements all across the periodic table, including all first row elements, metals, ceramics and ionic materials[2]. For all these elements and associated materials we have demonstrated that ReaxFF can accurately reproduce quantum mechanics-based structures, reaction energies and reaction barriers, enabling the method to predict reaction kinetics in complicated, multi-material environments at a relatively modest computational expense. At this moment, over 1000 publications including ReaxFF development of applications have appeared in open literature and the ReaxFF code has been distributed around the world and has been implemented in major open-source and commercial computational chemical software packages.
This presentation will describe the current concepts of the ReaxFF method, the current status of the various ReaxFF codes, including parallel implementations, new force field development algorithms that speed up the ReaxFF parameterization from months to weeks and acceleration methods that allow for microsecond-range predictions. Also, we will present and overview of recent and developing applications to complex materials, with a focus on 2D-material defect chemistry[3-4], metal deposition[5-6] and an expansion of ReaxFF for events in graphitic, metallic and polymer materials that require explicit electrons (e-ReaxFF)[7].

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3:30 PM MD01.04.06
Recursive Training for Deep Material Network and the Prediction of the Elastic-Plastic Behavior of Heterogeneous Microstructures Dongil Shin[1], Ryan Alberdi[1], Ricardo A. Lebensohn[2] and Remi Dingreville[1]; [1]Sandia National Laboratories, United States; [2]Los Alamos National Laboratory, United States

Recent developments to integrate micromechanics and neural networks are providing a promising path forward on rapid prediction of multiscale heterogeneous materials with similar accuracy as direct numerical simulations, such as finite-element analysis, for instance. Our approach here, called `Deep Material Network' (DMN), consists of a multi-layer network structure and micromechanics building blocks. DMN is trained on elastic properties data and provides a reduced-order model of the microstructures' representative volume elements (RVE), which can be extrapolated to non-linear constitutive behavior in an online mode. However, up-to-date training methods consisting of random initialization of the network parameters occur with inevitable uncertainty. Here, we present a recursive training strategy based on the visualization of the network as a DMN-RVE. In this methodology, the network is represented as a RVE derived from its architecture (number of layers) and parameters. The network is then trained recursively by using the converged DMN-RVE for a given number of layers, as a starting template for the initial parameters for the next DMN architecture with a higher number of layers. The result is an improvement in the training and performance of the network compared to random initialization, and the intuitive representation of the network during the training process. This approach opens new strategies for machine-learned, microstructure-based, and multi-scale modeling of complex materials.
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3:45 PM MD01.04.07
Ensemble Models for the Growth of Colloidal Sol-Gel Materials Tim Erdmann[1], Jason Chen[2], Sarathkrishna Swaminathan[1] and Dmitry Zubarev[1]; [1]IBM Research, United States; [2]The University of Chicago, United States

Sol-gel processes have been applied for the preparation of various high-performance and biocompatible solids ranging from ultra-light aerogels to sustained drug-release materials, metal oxide semiconductors, and tough ceramics. Using the sol-gel method to establish versatile functional modifications on various surfaces is furthermore a straight-forward and cost-efficient approach. To allow for operational flexibility, control and reproducibility of the process, knowledge about the reaction progress is crucial. This is however a non-trivial problem due to the competing underlying mechanisms of hydrolysis and polycondensation and the consequently resulting orthogonality of the reaction parameters. In our talk we will focus on spin-on-glass as an example for sol-gel materials and will discuss the selection of key reaction parameters, their translation into arguments experimentally executable by a synthesis robot, the analysis of the reaction progress by GPC, and how the workflow was established by hardware/software components. We will continue presenting how the sparse dataset – covering only 0.38 % of the experimental space resulting from the number of (semi-)continuous key reaction parameters and variability thereof (92,610 combinations) – was used for the development of ensemble models based on polynomial regression. In validation experiments the ensemble regressors correctly predicted the ranges for dispersity and molecular weight in about 70 % of the cases.

4:00 PM MD01.04.08
Inferring Interatomic Forcefields from Trajectories Using Graph Neural Network and Symbolic Regression Ruoxia Chen and Mathieu Bauchy; University of California, Los Angeles, United States

Classical molecular dynamics (MD)—the workhorse of computational material science—relies the accurate knowledge of the interatomic forcefields. In that regard, analytical forcefields are fast, physics-informed, and interpretable, but are hard to parameterize and often biased due to the choice of the underlying analytical form. On the other hand, machine-learned forcefields are non-biased, but are more computationally expensive and tend to offer poor generalizability to new phases or conditions. Here, we present a new approach that is able to infer analytical interatomic forcefields from trajectories produced by Density Functional Theory (DFT). Our approach is based on fitting DFT results by a message-passing graph neural network (GNN), which is then simplified into an analytical forcefield using symbolic regression—without any assumption regarding the nature of the analytical form. We show that the forcefields that are discovered offer an accuracy that matches that of machine-learned forcefields, at a fraction of the computing cost, and feature improved generalizability.

4:15 PM MD01.04.09
Forcefield Parameterization via Differentiable Molecular Dynamics Abhijeet S. Gangan and Mathieu Bauchy; University of California, Los Angeles, United States

In classical molecular dynamics, the quality of the forcefield is determined by how well it reproduces the desired physical properties in comparison to those achieved in experiment/*ab initio* settings. To achieve this the forcefield parameters are chosen either by physical intuition or are optimized with respect to some target (ground truth) properties like energies or forces. This makes it important to parametrize the forcefield in an accurate and efficient manner. Optimization of a forcefield is typically done using either gradient-free or gradient-based algorithms. In the case of gradient-based algorithms, the gradients of the loss function have to be computed. Since the analytic gradients are not known, approximations like the finite difference are made to compute the gradients. Such approximations introduce errors and their computation is inefficient in higher dimensions. Automated (algorithmic) differentiation (AD) solves this problem by enabling the computation of gradients in an efficient way. AD libraries like JAX have enabled end-to-end differentiable simulation packages like JAX-MD. JAX-MD provides a framework for physics simulation primarily focused on molecular dynamics. Differentiable simulation enabled by JAX and JAX-MD allows for the computation of gradients that are utilized for computing the relevant properties (forces etc) as well as in optimizers that use gradients of the loss function. This enables parametrization based on static (energy, forces, elastic constants, etc.) and dynamic properties (radial distribution function, etc.). We demonstrate this by parameterizing forcefields in an efficient manner by using gradient information provided by JAX and JAX-MD. We also compare it with gradient-free optimization methods and highlight the advantages offered by differentiable simulation.

SESSION MD01.05: Machine Learning V
Session Chairs: Ekin Dogus Cubuk and Sinan Keten
Wednesday Morning, April 12, 2023
Marriott Marquis, Second Level, Foothill C

8:30 AM *MD01.05.01
Virtual Inspection of Advanced Manufacturing via Digital Twins Brian Giera, Brian Au, Brian Weston, Kyle DeVlugt, Haicho Miao and Seth Watts; Lawrence Livermore National Laboratory, United States

A digital twin is an amalgam of physics-based (high fidelity or reduced order) and/or data driven models that describe a physical system, as shown below. Digital twins exist in a variety of settings ranging from manufacturing and inspection equipment, supply chains, city planning, and so on. In the context of advanced manufacturing (AM), the inputs/outputs of the digital twin and its real-world counterpart are indistinguishable, i.e., both operate on identical machine instructions and produce identical data structures. Like many, LLNL's approach requires continually refining the digital twin with real data to better capture behavior of its real counterpart via advanced analytical techniques. As such, a digital twin's evolving parameter set can inform of machine health and aging behavior, providing actionable insights on lifetime performance. Digital twins offer an inexpensive and risk-free environment for machine operator training and troubleshooting complex toolpaths. A suite of digital twins that capture all fabrication and inspection platforms of a given AM process can accelerate production for "born-qualified" parts at scale with minimized and quantified defects. This talk will walk through examples of how we are leveraging data from integrated pairs of real and digital twins of inspection and fabrication platforms to become more flexible and agile.

9:00 AM MD01.05.02
Continual Learning for Accelerating Flow Battery Redox-Active Material Development Yucheng Fu, Amanda A. Howard and Panos Stinis; PNNL, United States

Redox flow batteries hold great promise for large-scale energy storage applications due to their scalable capacity and low fire risks. The machine learning-based regression models have demonstrated their capability to provide high throughput performance predictions as a function of the battery cell design, operating conditions, and relevant material properties. However, due to the large design space of the molecular especially for the emerging organic redox-active materials, new datasets to be used for algorithm training can be available only incrementally. Moreover, it is computationally inefficient to simply add them to the existing material datasets and retrain the machine learning algorithms. To remedy these difficulties and help to accelerate the redox-active material design, we have developed continual learning methods for flow battery predictions that can train on incremental datasets, without a replay of previous datasets. Our multifidelity continual learning method takes advantage of correlations between the datasets to improve predictions without catastrophic forgetting that can occur for the earliest datasets. This approach can be combined with existing continual learning techniques, such as elastic weight consolidation, and other neural network training methods, such as physics-informed neural networks, to improve the flow battery performance predictions.

9:15 AM MD01.05.03
Unifying the Duality of Crystalline Order-Disorder Characterization with Denoising Score Function Model Yu-Ting Hsu[1], Babak Sadigh[1], Nicolas Bertin[1], Cheol Woo Park[1], James Chapman[2], Vasily Bulatov[1] and Fei Zhou[1]; [1]Lawrence Livermore National Laboratory, United States; [2]Boston University, United States

In atomistic modeling of solids, methods to elucidate structural phases and defects obscured by the noise of thermal fluctuations are essential for analyzing and understanding the simulated atomic order-disorder. With the perspective that the challenge of delineating order-disorder features from thermal perturbation is akin to determining signal from noise, we consider classifying the ordered phases and locating the disordered defects—two important tasks that are typically tackled separately—to be fundamentally the same problem and address it with a unifying approach complementary to current characterization techniques: a denoising score function that minimizes thermal noise. Our approach is based on a geometric and probabilistic standpoint of denoising structures to maximize their likelihood towards that of ideal reference structures, as opposed to traditional methods relying on structure/material-specific physical knowledge, or emerging data-driven approaches that rely on large datasets derived from interatomic potentials and MD simulation. The denoising score function is approximated with a rotationally equivariant graph neural network (NequIP) trained without physical knowledge about the reference structures. Focusing on single-element systems in this work, our denoising model effectively reduces molecular dynamics (MD) noise of perturbed BCC, FCC, and HCP structures up to the melting point and trivializes phase identification of an MD trajectory of Cu nucleation from melt. The denoising model is also shown to minimize thermal noise without impacting meaningful disordered features such as point defects, dislocations, and grain boundaries in MD simulations at elevated temperatures, thereby facilitating the identification of disordered defects. The denoising model, trained without any simulation data, is potentially a powerful, flexible denoising filter that can be integrated in the analysis workflows of massive atomic simulations. Lastly, future work for generalizing the denoising model to multi-element systems and other complex structure and defect types is discussed.

9:30 AM MD01.05.04
Weak-Formulated Physics-Informed Machine Learning for Nondifferentiable Heterogeneous Material Domains Zhizhou Zhang and Grace Gu; University of California, Berkeley, United States

Physics-informed machine learning has attracted great research interest for its ability to perform data-free training by direct supervision of partial differential equations (PDE). Recent advancement in operator learning further allows deep neural networks to not only learn functional solutions, but also projections between input and output fields, which can potentially be used as surrogate physics models. Despite the abovementioned achievements, there has been limited attention on solving balance of linear momentum for solid heterogeneous material mediums, where physics-informed learning is difficult to implement due to nondifferentiable constituent material domains and irregular boundaries subject to deformation. In this work, we propose a weak formulated physics-informed loss based on the deep operator network architecture to tackle the challenges in solid mechanics. Without loss of generality in network architecture, sensor points are sampled based on the nodes of a lagrangian mesh. Numerical integration will be performed over the sensor points to estimate the system energy which serves as part of the loss to be minimized. Such weak formulation converts spatial divergence into integral and provides precise tracking of material points and boundary deformation. Additional sensor points are sampled within each Lagrangian element where the material is assumed homogeneous to allow regularization of training via the strong form PDE. Our method is expected to achieve over 97% R^2 accuracy under a purely data-free training scheme for arbitrary material domain shape, with a fully generalized model that performs single solution learning as well as operator learning under a universal architecture.

9:45 AM MD01.05.05
Automated Chemical Structure Prediction Using Multi-Modal Spectral Data and Machine Learning Peggy P. Li, Evan Antoniuk, Bhavya Kailkhura and Anna Hiszpanski; Lawrence Livermore National Laboratory, United States

Spectroscopic data of various types – infrared (IR), mass (MS), or nuclear magnetic resonance (NMR) – are critical tools chemists use to deduce the chemical structure of molecules present in samples. However, this exercise becomes increasingly challenging when the sample is unknown or contains a mixture of molecules. In such cases, a primary method of structure elucidation is by pattern-matching the spectra against large libraries of reference spectra or standards using rule-based software. While useful, these softwares fail when they encounter samples whose spectra are not available, and for this reason, standardless and machine-learning-driven approaches of chemical structure elucidation from spectra data are highly desired. We build upon prior machine learning work for structure elucidation, focusing on multi-modal spectral data.

We have developed models that predict chemical structure directly from four types of spectral data - IR, MS, H-NMR, and C-NMR, without requiring a library of reference spectra, as well as evaluated different combinations of those four spectra. The ability to incorporate these different data modalities and evaluate their relative importance to structural elucidation is a unique benefit of these machine learning approaches. Our model is a multilayer perceptron, the simplicity of which was more suitable for our relatively small dataset. This dataset contains around 7k molecules, from the NIST WebBook. Based on the input spectra, the models output for several hundred substructures the probabilities that they are present in the sample. These probabilities then serve as input to a beam search algorithm previously developed by the Markland and Kanan group (Huang Z. et al. Chem. Sci., 2021, 12 (46), 15329), which generates a ranked list of the potential chemical structures. From these molecule prediction results, we see that using all four modalities of spectra indeed gives us the best top-1 and top-10 scores, with a top-1 score 8% better and a top-10 score 7% better than the best single modality model (IR). This increase in performance could be useful to improve the performance of a machine learning model that lacks a large training dataset. Interestingly, the MS modality does not increase performance by as much as we expected, and we are investigating that further. This is surprising as NMR and MS is commonly used for structure elucidation by chemists. Our hypothesis is that our substructures need to be curated to better work with our MS spectra.

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

10:00 AM BREAK

10:30 AM *MD01.05.06
Data-Driven Approaches to Accelerate Experimental Discoveries Xiaolin Zheng; Stanford University, United States

Experimental researches are typically labor-intensive, especially when multiple parameters affect the experimental output. The amount of control experiments needed is enormous to understand and optimize those parameters. The rapid advancement and easy access to machine learning offer great opportunities to accelerate experimental discoveries. In this talk, I will present two examples of using machine learning to guide experimental research. The first example demonstrates a data-driven approach to designing soft materials that predict experimental synthetic recipes based on specified mechanical properties. We use polyurethane (PU) elastomer as a model soft material and experimentally varied the mechanical properties of the PU elastomer by modulating the mixing ratio between components of the elastomer. We used the experimental data to train a regression model. The resulting model takes desired mechanical properties as input and returns synthetic recipes of a soft material, which is subsequently validated by experiments. The second example studies the electrochemical production of valuable chemical hydrogen peroxide (H_2O_2). We apply a machine learning-assisted prediction to map out the performance of electrochemical H_2O_2 production over the continuous parameter space of electrolyte composition and applied potential. The continuous model enables us to evaluate the thermal efficiency, H_2O_2 electricity cost, and time needed to produce H_2O_2 over a broad range of electrolytes and applied potential conditions.

11:00 AM MD01.05.07
CHGNet: Pretrained Neural Network Potential for Fast and Accurate Charge-constrained Molecular Dynamics Bowen Deng[1,2], Peichen Zhong[1,2] and Gerbrand Ceder[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Molecular dynamics (MD) simulation coupled on systems with complex electron interactions remains one of the biggest challenges for atomistic modeling. While classical force fields often fail to describe the electronic coupling with ionic rearrangements, the more accurate spin-polarized *ab initio* molecular dynamics (AIMD) suffer from the computational complexity that prevents long-time and large-scale simulation, which are essential to study ion migrations and phase transformations.
In this work, we present the Crystal Hamiltonian Graph Neural Network (CHGNet) as a novel approach that uses a graph neural network (GNN) based force field to model a universal potential energy surface that can describe both atoms and electrons. CHGNet is pretrained on a large Materials Project Trajectory (MPtrj) Dataset, which consists of over 1 million inorganic structures from over 10 years of density functional theory (DFT) static and relaxation trajectories at the Materials Project. We demonstrate the performance of CHGNet molecular dynamics in Li-ion solid-state electrolyte and phase transformation in Li-ion cathode materials.

11:15 AM MD01.05.08
Accelerated Modelling of Interfaces for Electronic Devices using Graph Neural Networks Pratik Brahma[1], Sinead Griffin[2] and Sayeef Salahuddin[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

The modern Si transistor gate stack is comprised of multiple material interfaces whose electronic interactions greatly affect the electron transport and ultimate transistor performance. In particular, the heterogeneous semiconductor-dielectric gate stack introduces many atomic-scale modelling challenges, which if addressed, can help design higher performance gate sacks for next generation transistors. Towards this goal, grand challenges for the electronic device modelling community include: (i) incorporating the physics of defect formation across a large number of interfaces, (ii) adjusting for ultrathin layers, which leads to surface energy and interface interactions dominating the electronic transport properties rather than bulk interactions, and (iii) accounting for different crystalline states across the gate stack (e.g., single crystalline channel, amorphous and polycrystalline gate dielectrics). There are currently two primary methods to model these complex systems: (i) Empirical methods which fit material parameters to experimental results that are scalable but suffer from accuracy limitations due to neglection of ab-initio physical equations, and (ii) Ab-initio methods which accurately solve the quantum Hamiltonian of the heterostructure system but are time consuming and impractical for large systems containing thousands of atoms and varied crystalline states.

In this work, we aim to overcome the scalability-accuracy trade-off in modelling electronic heterostructures by using graph neural networks [1] with the scalability and flexibility of empirical methods and with the accuracy of ab-initio methods like density functional theory (DFT). Machine learning techniques help to characterize the relationships between local atomic chemical environments and global electronic transport properties e.g. injection carrier velocity, gate capacitance, band gap, etc. We focus on the model system HfO2-SiO2-Si, the gate stack for state-of-the-art transistors, in which hafnium dioxide and silicon dioxide are amorphous and silicon is crystalline. The neural network is trained on data generated using DFT for a small number of atoms (~ 50 -100) to capture the local chemical correlations and learn the energy-conserving force fields. Thus, the network can efficiently generate samples to produce histograms needed to calculate the properties of an amorphous/polycrystalline heterostructure and predict electronic properties accurately for up to system sizes of five hundred atoms. This work paves the way for a fast and scalable method to model modern advance electronic transistors with ab-initio accuracy.

[1] Schütt, K. T., Sauceda, H. E., Kindermans, P. J., Tkatchenko, A., & Müller, K. R. (2018). SchNet - A deep learning architecture for molecules and materials. *Journal of Chemical Physics*, *148*(24)

11:30 AM MD01.05.09
Predicting Secondary Phase Formation at the Solid-Electrolyte/Cathode Interface Using Machine-Learning Interatomic Potential Wonseok Jeong, Aniruddha M. Dive, Kwangnam Kim, Brandon Wood and Liwen Wan; Lawrence Livermore National Laboratory, United States

All-solid-state Li-ion batteries are attractive next-generation energy-storage devices that offer potential improved safety, energy density, and durability in comparison with conventional Li-ion batteries. One of the key phenomena that deteriorate the performance of all-solid-state Li-ion batteries is the side reaction occurring at the solid-electrolyte/cathode interface, which exacerbates at elevated temperatures during co-sintering and can lead to formation of unwanted phases that impede Li-ion transport. It is unclear how these secondary phases are dynamically formed at the atomic scale and under what conditions. In this work, we explore the nucleation and evolution of secondary phases, such as La-Co-O, at the $Li_7La_3Zr_2O_{12}$ (LLZO) solid-electrolyte and $LiCoO_2$ (LCO) cathode interface, from atomistic simulations. To start, we set up a series of ab initio molecular dynamics (AIMD) simulations of small LLZO|LCO interfacial model, to probe early-stage interfacial degradation and to identify chemical motifs that can lead to the formation of La-Co-O secondary phase. We then directly simulate the phase evolution of La-Co-O using metadynamics and machine-learning interatomic potential. Adopting machine-learning interatomic potential allows us to perform large-scale simulations in close-to-real time and length scale with quantum-level of accuracy. In addition to the dynamics simulations, we also carry out crystal structure prediction (CSP) simulations for La-Co-O and Li-La-Co-O systems. For multi-component systems such as (Li)-La-Co-O system, CSP involves extensive search of the energy landscape, thus we adopt the machine-learning potential for CSP within the SPINNER framework to predict meta-stable structures that may be formed at the LLZO|LCO interface during operation.[1]

This work was sponsored by the Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office and was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. A portion of this research was performed using computational resources sponsored by the Department of Energy's Office of Energy Efficiency and Renewable Energy and located at the National Renewable Energy Laboratory.

[1] Kang, S.; Jeong, W.; Hong, C.; Hwang, S.; Yoon, Y.; and Han S. Accelerated identification of equilibrium structures of multicomponent inorganic crystals using machine learning potentials *Npj Comput. Mater.* **8**, 108 (2022).

SESSION MD01.06: Machine Learning VI
Session Chairs: Mathieu Bauchy and Brian Giera
Wednesday Afternoon, April 12, 2023
Marriott Marquis, Second Level, Foothill C

1:30 PM *MD01.06.01
Towards Predictive Constitutive Models of Biomaterials Using Machine Learning and Molecular Simulations Sinan Keten; Northwestern University, United States

Transitioning from plastic to synthetic biomaterials is important for producing biodegradable packaging, manipulating food texture, developing biocompatible medical grafts, and enhancing durability of textiles. Structural biomaterials such as titin, silk, collagen, resilin and mussel foot proteins exhibit fascinating mechanical behavior. These model materials are critical starting points for identifying relationships between sequence and mechanical properties and are often used as templates to design synthetic biomaterials with tunable properties. Current experimental and computational methods for characterizing structural proteins are time and resource intensive, which hinders the rate at which favorable sequence mutations can be tested. Complex strategies for developing constitutive relations of these materials are most successful when computational and experimental techniques are combined to account for variable pre and post yield behavior. For resilin, silk, and other protein families, sequences vary across species producing an envelope of material properties related to sequence variability. In this work, we aim to establish a connection between molecular mobility and mechanical properties of protein-based materials using existing data sets, and molecular dynamics simulations, and machine learning methods trained on molecular-scale data. We then explore how predictions from these models can be utilized develop predictive constitutive models that can sequence-dependent mechanical properties of these protein-based materials.

2:00 PM MD01.06.02
Mixed-Variable Adaptive Design Framework with Bayesian Optimization for Multi-Property Optimization of Anisotropic Nanodielectric Materials using "on-demand" Simulations Yigitcan Comlek[1], Prajakta V. Prabhune[2], Ravishankar Sundararaman[3], Linda S. Schadler[4], Catherine Brinson[2] and Wei Chen[1]; [1]Northwestern University, United States; [2]Duke University, United States; [3]Rensselaer Polytechnic Institute, United States; [4]The University of Vermont, United States

Design and development of novel polymer nanodielectrics still remains a challenge due to high number of parameters and properties from different domains involved with the process. Specifically, the mixed-variable multi-scale design space formed by interface choices, and microstructural variations creates a bottleneck in the design optimization. We propose a physics-based adaptive nanodielectrics design framework for multi-property optimization. The framework adopts a descriptor based anisotropic microstructure design technique that controls the non-spherical filler design variables, namely volume fraction, orientation, dispersion, and aspect ratio to generate microstructures, and incorporates attractive extrinsic and intrinsic interfaces as supportive mechanisms into the design. A novel and interpretable machine learning model, Latent Variable Gaussian Process (LVGP), is trained to capture and understand the underlying relationship between mixed-variable design space, interface (qualitative) and microstructural (quantitative) variables, and the properties. Finally, a multi-property Bayesian optimization is performed with the help of "on demand" finite element simulations to find the Pareto Front between mechanical and dielectric properties of anisotropic nanodielectric materials, while providing interpretability about the design process through global sensitivity analysis.

2:15 PM MD01.06.03
Random Forest Prediction of Crystal Structure from Diffraction Patterns Samuel P. Gleason[1,2], Alexander Rakowski[2], Jim Ciston[2] and Colin Ophus[2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Electron microscopy, and specifically diffraction patterns, contain a wealth of information regarding the structure of a crystalline material. Specifically, electron diffraction can be used to determine crystal phases of nanoscale sample volumes produced by synthesis methods, track how chemical processes alter crystals, and provide quantitative information on a crystal's lattice structure. However, it is a consistent challenge to determine this information for a new material or even a new phase of an existing material. This challenge is exacerbated by the high electron scattering cross section, frequently leading to multiple scattering in a specimen and breaking the direct relationship between structure factors and diffraction intensities often present in x-ray and neutron diffraction experiments. In these situations, manual exploration of fully dynamical simulated diffraction patterns of individual crystals, and then mapping these patterns to the experimental pattern, is required. This is often a time consuming process with no obvious start point when many very similar structures are possible. Therefore, this project developed a predictive model to make inferences about the crystal structure of a material from its diffraction pattern.

In this work, py4DSTEM was used to simulate diffraction patterns for thousands of unique materials extracted from the materials project [1],[2]. Our database contains 100 unique zone axes for each material and a range of material thicknesses, providing a database containing millions of patterns. These patterns were then used to build a random forest model capable of predicting the space group, point group, crystal system, lattice parameters and thickness of an unlabeled pattern [3]. This model achieves a reasonably high top line accuracy for crystal structure prediction, correctly identifying the crystal system from an indivudual diffraction pattern of arbitrary zone axis and thickness greater than 60% of the time. However, top line accuracy is not the only, or even the primary, value of this model, as a significant utility of this approach is the ability to return a complete set of predictions for each tree in the random forest model. By examining the spread of predictions for an individual pattern across all the decision trees that make up the random forest model, the correct crystal system can often be deduced, even if the top line prediction is incorrect. In cases such as these, the spread of predictions may indicate a great deal of uncertainty between two similar crystal systems, providing a significant boost for a user searching for a theoretical crystal which matches the experimental pattern. Additionally, the spread of the lattice parameters, the lengths of the three lattice vectors and their angles, further narrow down the possible structures, even in situations where the top line prediction is inaccurate for these quantities. This model can be used to significantly accelerate the analysis diffraction patterns, especially for situations where the crystal hasn't been seen in experiments before. Additionally, integration of this model with a 4DSTEM experiment would allow on the fly labeling of an entire sample with phase and thickness information.

References:
[1] Savitzky, B. et al. Microscopy and Microanalysis (2021) 27 (4), 712-743
[2] A. Jain, et al. APL Materials 1, 011002 (2013)
[3] Pedregosa et al., Journal of Machine Learning Research (2011) 12, 2825-2830

2:30 PM MD01.06.04
Data-Driven Discovery of Dynamics from Time-Resolved Coherent X-Ray Scattering Nina Andrejevic, Qingteng Zhang, Tao Zhou, Mathew Cherukara and Maria K. Chan; Argonne National Laboratory, United States

Coherent X-ray scattering techniques are often used to interrogate materials' structural and dynamical properties at mesoscopic time and length scales. In particular, X-ray photon correlation spectroscopy (XPCS) exploits correlations between scattered intensity fluctuations over time to derive insights about microscopic sample dynamics, from particle diffusion in colloidal suspensions to fluctuations of magnetic domains. However, the interpretation of complex XPCS signatures is often challenging or only in terms of approximate phenomenological models. In this work, we develop a machine learning framework to uncover mechanistic models from time-resolved coherent scattering measurements directly from data. Combining the method of neural differential equations with a computational forward model of the scattering method, we recover the time evolution of several model dynamical systems without access to real-space dynamics. We evaluate our approach against experimental considerations such as sampling and noise and discuss the interpretability of the learned models. Finally, we demonstrate a simple proof of concept for applying our framework to experimental data.

2:45 PM MD01.06.05
Multi-Objective Bayesian Optimization of Complex, Concentrated Alloys Jacob Startt[1], Sean Donegan[2], Megan Mccarthy[1], Mitchell A. Wood[1] and Remi Dingreville[1]; [1]Sandia National Laboratories, United States; [2]Air Force Research Laboratory, United States

High-entropy alloys (HEA) and the broader class of multi-principal element alloys (MPEA) and baseless alloys, collectively called complex, concentrated alloys (CCA), sit at the forefront of the state-of-the-art in high-strength metals research. The near equiatomic concentrations of components in these alloys promote a multitude of desirable effects, ranging from entropic phase stabilization to atomic size mismatch and local magnetic strengthening mechanisms. Often, the combined effects of these properties lead to CCAs with high temperature mechanical strengths that far surpass that of our best high-strength steels and Ni superalloys. While the origins of these properties are typically rooted in the compositional disorder of CCAs, their complex compositional domain is also what ultimately makes the task of engineering or tailoring specific properties a nearly insurmountable hurdle when approached with traditional experiment-based optimization techniques. In this work, we demonstrate how Bayesian inference led multiscale modeling of relevant atomic and microscopic properties can instead be used to efficiently navigate the vast compositional space of these CCAs to optimize multiple properties at the same time. We utilize a diversity guided multi-objective Bayesian optimization (MOBO) scheme, involving objective modeling via Gaussian processes (GP), to optimize sets of mechanical and thermodynamic properties in several refractory body-centered cubic (BCC) CCA systems, including MoNbTaTi, MoNbTaWVCrMn, and MoNbTaWTiV. In doing so, we also attempt to base descriptions of important macroscopic properties on easy-to-obtain atomic level properties from multiscale ab-initio and molecular dynamics calculations to best expedite the process of data generation and objective optimization. By identifying the compositional neighborhoods that yield the best combinations of desired alloy properties, a large portion of the legwork can be eliminated before any physical experiment is performed, greatly reducing the associated cost and time to develop new state-of-the-art CCAs.

SAND2022-15070 AX

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3:00 PM BREAK

3:30 PM *MD01.06.06
Uncovering Fast Solid-Acid Proton Conductors Based on Dynamics of Oxyanion Groups and Proton Bonding Strength Konstantin Klyukin[1,2], Pjotrs Zguns[1], Ju Li[1,1] and Bilge Yildiz[1,1]; [1]Massachusetts Institute of Technology, United States; [2]Auburn University, United States

Achieving high proton conductivity in inorganic solids is very attractive for many electrochemical devices such as in required for low-power nanoelectronics and energy-efficient fuel cells and electrolyzers. A deeper understanding of physical traits of the material to regulate the Grotthuss mechanism of proton diffusion is crucial to accelerate the discovery of new electrolytes with high proton conductivity. In this work, we investigated proton conductivity in electrolyte materials from the solid-acids family. We have performed ab initio molecular dynamics, phonon spectra and atomic structure calculations to map structural, chemical, and dynamic properties of the material to rate-limiting steps of proton diffusion. We have identified a set of physical descriptors, specifically the acidity of donor/acceptor groups, bond lengths, and vibrational frequencies of cation framework, that control the kinetics of local proton hopping and structural reorganization to facilitate long-range proton diffusion. Finally, we use these descriptors for high-throughput screening of materials databases and discuss how our results can be useful in the design of novel electrolytes with high proton conductivity.

4:00 PM MD01.06.07
A Crystal Generative Model Conditioned on Space Group Rees Chang[1], Nick Richardson[2], Alex Guerra[2], Angela Pak[1], Ni Zhan[2], Alex M. Ganose[3], Adji B. Dieng[2], Ryan Adams[2] and Elif Ertekin[1]; [1]University of Illinois at Urbana-Champaign, United States; [2]Princeton University, United States; [3]Imperial College London, United Kingdom

This presentation will highlight our explorations of approaches to deep generative models for atomic crystals. Generative modeling of crystals is challenging due to the hard constraints with respect to symmetry and stability, variable lattice sizes and numbers of atoms, and mix of both discrete and continuous attributes. Existing methods aim to learn the distribution of stable atomic configurations without consideration of space group symmetries. To overcome this limitation, we are using highly interpretable GFlowNets to generate crystals approximately from the Boltzmann distribution and conditioned on space group and/or chemistry. The model is also explicitly trained to avoid creating invalid structures. We will present the performance and implications of our framework, highlighting the advantages of symmetry-aware generation towards inverse design of materials.

4:15 PM MD01.06.08
Interpretable Physics-Inspired Graph Neural Network Force Fields for Atomistic Modeling Hong Sun[1], Zhitao Chen[2,1] and Amit Samanta[1]; [1]Lawrence Livermore National Laboratory, United States; [2]University of California, Santa Barbara, United States

Graph neural networks have attracted enormous attention in atomistic simulations due to its natural ability to capture geometric information about the distribution of atoms in a structure. Many graph neural network (GNN) models proposed in the literature for atomistic modeling involve massive high-dimensional atomistic features, typically ~100-300 basis functions, and complex message passing mechanisms between different GNN layers and stacks that are coupled with complicated node and edge update operations. However, training such a complex GNN model requires a huge training set, a lot of memory, and often the high flexibility comes at the cost of low scalability and poor interpretability. To address this limitation, we propose a physics-informed GNN interatomic potential which generalizes the concept of embedded atom method (EAM) by combining pair and many-body interactions with nonlocal embedding energy interactions that incorporates long-range and high order interactions. The proposed GNN framework adopts a gated workflow with two message passing layers, which allows us to seamlessly model the pair and many-body energy contributions from the traditional EAM model while learning the complex, high-order interactions in the nonlocal embedding energy through message aggregation. In contrast to many, evenly spaced radial basis functions used in other GNN models, only 10-20 atom-centered, even-tempered Gaussian functions are sufficient to featurize our GNN model. This hybridization of physics informed EAM with a nonlocal embedding energy using GNN makes the proposed machine learned interatomic potential more computationally efficient and interpretable. The ability of the proposed GNN framework to model complex energy landscapes is demonstrated by developing potentials for elemental systems, like Nb, Pt, C and benchmarking with existing state-of-the-art GNN potentials. Our EAM inspired GNN model provides a new way of integrating established physics principles with modern deep learning models, which makes the predicting of materials properties more efficient and interpretable.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory (LLNL) under Contract DE-AC52-07NA27344. This work was funded by the Laboratory Directed Research and Development (LDRD) Program at LLNL (project tracking code 21-ERD-005). Computing support for this work came from the LLNL institutional computing facility.

4:30 PM MD01.06.09
An Unsupervised Data Mining Methodology for Analysis of Molecular Dynamics Sampling of Local Coordination Fabrice Roncoroni, Ana Sanz-Matias, Siddharth Sundararaman and David Prendergast; Lawrence Berkeley National Laboratory, United States

Molecular dynamics (MD) simulations present a data-mining challenge, given that they can generate a considerable amount of data but often rely on limited or biased human interpretation to examine their information content. By not asking the right questions of MD data we may miss critical information hidden within it. We combine dimensionality reduction (UMAP) and unsupervised hierarchical clustering (HDBSCAN) to quantitatively characterize the coordination environment of chemical species within MD data. By focusing on local coordination, we significantly reduce the amount of data to be analyzed by extracting all distinct molecular formulas within a given coordination sphere. We then efficiently combine UMAP and HDBSCAN with alignment or shape-matching algorithms to classify these formulas into distinct structural isomer families. The outcome is a quantitative mapping of the multiple coordination environments present in the MD data. The method was employed to reveal details of cation coordination in electrolytes based on molecular liquids and polymers.
The tool is written in python, leverages available open-source data science modules and integrates with the Atomic Simulation Environment (ASE).

4:45 PM MD01.06.10
Transferability of Machine-Learned Force Fields to Capture Material Properties Shaswat Mohanty[1], SangHyuk Yoo[2], Keonwook Kang[2] and Wei Cai[1]; [1]Stanford University, United States; [2]Yonsei University, Korea (the Republic of)

Molecular dynamics (MD) based techniques have been widely applied to materials science, polymer chemistry, biochemistry, and medical science. One of its underlying shortcomings is the insufficient accuracy of the force fields used. Machine-learned approaches to aid MD simulations are of growing interest with efforts focused on developing accurate and efficient force fields. Graph neural networks (GNN) provide a scalable force field with limited computational expense to predict the atomic forces. This paves way for a promising approach to obtaining a O(N) scaling for force fields trained on ab-initio data as opposed to the $O(N^3)$ scaling of ab-initio simulations.

However, before we deploy GNN-based force fields, we need to test their reliability and accuracy. Most existing studies focus on the radial distribution function and self-diffusivity to assess reliability, which is not a sufficient test. To this end, we present a series of benchmarking tests, including the equivalence of the radial distribution function and self-diffusivity from MD and GNN-MD simulations on a set of GNN-based force fields (Li et al. (2022)). The force field is trained on liquid and solid configurations with the Lennard-Jones interatomic potential. We also compare the computational X-ray photon correlation spectroscopy (XPCS) analysis to test the density fluctuations induced by the dynamics. A model trained exclusively on liquid configurations can capture the equilibrium lattice spacing in solid phase but it cannot accurately capture the vibrational frequency distribution. As a consequence, we show that a model also needs to be trained on solid configurations to successfully capture the spectrum of vibrational frequencies and the phonon density of states. We finally demonstrate the extensibility of the force field to capture rare events of defects in solids such as vacancy diffusion and the training procedure that needs to be employed to accurately capture the rate of such events. In summary, (i) these benchmarking tests provide a more expansive test on the reliability of the GNN-based force fields that are being trained and (ii) the model preparation techniques provide a guide on how dataset engineering (as opposed to feature engineering) can capture rare events such as vacancy diffusion in GNN-MD simulations.

SESSION MD01.07: Poster Session
Session Chairs: Ekin Dogus Cubuk and Bilge Yildiz
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM MD01.07.01
Designing Beam Shape of Lattice Structure for Enhancing Mechanical Characteristics Based on Multi-objective Bayesian Optimization Jinwook Yeo and Seunghwa Ryu; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Lattice structures, a kind of metamaterial, with high strength and low density have gained significant attention due to the ever-increasing need for designing lightweight strong parts. Most existing studies examined a variety of lattice structures made of uniform cross-section beams, which does not encompass a vast design space related to the beam shape. Moreover, very sharp corners formed at the cross-sections of the beams serve as the source of stress concentration that significantly hampers the strength of the lattice structures. In this research, we explore the beam shape thoroughly as a new design space in a variety of lattice structures based on smooth Bezier curve generations and search for the ultimate performance of the lattice structures. The elastic modulus of the lattice structures with the free-form beam shape is evaluated via finite element method, and the optimal beam shape for the ultra-stiffness and low density is designed through multi-objective Bayesian optimization (MBO). The efficient search of the optimal shape via MBO enables us to search for the optimal beam shapes for many different lattice structures. The lattice structures with optimal shapes are manufactured using 3D printing, and significant improvement in specific stiffness is confirmed in comparison with existing designs.

5:00 PM MD01.07.02
Deep Learning Algorithm to Improve Predictive Performance of Strain Fields in Grid Composites Donggeun Park and Seunghwa Ryu; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

For design problems concerning astronomically large number of configurations in multimaterial 3D printers, multiple optimization frameworks have been suggested that efficiently leverage the predictive power of deep neural network (DNN). Especially, the design of grid composites with superior mechanical properties has gained significant attention as a testbed for the DNN-based optimization methods. However, publicly available DNN architectures have been utilized so far that were not specifically developed for the grid composites and thus show weak generalizability in exploring unseen configurations away from training datasets. Here, we propose a multiscale kernel neural network (MNet) that can efficiently predict the strain field within a grid composite subject to an external loading. MNet enables accurate prediction of the strain distribution for completely new configurations in unseen domain, and reduced mean absolute percentage error (MAPE) by 50% compared to a benchmark, U-Net. MNet maintained superb performances with less than one-third of dataset, and can be applied to grid composites larger than the composite configurations used for the initial training. By investigating the inference mechanisms from the kernels of multiple sizes, we revealed that the MNet efficiently extracted various spatial correlations from the material distribution. It is envisioned that MNet can be applied to design problems concerning random checkerboard configurations in various engineering disciplines.

5:00 PM MD01.07.04
Virtual Node Augmented Machine Learning for Material Property Prediction Ryotaro Okabe, Abhijatmedhi Chotrattanapituk, Zhantao Chen and Mingda Li; Massachusetts Institute of Technology, United States

Graph Neural Network (GNN) has been broadly used in material science to understand the material properties related to the interactions among atoms[1]. We deal with the atom and the interactions among neighborhoods as nodes and edges of the graph, respectively. By aggregating the node features of the output layer, we can get unique prediction results of material properties. However, there is a risk that the aggregation process, such as summation and averaging, in the final layer could cause the loss of essential information. Therefore, it is demanding to develop a GNN model that allows us to decide the dimension of output features flexibly.

In this presentation, we present a GNN model that directly predicts the physical properties of materials only with simple inputs like atomic coordinates. We have augmented virtual nodes[2] to the existing Euclidean neural network of E(3)NN[3] as output nodes. Depending on the model and property, we can decide the number and the positions of virtual nodes. This approach has made it possible to deal with the outputs whose dimension varies among different materials.

We have applied the GNN model augmented with virtual output nodes for predicting properties like phonon bands[4] and magnetic structures[5]. This work could lead to deeper insights into the material's microscopic dynamics and interactions of magnetic moments inside the materials.

[1] Xie et al., *Phys. Rev. Lett.* **2018**, 120, 145301.
[2] Pham et al., *Arxiv.* **2017**, 1708.04357.

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5:00 PM MD01.07.05
Machine Vision for Optoelectronic Perovskite Film Characterization Milan Harth[1], Ioannis Kouroudis[1], Luigi Vesce[2], Maurizio Stefanelli[2], Aldo Di Carlo[2] and Alessio Gagliardi[1]; [1]TUM - SNE, Germany; [2]University of Rome "Tor Vergata", Italy

We present our research for fast and reliable bandgap and absorption quality value extraction for triple-cation perovskite thin films from sample scans. To this end, thin film samples were synthesized via blade-coating and their photoluminescence, ultraviolet-visible spectra and the film thickness were collected. For qualitative evaluation of the absorption of perovskite films for use in photovoltaic modules we propose a method of computing a dimensionless figure of merit we called the Area Under Absorption Coefficient (AUAC). Our approach consists of perform regression tasks aimed at predicting the properties of interest using machine learning methods, namely convolutional neural networks. Similar methods have been reported in literature before [1,2,3], while the novelty lies in using very simple imaging techniques, as well as the concept and prediction of the AUAC.
This work demonstrates the usability of simple imaging techniques to characterize repeatedly fabricated experimental samples while requiring only a feasibly acquirable initial amount of data. Our reported method can help speed up time consuming material optimizations by reducing lab time spent on recurrent characterizations, nicely synergizes with high throughput production lines and could be adapted for quick extraction of other optoelectrical quantities.

[1] Srivastava, M., Howard, J. M., Gong, T., Rebello Sousa Dias, M., & Leite, M. S. (2021). Machine Learning Roadmap for Perovskite Photovoltaics. The Journal of Physical Chemistry Letters, 12(32), 7866–7877. doi:10.1021/acs.jpclett.1c01961
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[3] Chenyu Zhang, Jie Feng, Luis Rangel DaCosta, Paul.M. Voyles, Atomic resolution convergent beam electron diffraction analysis using convolutional neural networks, Ultramicroscopy, Volume 210, 2020, 112921, ISSN 0304-3991, https://doi.org/10.1016/j.ultramic.2019.112921.

5:00 PM MD01.07.07
Toughness Optimization of Grid Composite Using Hierarchical DNN-based Genetic Algorithm and Active Learning. Jaemin Lee, Donggeun Park and Seunghwa Ryu; Korea Advanced Institute of Science & Technology, Korea (the Republic of)

A grid composite consists of heterogeneous materials arranged in a grid lattice and has been studied extensively with the advancement of 3D printing. Because it offers an astronomically large design space that cannot be explored with conventional composite optimization methods, significant efforts have been paid to devise a systematic design framework that leverages the superior inference of deep learning for optimal configurations with desired properties. In previous studies, the optimum configurations with high stiffness or high strength were sought successfully because one can train a deep neural network (DNN) to predict stiffness or strength from a given composite configuration. However, there have been no studies succeeding in optimizing its toughness that can only be obtained by considering the full crack propagation process, due to the difficulty in training a deep learning model for predicting the toughness. In this study, a novel hierarchical DNN architecture is devised that takes not only the configuration but also the initial stress distribution deduced by a sub-NN trained from a minimal set of simulations for accurately predicting the toughness, and a grid composite configuration with high toughness was successfully designed based on the DNN-based genetic algorithm and active learning. In the optimized configuration, multiple distributed crack nucleation occurs simultaneously and propagates independently without being interconnected to each other, absorbing significant energy until the fracture, which allowed them to have high toughness. The proposed hierarchical DNN architecture that simultaneously takes the 'configuration' and 'easily deducible physical quantity from sub-NN' is expected to be applicable to solve various composite design problems concerning highly complex and nonlinear properties of materials.

5:00 PM MD01.07.08
Performance Enhancement of the Photovoltaic Cell via Support Vector Machine Based Nanograting Optimization Wonkyeong Jeong, Ki-Hoon Kim and Min Ho Seo; Pusan National University, Korea (the Republic of)

Exploiting a nanostructure is one of the promising strategies for the performance enhancement of a photovoltaic cell, but optimizing the dimension of the nanostructure is still challenging, because of the complexity of the physics of light around nanostructures. Conventionally, to optimize the nanostructure for performance-improved photovoltaic cells, researchers have utilized numerical simulation, such as finite-difference time-domain (FDTD). However, the conventional methods inevitably require massive calculations considering numerous structures for the design optimization, implying extremely time- and resource-consuming. Recently, being more efficient, deep learning-based design optimization has been reported, however, it also requires massive initial expenses of securing more than thousands of big data for accurate theoretical optimization. Thus, there is a huge demand for a more efficient and simpler method to predict the structural optimization of the nanostructure with high accuracy and to demonstrate the performance-enhanced photovoltaic cell.

Here, we introduce a performance-enhanced photovoltaic cell exploiting a nanograting structure, on the surface, that is optimized by a simple support vector machine (SVM) based nanostructure designing method. Using numerically calculated transmittances with respect to various nanostructures in the visible light range as a training set, we first developed the learning model based on the SVM. Importantly, the developed learning model utilizes a Gaussian Radial Basis function (RBF) kernel that is appropriate to the accurate prediction for regression of data having non-linearity. Compared to other models, for example, polynomial (mean squared error, MSE = 0.654) kernel with SVM model or multi-layer regression (MSE = 0.614) model, the developed model with RBF kernel does not show simplicity and efficiency with the far less initial expense (number of learning data = 125) than the conventional method, but it also shows the highest accuracy (MSE = 0.006). Using the developed model, we plotted a contour map of the predicted transmittance of various dimensions of nanograting and through the map, we confirmed that the nanograting of pitch = 200 nm, width = 100nm, and height = 250nm can show the highest transmittance in visible light. To demonstrate the optimized nanograting structure on the photovoltaic cell, we developed a nanofabrication method, combining a conventional semiconductor process and nanoimprinting lithography. Using the developed method, the optimized nanograting transparent polymer film (pitch = 200 nm, width = 100nm, height = 250nm) is fabricated and it is assembled with a commercial photovoltaic cell. Finally, from the measured conversion performance of the fabricated photovoltaic cell, the device with the nanograting showed significant performance enhancement, a 6.6% improvement in efficiency, compared to a control sample without the nanograting.

In summary, we proposed a simple and efficient optimization method of a nanograting dimension for the high-performance photovoltaic cell. Through the theoretical and experimental verification of the developed method, we confirmed that is practically valid to demonstrate the performance-enhanced photovoltaic cell with high efficiency. We expect this method can be widely used for diverse photoelectric energy and sensor applications.

5:00 PM MD01.07.10
Pneumatic Soft Grasping Robotic Devices Using Reinforcement Learning Zeqing Jin, Zhizhou Zhang and Grace Gu; University of California, Berkeley, United States

Advances in soft grippers have achieved remarkable success in grasping tasks providing superior flexibility compared to rigid grippers. However, challenges still remain in limited loading capacity and understanding the working mechanism of the soft gripper due to its nonlinear behavior and deformation. In this study, by leveraging both soft pneumatic joints and rigid components, a hybrid grasping device is developed to provide superior dexterity compared to conventional electromechanical grippers. A grasping platform is established using a robot arm equipped with the designed hybrid gripper and a depth camera imaging system. Simple and difficult grasping tasks are conducted on multiple objects indicating different difficulty levels using imitation learning methods. Two model-based approaches including CNN and PointNet models are implemented and show good performance on grasping predictions. An average error of 5 mm towards desired grasping spatial locations is reached for the simple grasping task. It is envisioned that such platforms and reinforcement learning approaches can be applied to more complicated grasping problems including irregular shaped objects that requires tailored gestures and grasping trajectories.

SESSION MD01.08: Machine Learning VII
Session Chairs: Pawan Goyal and N M Anoop Krishnan
Thursday Morning, April 13, 2023
Marriott Marquis, Second Level, Foothill C

8:00 AM *MD01.08.01
Combining Cluster Expansion and Machine Learning Towards Non-Linear Modeling and Classification Claudia Draxl[1], Santiago Rigamonti[1], Adrian Stroth[1], Manish Kumar[1], Mao Yang[1,2] and Peter Benner[2]; [1]Humboldt-Universität zu Berlin, Germany; [2]Max Planck Institute for Dynamics of Complex Technical Systems, Germany

Despite the success of the cluster expansion (CE) approach demonstrated by numerous applications to alloys, CE may perform poorly in two cases which are common in materials science. These concern properties which depart from linearity as a function of concentration, and properties which split into sub-domains in configuration space, each having distinct physical behavior. Examples include kinks in the energy of formation [1] and metal to insulator transitions in complex alloys [2]. In this work, we combine CE with machine-learning techniques toward non-linear modeling and classification such to overcome these problems. First, the input space is significantly augmented by adding mathematically complex but potentially more descriptive features built upon cluster correlations. Second, state of the art techniques including compressed sensing and support vector machines, are employed to find sparse models that generalize well. Compared to standard CE approaches, the larger input space of the introduced methodology leads to steeper learning curves, which generally means higher requirements with respect to the amount and variety of training data. Since producing DFT data is costly, we make use of an iterative approach that allows for reaching fast convergence, by automatically detecting and adding data from regions in configuration space which are either unexplored or more relevant for the property to be modeled. This approach is especially important for systems with large parent cells [1], where the combinatorial explosion cannot be restrained by limiting the supercell size. All developments are implemented in the CE Python package CELL [3]. We demonstrate our approach by addressing the stability and electronic structure of complex materials, including intermetallic thermoelectric clathrates that are of interest for waste-heat recovery and oxide perovskites that are promising candidates for optoelectronic applications. The modeled properties include the energy of formation, the conducting behavior (metal vs. semiconductor), as well as concentration- and temperature-dependent band gaps.

[1] M. Troppenz, S. Rigamonti, and C. Draxl, Chem. Mater. 29, 2414 (2017).
[2] M. Troppenz, S. Rigamonti, J. O. Sofo, and C. Draxl; https://arxiv.org/abs/2009.11137v1.
[3] S. Rigamonti et al., CELL: a Python package for cluster expansion with a focus on complex alloys, preprint; https://sol.physik.hu-berlin.de/cell/

8:30 AM MD01.08.03
Billions of Atoms with Machine Learning Interatomic Potentials: Application to Direct Heterogeneous Reactive Dynamics Anders Johansson, Yu Xie, Cameron J. Owen, Jin Soo Lim, Lixin Sun, Jonathan Vandermause and Boris Kozinsky; Harvard University, United States

Machine learning interatomic potentials (MLIPs) have become a prevalent approach to bridging the gap between slow-but-accurate ab initio calculations and fast-but-inaccurate empirical potentials for molecular dynamics. Among MLIPs, there is a pareto front of models with different tradeoffs between accuracy and speed. The FLARE interatomic potential aims to push the boundary of scalability and performance, while maintaining sufficient accuracy to study complex, reactive systems.

FLARE combines the atomic cluster expansion with a sparse Gaussian process. Bayesian uncertainties enable efficient training with active learning and uncertainty-aware, large-scale molecular dynamics simulations. We implement FLARE in LAMMPS with the Kokkos performance portability library, enabling efficient molecular dynamics simulations on GPUs across a wide range of system sizes. Using 27336 GPUs, we demonstrate state-of-the-art scaling and performance in micrometer-scale heterogeneous catalysis simulations with up to half a trillion atoms [1].

[1] arXiv:2204.12573

8:45 AM MD01.08.04
Adversarial Sampling of Geometries Using Uncertainty Quantification from Single Neural Networks Aik Rui Tan, Samuel Goldman and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States

In recent years, neural network (NN) interatomic potentials have been increasingly applied to construct potentials for a wide range of systems since they provide high numerical accuracy like in electronic structure methods and low computational cost comparable to that of analytical interatomic potentials. However, due to architectural limitations, NN interatomic potentials are still constrained by their inability to extrapolate well. In high-dimensional systems such as crystal or molecular structures, NN interatomic potentials often fail to perform robustly in regions outside of well-learned training domains. To expand this learning space, many methods in the realm of active learning and uncertainty quantification (UQ) have been proposed. Here, we apply multiple UQ methods ranging from ensembling, mean-variance estimation, and deep evidential regression, and exploit a differentiable sampling technique based on adversarial attacks to sample atomic configurations with high uncertainty. Evaluation of these methods allow us to benchmark performance of single deterministic networks against ensemble methods for UQ task, especially for large bulk material systems which are restricted by their expensive training costs. Coverage of sampled regions is also evaluated for these UQ methods using statistical analysis after several active learning loops. These models are benchmarked on kinetic barrier sampling in ammonia and bulk interactions in silica glass systems.

9:00 AM MD01.08.05
Physics-Informed Deep Learning for Elasticity—Forward, Inverse and Mixed Problems Chun-Teh Chen and Grace Gu; University of California, Berkeley, United States

Elastography is an emerging imaging modality to estimate the elasticity of biological tissues by comparing ultrasound signals before and after a light compression. Ultrasound examinations are much more accurate in the axial direction than in the lateral direction. However, current elastography methods generally require both axial and lateral displacement components, making them ineffective for clinical applications. Additionally, the assumption of incompressibility adopted in current elastography methods results in inaccurate Young's modulus reconstructions. Here, we introduce a new physics-informed deep learning method for elastography. By integrating a displacement network and an elasticity network, the proposed method can reconstruct the Young's modulus field of a heterogeneous object based on only a measured axial displacement field. Moreover, the proposed method can remove the assumption of incompressibility and reconstruct the Young's modulus and Poisson's ratio fields at the same time. We show that the "egg shell" effect where the stiff material prevents the generation of strain in the soft material could be a source of error, and using multiple measurements can help mitigate this potential problem and increase the prediction accuracy. While the proposed method is an iterative approach, we demonstrate that the initial guess has no significant effect on the final prediction. Lastly, we show that activation functions play an important role when using deep neural networks to approximate physical fields. The proposed method opens new venues for efficiently and accurately solving inverse problems in materials characterization, medical imaging, and beyond.

9:15 AM MD01.08.06
Large Scale Simulations of Soft Materials with Equivariant Deep Learning Potentials Simon L. Batzner, Albert Musaelian, Anders Johansson and Boris Kozinsky; Harvard University, United States

Accurate computationally efficient predictions of the energy and atomic forces of many-atom systems are a long-standing goal in the natural sciences. Interatomic potentials based on Message-Passing Neural Networks have emerged as the leading paradigm toward this goal over the past years. Their propagation mechanics, however, make parallel computation challenging and limit the length scales that can be studied. Strictly local descriptor-based methods on the other hand, have been scaled to massive systems, however, they currently fall short of the accuracy seen in message passing approaches. We have recently introduced the Allegro model, a fully local equivariant deep learning interatomic potential that is massively parallelizable while retaining the high accuracy of equivariant message passing potentials. Molecular dynamics simulations using the Allegro potential recover structural and kinetic properties of an amorphous phosphate electrolyte in great agreement with first principles calculations and can be scaled to 100 million atoms. Here, we demonstrate how Allegro can be used to study complex, soft materials using large-scale Molecular Dynamics simulations.

9:30 AM MD01.08.07
Creating Knowledge Maps from Literature to Accelerate Catalytic CO_2 Conversion Development Anna M. Hiszpanski, Juanita Ordonez, Aditya Prajapati, Huiyun Jeong and David Buttler; Lawrence Livermore National Laboratory, United States

Natural language processing (NLP) is a useful tool for extracting and organizing information from scientific papers, thereby expediting the creation of materials science databases for downstream machine learning. However, less well-explored in the materials science domain is the use of NLP to create knowledge maps – rather than databases – which requires extracting overarching concepts and relationships from documents rather than specific detailed information. Such "knowledge maps" provide better organization, searching, and querying of materials science document sets of interests and can be used as a pedagogical tool, enabling a holistic view of the field and creating non-intuitive connections. We have developed NLP tools for the creation of such a conceptual map for the field of catalytically driven CO_2 conversion. We focus on this field given its global importance and the fact that it has experienced a high volume and diversity of publications in recent years, making it challenging for subject matter experts and newcomers to the field alike to keep up with the literature. Our corpus consists of ~37.7k abstracts and ~9.6k full-text articles broadly pertaining to CO_2 conversion. The key tool to create such conceptual mappings is creating document encoders that accurately capture and represent the concepts contained in papers. For our document encoder, we evaluated several transformer models, including MatBERT, MatSciBERT, and ROBERTa. For each, we analyzed the effect that encoding whole versus partial documents and the order in which text is encoded (randomly or in order as it's written) can have. Our findings show that the MatBERT transformer with the use of more text sampled in a random order tends to best encode documents and capture the concepts contained within them. As an example, this model is able to classify the CO_2 catalytic literature according to the type of catalytic reaction – photocatalytic, electrochemical, or thermohydrogenation – with up to 83% accuracy.

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

9:45 AM BREAK

10:15 AM MD01.08.09
Data-Driven Identification of an Interpretable Model for Diffusivity by Generating the Largest Amorphous Materials Database from *Ab Initio* Molecular Dynamic Calculations Hui Zheng, Eric Sivonxay and Kristin Persson; Lawrence Berkeley National Laboratory, United States

All-solid-state batteries (SSB) are promising to address a portion of the increasing need for energy storage. Amorphous materials demonstrate unique advantages in tunability and processability in electrodes, electrolytes, and their interface coating materials. Investigating the relationship between ion conduction in amorphous materials can provide guidance in selecting materials. However, a comprehensive database is missing to enable such analysis. In this work, we generated the largest diffusivity database of amorphous materials to fill this gap using the AIMD workflow. The database covered a total of 4886 distinct compositions, and 3383 of them include Li. The amorphous structures are generated using the melt-quench procedure. The diffusivities of a subset of amorphous materials at four temperatures from 2500 K to 1000 K with 500 K intervals were calculated. We developed an analytical machine learning model from this diffusivity database using the sure independence screening and sparsifying operator (SISSO) method. The model can predict the temperature-dependent diffusion coefficient from compositional and structural features with high accuracy (R^2=0.95). The model enables a rapid evaluation of diffusion in amorphous solids of different compositions, which can be used to screen suitable candidates for different parts in SSB.

10:30 AM MD01.08.10
Melting and Phase Separation of SiC from Large-scale Machine Learning Molecular Dynamics Yu Xie[1], Senja Ramakers[2,3] and Boris Kozinsky[1,4]; [1]Harvard University, United States; [2]Robert Bosch GmbH, Germany; [3]Ruhr-Universität, Germany; [4]Robert Bosch LLC, United States

Incongruent melting has been reported by many experimental studies with the observation that the SiC decomposes into liquid silicon and solid carbon upon heating. However, contradictory results have also been reported that SiC melts congruently with no decomposition. Ab initio MD provides evidence of carbon clustering during the melting process but did not capture the phase separation limited by the small supercell. Empirical potentials give good approximations of the melting points but all of them have limited ability to describe other phases and thus cannot capture the decomposition in the MD simulation. In this work, we use Bayesian active learning to train a machine learning potential for SiC at a wide range of temperatures and pressures, and observe the phase decomposition process into Si and C-rich phases in both the active learning and the large-scale MD stages. Our results provide a microscopic validation of the incongruent melting hypothesis, resolving the disagreement among experiments of the SiC melting behavior. The occurrence of decomposition also indicates that amorphous SiC can not be produced by melting and quenching but only with irradiation, consistent with existing experimental approaches of the amorphization of SiC.

10:45 AM MD01.08.11
Matbench Discovery - An Automated Benchmark for ML Energy Models Janosh Riebesell[1,2], Rhys Goodall[2] and Anubhav Jain[1]; [1]Lawrence Berkeley Lab, United States; [2]University of Cambridge, United Kingdom

The past 2 years have seen the release of several machine learning models specifically designed to predict the DFT final energy given only the unrelaxed crystal structure. Such models are suited for a materials discovery workflow in which they pre-filter and/or pre-relax structures that are then fed into high-throughput DFT. Examples of such models include
- [BOWSR](https://sciencedirect.com/science/article/pii/S1369702121002984): Bayesian optimizer taking crystal symmetries into account when exploring/exploiting known samples of a crystal's potential energy surface
- [Wren](https://www.science.org/doi/10.1126/sciadv.abn4117) [[arxiv](https://arxiv.org/abs/2106.11132)]: uses composition, spacegroup and Wyckoff symmetries as coarse-grained, relaxation-invariant, enumerable descriptors of a crystal structure to predict the post-relaxation energy
- [M3GNet](https://arxiv.org/abs/2202.02450): trained on VASP relaxation trajectories, M3GNet predicts forces and stresses acting within a structure to perform pseudo-relaxation that yields the energy of a structure more closely resembling the DFT-relaxed crystal

However, even closely following the literature, it remains unclear which methodology and in particular which model performs best.
Matbench Discovery extends the growing Matbench ecosystem by building on the dataset published in Wang 2021 npj Comput Mater. This work generated ~250k structures with chemical similarity-based element substitution. After DFT relaxation, they found 10% (~20k) to lie on the Materials Project convex hull. Our benchmark measures how precisely models identify the 20k stable structures from the 250k search pool, as well as how many false positives each one incurs. The latter lead to wasted compute for relaxing unstable structures.

One unusual but compelling feature of test set is that it was generated by 5 rounds of elemental substitution, each time feeding newly found stable structures back into the pool. This allows for out-of-distribution testing as repeated substitutions on average increase chemical dissimilarity from the training set. Indeed we see a decline in model performance with substitution count which is more pronounced for some models than others. This becomes an important metric that influences model ranking as any prospective discovery campaign for exceptional materials will require models to operate robustly on out of distribution crystals. Models that estimate their own predictive uncertainty in good correlation with their error receive bonus points.

We also look at how model errors compare across crystal structures and identify classes of materials on which all models perform poorly, indicating a lack of attention from the community and/or lower quality training data in certain areas of materials space.

Like the original Matbench, Discovery will grow over time as new models are released. To that end, we publish our train and test data along with code to quickly deploy models on them as a `pip`-installable Python package. This allows model authors to add their models to our automated leaderboard by making pull requests to the [Matbench Discovery repo](https://github.com/janosh/matbench-discovery) with their benchmark results and code used to generate them. The Discovery website is kept up to date through continuous deployment.

The utility of this work is twofold:
1. Make it easy for future researchers to identify SOTA ML models that predict stability given only the unrelaxed crystal. This enables informed decisions when choosing ML filters for high-throughput discovery projects.
2. On a more philosophical note, by keeping the leaderboard up to date with new model releases, we ultimately hope to answer the question which methodology works best; DFT emulators like M3GNet, one-shot predictors like Wren or a new method yet to be released?

11:00 AM MD01.08.12
A Lightweight and Flexible Schema for Materials Data to Interface with Self-Driving Laboratories Rishi Kumar and Anubhav Jain; Lawrence Berkeley National Laboratory, United States

The advent of machine learning and laboratory automation in materials science has reinforced the need for a performant and flexible solution for materials data storage. Self-driving laboratories in particular require that data be available and malleable for any analysis required during online learning by an AI agent. We propose a graph-based database schema and associated python library for the entry and retrieval of experimental and computed materials data. In contrast to rigid table-based schemes, our graph approach accommodates the evolving workflows of a research setting. Furthermore, we keep the data structure similar to that generated by recent text-mining efforts to facilitate fusion of local data with the literature. This database was developed to support self-driving labs at Lawrence Berkeley National Lab executing diverse experiments ranging from spincoating to solid-state synthesis.

Our schema is designed to be lightweight and flexible while adhering to FAIR principles. Data is entered (either by operators or the self-driving lab codebase) from the perspective of the experimentalist as a directed acyclic graph (i.e. sequence) of nodes (i.e. steps) which process, measure, and analyze materials. Analysis is distinguished from measurement to establish extracted features as first-class components, as well as to enable multiple interpretations of the raw data. The directed graph structure naturally captures material flows within and across experiments; an experiment that uses a material generated by another experiment will generate an edge which connects the two graphs. Finally, the data can be filtered by any step of the experimental life cycle (e.g. by input material, by process variables, or by analysis results) to generate tabular datasets amenable to downstream analysis.

We conclude by demonstrating this schema for the storage and manipulation of data generated by self-driving laboratories at Lawrence Berkeley National Lab. In particular we show how text-mined recipes for solid-state synthesis are joined with experimental data in our database to inform experimental campaigns. While we show this in an automated laboratory setting, we stress that our schema has been kept lightweight to ease its adoption in traditional laboratory environments. The code to deploy this schema is publicly available on our GitHub repository.

SESSION MD01.09: Machine Learning VIII
Session Chairs: Grace Gu and Adana Tandia
Thursday Afternoon, April 13, 2023
Marriott Marquis, Second Level, Foothill C

1:30 PM *MD01.09.01
Structure Generation in the Representation Space Victor Fung; Georgia Institute of Technology, United States

Data-driven methods have the capability to greatly accelerate the rate of materials discovery and design over conventional human-guided approaches. Generative models are one such recent example which could potentially be used to generate completely novel materials with specified functional properties. When applying generative models for determining atomic structures, a key prerequisite lies in using suitable structural fingerprints or representations for the machine learning model, analogous to the graph-based or SMILES representations used in molecular generation. These representations would need to be invariant to translations, rotations, and permutations, while remaining invertible back to their Cartesian coordinates. The challenges associated with simultaneously meeting both invariance and invertibility requirements have prompted us to propose an alternative approach to this problem by developing methods for accurately reconstructing the structure using optimization-based techniques which can be applied towards non-invertible representations. Our recent findings show this approach can reliably reconstruct atomic structures with high accuracy, and when paired with a generative model, can produce diverse structures with very high data efficiencies.

2:00 PM MD01.09.02
Accurate Simulation of Precipitation Events Using Diffusion Probabilistic Models Cheol Woo Park, Babak Sadigh, Yu-Ting Hsu and Fei Zhou; Lawrence Livermore National Lab, United States

Simulation of microstructure evolution have largely relied on coarse-grained models that obey evolution principles described by partial differential equations. However, quantitatively capturing the precipitation kinetics in these models remains a challenge. In this talk, we show that stochastic dynamics that occur on the coarse-grained level in microstructure evolution can be learned in a data-driven manner using a diffusion probabilistic model (DPM) which enables the model to accurately reenact nucleation and growth. We demonstrate the capability of DPM by replicating the precipitation dynamics of a symmetric Lennard-Jones binary mixture. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

2:15 PM MD01.09.03
Multitask Learning of Collective Variables and Reactive Force Fields for Enhanced Sampling of Rare Catalytic Events Boris Kozinsky[1,2], Lixin Sun[1], Simon L. Batzner[1], Albert Musaelian[1], Jonathan Vandermause[1], Yu Xie[1] and Steven B. Torrisi[1]; [1]Harvard University, United States; [2]Bosch Research, United States

Accurate reaction rate prediction is crucial for designing highly efficient heterogeneous catalysis. Ab initio molecular dynamics can be used because it precisely models chemical reactions. But they often scale poorly and thus are prohibitive for long simulation time to accumulate sufficient statistics. On the other hand, enhanced sampling techniques can accelerate the simulation but require good collective variables, which can be hard to design for complex reactions.
In this work, a data-driven method is used to address these two problems using a multitask learning framework [1] based on Neural Equivariant Interatomic Potentials (NequIP) [2]. The framework trains force fields with quantum chemical accuracy and discovers critical collective variables for highly efficient free energy landscape exploration. This learning framework is demonstrated on estimating the reaction free energy of formate dehydrogenation on a Cu(110) surface.

[1] L. Sun, J. Vandermause, S. Batzner, Y. Xie, D. Clark, W. Chen, B. Kozinsky, "Multitask machine learning of collective variables for enhanced sampling of rare events", J. Chem. Theory Comput. 18, 2341 (2022)
[2] S. Batzner, A. Musaelian, L. Sun, M. Geiger, J. Mailoa, M. Kornbluth, N. Molinari, T. Smidt, B. Kozinsky, "E (3)-Equivariant Graph Neural Networks for Data-Efficient and Accurate Interatomic Potentials", Nature Comm. 13, 1 (2022)

2:30 PM BREAK

3:30 PM *MD01.09.04
Pretraining for Property Prediction of Crystalline Materials Kishalay Das[1], Bidisha Samanta[2], Pawan Goyal[1], Seung-Cheol Lee[3], Satadeep Bhattacharjee[3] and Niloy Ganguly[1]; [1]IIT Kharagpur, India; [2]Google, India; [3]Indo Korea Science and Technology Center, India

In this talk, we will describe our attempts towards large-scale pretraining to be able to predict properties of crystalline properties to lower the need for large property tagged datasets. We will present a deep-learning framework, CrysXPP that uses an autoencoder, CrysAE. The important structural and chemical properties captured by CrysAE from a large amount of available crystal graphs data helped in achieving low prediction errors. Moreover, we design a feature selector that helps to interpret the model's prediction. Most notably, when given a small amount of experimental data, CrysXPP is consistently able to outperform conventional DFT. A detailed ablation study establishes the importance of different design steps. We release the large pre-trained model CrysAE. We believe by fine-tuning the model with a small amount of property-tagged data, researchers can achieve superior performance on various applications with a restricted data source.

4:00 PM MD01.09.05
Predicting the Synthesizability of All Crystalline Inorganic Materials with Semi-Supervised Machine Learning and Learned Atomic Embeddings Evan Antoniuk[1,2], Gowoon Cheon[3], George Wang[2], Daniel Bernstein[2], William Cai[2] and Evan Reed[2]; [1]Lawrence Livermore National Laboratory, United States; [2]Stanford University, United States; [3]Google Inc., United States

The autonomous computational design of new materials is being actively pursued as a new paradigm of materials science research. However, the current lack of predictive capabilities for directly identifying synthesizable inorganic crystalline materials is a significant roadblock for achieving autonomous materials discovery. Computationally, inorganic material synthesizability has been assessed by employing high throughput density-functional theory (DFT) to calculate the formation energy of a material or through the enforcement of a charge-balancing criteria. However, using DFT and charge-balancing as proxy methods for assessing synthesizability can only account for 50% and 28% of all previously synthesized inorganic crystalline materials, respectively.

In this work, we develop a deep-learning classification model (*SynthNN*) to directly predict the synthesizability of inorganic chemical formulas without requiring any structural information. We accomplish this goal by training *SynthNN* on a database of chemical formulas consisting of previously synthesized crystalline inorganic materials that has been augmented with artificially generated unsynthesized materials. Chemical formulas are represented by learning an optimal set of descriptors for predicting synthesizability directly from the corpus of synthesized materials, allowing our approach better capture the complex array of factors that influence synthesizability. *SynthNN* offers numerous advantages over previous methods for identifying synthesizable materials. Whereas expert synthetic chemists typically specialize in a specific chemical domain of a few hundred materials, this approach generates predictions that are informed by the entire spectrum of previously synthesized materials. Additionally, since this method trains directly on the corpus of synthesized materials (rather than employing proxy metrics such as energy above the hull or charge-balancing), this approach also eliminates questions of how well these metrics can describe synthesizability. Finally, this method is computationally efficient enough to enable screening through billions of candidate materials.

We benchmark the performance of *SynthNN* in a head-to-head material discovery comparison against 20 expert chemists and material scientists. *SynthNN* outperformed all experts, achieved 3.6X higher precision and completed the task five orders of magnitude faster than the average human expert. Remarkably, without any prior chemical knowledge, our experiments indicate that *SynthNN* learns the chemical principles of charge-balancing, chemical families and ionicity, and utilizes these principles to inform synthesizability predictions. Since *SynthNN* can be seamlessly integrated with Materials Screening or Inverse Design workflows, the development of *SynthNN* serves to greatly improve the success rate of computational material discovery efforts by ensuring that the candidate materials discovered through these efforts are synthetically accessible.

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

4:15 PM MD01.09.06
End to End Force Field Parametrization for Polymer Electrolytes Using Machine Learning Pablo A. Leon and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States

Solid polymer electrolytes (SPEs) are seen as promising alternatives to conventional liquid electrolytes in lithium battery systems due to their low density, mechanical compliance, and low flammability but are challenged by lower ionic conductivity. Molecular dynamics (MD) simulations can be used to guide the design of novel SPEs by allowing quantitative determination of separable anion and cation diffusions as well as local solvation environments. Classical potential MD simulations update molecular conformations by the net force on each atom due to covalent and nonbonded interactions. However, these classical potentials are often not well defined for novel systems as they require materials- and local environment-specific parameters such as unique bond stiffnesses which are either meticulously hand-tuned across decades or unchangeable due to proprietary licenses.

In this work, we explore the effects of anharmonic bonded interactions on ionic solvation and conductivity in polymer and liquid electrolyte systems. An in-house, machine learning-based workflow, named AuTopology, was used to autonomously learn the interatomic potential parameters of distinct atomic environments for two different classical models from DFT forces as training data. In particular, the effect of machine learning regularization on dihedral parameters and resulting polymer behavior is highlighted. The learned harmonic OPLS model and anharmonic PCFF+ model parameters were then used to equilibrate condensed-phase simulations at a variety of experimentally-relevant concentrations. These simulations were allowed to run for hundreds of nanoseconds to determine the individual anion and cation diffusivities and resulting conductivities. Using this framework and an in-house database of molecular conformations, we have been able to reproduce wB97XD3-level DFT forces from trained OPLS force fields to within 5.5 kcal/mol-A. Lithium solvation environments and ion diffusivities were found to match legacy parameterizations to the same order of magnitude.

4:30 PM MD01.09.07
AI as a Peer: Polymer Discovery with Neuro-Symbolic In-telligent Agents Sarathkrishna Swaminathan, Dmitry Zubarev, Tim Erdmann, Subhajit Chaudhury and Asim Munawar; IBM Research, United States

Materials discovery, in the most general form, is a search for materials whose usefulness exceeds available ones. This is a sequential process, such as synthesis and formulation of a polymer, and in executing complex experimental plans at each stage that favor synthesis of polymer with desired molecular weight. The burden of sequential decision-making in experimental material science rests on subject matter experts (SMEs). Artificial intelligence (AI) systems with direct access to the experimental equipment platforms and general capability to plan sequences of experiments show enormous promise in sharing this burden while improving the characteristics of discovery processes. Neuro-symbolic (NS) variant of AI, combining concepts of logic-based reasoning and connectivism, is especially attractive because of highly desirable characteristics in the context of experimental materials discovery. First, explicit symbolic rules that can be reviewed by a SME serve as a safeguard against undesirable experiments. Second, symbolic rules congruent with conceptual structure of SMEs knowledge can be adjusted pro-actively by SME thus reducing learning budget and improving sample efficiency.

Here, we discuss a practical example of SME interactions with logical optimal action reinforcement learning (LOA RL) agent working on synthesis of spin-on-glasses. Our implementation of LOA RL explicitly considers logical structure of the interactions between the agent and the environment. We define the environment as the space of experiments accessible via an automated pipetting reactor and pursue training generalizable RL agents skilled in traversing the space of polymer synthesis. We demonstrate and quantify basic aspects of peer-like interactions between SME and LOA RL agents.

4:45 PM MD01.09.08
Proton Dynamics Simulations of Solid-Acid Electrolytes Using Active Learning and Equivariant Neural Network Force Fields Menghang Wang, Cameron J. Owen, Yu Xie, Simon Batzner, Albert Musaelian, Anders Johansson and Boris Kozinsky; Harvard University, United States

Understanding the rate-limiting steps of proton conduction across various solid acid electrolytes and the mechanisms behind superprotonic phase transition is crucial for designing next generation energy fuel cells. Due to the high computational cost of ab-initio molecular dynamics, previous studies of proton dynamics were constrained to a hundred atoms within a few hundred picoseconds and thus led to a limited statistics of proton-hopping events. Previous work has used material-specific empirical force fields to study the phase transition of CsHSO4, but it cannot be generalized to understand the mechanism of other solid acid materials.
In this work, we develop machine learning interatomic force fields for CsH2PO4 and CsHSO4 superprotonic conductors combining ab-initio accuracy with scalability to large system sizes and nanosecond time scale. First, we use Bayesian active learning framework FLARE[1] to generate training data containing various atomic configurations. Then, we train an equivariant neural network potential Allegro[2] and deploy it in large-scale molecular dynamics. After demonstrating the fidelity of the machine learning potential by comparing with experimental diffusivities and activation energies, we study the dynamics of oxyanions and protons to identify the rate-limiting step for conduction.
[1] arXiv:2203.03824
[2] arXiv:2204.05249

SESSION MD01.10: Machine Learning IX
Session Chairs: Mathieu Bauchy and Adana Tandia
Friday Morning, April 14, 2023
Marriott Marquis, Second Level, Foothill C

8:15 AM *MD01.10.01
Ab Initio, Classical and Machine-Learning MD Simulations for Modeling Lithium Borosilicate Glasses Shingo Urata; AGC Inc., Japan

Lithium borosilicate (LBS) glass is a typical oxide glass applicable for all solid electrolyte to reduce interfacial resistance between the electrolyte and electrode. Because understanding in the microstructure is essential to improve the ion conductivity, accurate modeling in nanoscale is demanded. However, it is often difficult to reproduce boron coordination change from three-fold (^{3}B) to four-fold (^{4}B) coordinate using a conventional functional type of force-field, which hinders designing high ion-conducting glasses using molecular simulations.

This study, therefore, tried to apply machine-learning potential (MLP) for modeling a series of LBS glasses using DeepMD. The MLP was trained to reproduce a number of data on force and energy calculated by density functional theory (DFT) for crystals and amorphous glass models. The MLP successfully reproduced ^{3}B/^{4}B ratio in the LBS glasses with a few exceptions. Specifically, three-membered rings including boroxol ring, which is composed of three ^{3}B, were generated in high boron-containing LBS glasses in contrast to classical MD simulations with the functional force-field. Ion conductivity and glass transition temperature were also qualitatively reproduced by the MLP, which proved the applicability of MLP to investigate oxide glasses composed of network formers, which flexibly change their coordination.

In this talk, *ab initio* and classical MD simulations will be compared with the MLP-MD. For the classical MD simulations, a Buckingham type of force-field was developed to model LBS glasses by introducing a composition-dependent correction. In comparison with the CMD, the MLP was found to construct energetically more stable glass structures including the three-membered rings more in the microstructures. These results highlighted the advantages of the MLP. In contrast, five-hold coordinated silicon atoms were unreasonably generated, and the glass structures were disrupted at high temperature. This talk will also share these issues when applying MLP for modeling amorphous materials.

8:45 AM MD01.10.02
Investigating Representation Schemes For Surrogate Modeling Of High Entropy Alloys (HEAs) Arindam Debnath and Wesley Reinhart; The Pennsylvania State University, United States

In recent years, High Entropy Alloys (HEAs) have emerged as suitable candidates to replace Ni-based superalloys in gas turbines and jet engines due to their exceptional properties at extreme temperatures. However, the design of HEAs with desired value of properties is a challenging task due to the large and mostly uncharted design space and the difficulty in predicting the non-linear relationships between structure, property, and processing parameters. To further complicate matters, the three traditional paradigms of materials design, namely the trial-and-error method, chemical intuition governed by physical and chemical rules, and computer simulations are also unsuitable for designing HEAs with target properties. The advent of machine learning and data-driven methods has unlocked a new paradigm in the field of materials discovery and is perfectly poised to solve the problem of inverse design of HEAs. However, there are certain challenges that need to be addressed when it comes to utilizing ML tools for materials science problems, most of which arise because of adapting pre-existing methods to solve specific problems.

One such challenge is representing the material system of interest (in this case HEAs) in a format that is machine readable while also incorporating sufficient information. Unlike crystalline materials, where structural information is widely available, such vital information is lacking in HEAs as they mostly exist as random, non-periodic solid solutions. Therefore, most ML studies involving HEAs derive the input features for their model from the chemical composition. Primarily, the atomic fractions of the elements present in the composition are encoded as vectors, which can be either randomly arranged or follow a logical arrangement (like a 1D vector where the elements are arranged according to their atomic numbers or a 2D matrix that follows the periodic table arrangement). Additionally, studies have also utilized some material properties that can be derived from the composition by applying some stoichiometric and thermodynamic rules as features. While all of these feature schemes have yielded great results for predicting specific HEA properties, there has not been a systematic effort to benchmark these schemes.

Therefore, we investigate several commonly used representation schemes for HEAs for predicting thermodynamic and mechanical properties of interest like phase, hardness, and yield strength. The performance of the different models using the different representation schemes on these material properties would indicate the scheme's transferability. To assess the generalizability of the representation schemes, we create multiple scenarios by omitting specific element containing compositions from the training of the respective models and using these omitted compositions as the test set. We anticipate that the insights from these results will help us understand which representation scheme manages to retain the most chemical information and therefore is best suited to solve real-world design tasks.

9:00 AM MD01.10.03
Exploring the Discrepancies, the Extrapolability, and the Interpolability of Machine Learning Interatomic Potentials Yunsheng Liu and Yifei Mo; University of Maryland, United States

Machine learning interatomic potentials (MLPs) are a promising technique for atomic modeling. Despite its low computation cost, high accuracy, and small errors that are widely reported for MLPs, an open concern is whether MLPs can always accurately reproduce atomistic dynamics and related physical properties in their applications in molecular dynamics (MD) simulations. By testing a number of current state-of-the-art MLPs, we examine the extrapolability and interpolability of MLPs and reveal quite a few discrepancies related to defects and rare events (REs), especially the predicted diffusional properties of the MLP-MD simulations and the phonon dispersion with vacancy defect, comparing with the ab initio computation. Our analyses on atomic dynamics, including defect formation energies, atomic vibrations around the defects, and atom migrations, reveal that the current testing for MLPs based on low average errors is in adequate. To fully capture the true performance of MLPs on extrapolability and interpolability, we further develop and demonstrate quantitative metrics, which are better indicators for the prediction of atom dynamics properties in MD simulations. Leveraging these findings, we develop a RE-enhanced workflow of MLP training consisting of identifying RE data, enhancing training sets, and optimizing MLPs by RE-enhanced force performance scores. The MLPs trained by the RE-enhanced workflow are demonstrated to have improved prediction in diffusional properties. Given the identified errors and improved workflow are general to all MLPs, our study provides guidance for further development, improvements, and wide adoption of accurate, robust, and reliable MLPs for atomistic modeling.

9:15 AM MD01.10.04
Predicting Small-Molecule Viscosities Using Machine Learning and Physics-Informed Approaches Alex K. Chew, Mohammad Atif Faiz Afzal, Matthew Sender, Anand Chandrasekaran, Lihua Chen, Andrea Browning and Mathew Halls; Schrödinger, United States

Viscosity is a fundamental property that measures how "sticky" - or how resistant to flow - a fluid is, which dictates the performance of a wide range of materials, such as batteries, cosmetic formulations, and pharmaceuticals. Measuring viscosities using experiments or physics-based simulations is slow and tedious, which motivates the use of alternative, fast data-driven approaches to accelerate viscosity estimations. In this work, an extensive collection of over 4,000 experimental viscosity and temperature values for small organic molecules were curated from scientific literature and databases to develop quantitative structure-property relationship (QSPR) models. We compared both traditional-learning and deep-learning QSPR models and identified models that can accurately predict viscosities using molecular descriptors and temperature as inputs. To further improve model accuracy, we added physically relevant descriptors, extracted using classical molecular dynamics simulations, and encoded them into our QSPR models. We employ feature importance analysis tools to evaluate the influence of molecular-based and physics-informed descriptors on QSPR model performance. The data curation of a large viscosity dataset and the development of accurate, physically informed machine learning models enables the screening of viscosities for the design of new materials.

9:30 AM MD01.10.05
Atomistic Dynamics Simulations of Complex Materials and Interfaces with Machine-Learned Force Fields Anders Blom, Julian Schneider, Suresh K. Natarajan, Deb De, Jan-Niclas Luy and Søren Smidstrup; Synopsys, United States

Atomistic modeling is a powerful way to predict the properties of new materials. Progress in computer speed combined with more efficient algorithms have enabled accurate studies even for complicated materials like alloys and interfaces. Static simulations can now be performed for systems containing hundreds or even thousands of atoms using methods such as density-functional theory (DFT), and even millions of atoms with classical interatomic potentials (force fields). Unfortunately, the situation is quite different if one is interested in performing dynamical calculations, which includes studies of thermal conductivity or expansion coefficients, mechanical strength, or structure prediction.

Although DFT can be used for almost any material, the simulation times quickly become unmanageable, as a single molecular dynamics (MD) run over a few nanoseconds could take years for a big system, even if the calculations were heavily parallelized. Conversely, using force fields one could run the simulations in a fraction of the time, but sufficiently accurate force fields are only available for a few selected materials, and usually rather simple ones. For instance, the force field parameters might be fitted for a crystalline material, but the application calls for calculations of an amorphous cell. Parametrizing a new traditional force field for a novel material is a very time-consuming task, and the accuracy is often strongly limited by the functional form of the potentials used; the potentials often fail in high-temperature situations or when trying to predict atom diffusion energy barriers or phase transitions. Moreover, these potentials are rarely able to describe complicated situations such as interfaces or materials with many elements.

Recent efforts in the development of machine-learned (ML) force fields are now however enabling new and exciting quantitative studies of a wide range of problems. ML force fields can in theory be fitted for complex materials and interfaces, work well in sitations far from equilibrium (if properly trained), and are almost as efficient as traditional force fields when running long MD simulations. The one caveat that remains is that while it is possible to obtain near-DFT accuracy in a wide variety for scenarios, the training data used for the fitting must be very carefully chosen, and this is no small or simple task. The challenge is to generate an sufficient quantity of significantly different geometries which still cover the desired application space, as efficiently as possible, in order to minimize the time used to generate the reference DFT data for the fitting.

In this presentation, we will describe how we have created a set of automated protocols that can generate curated training data sets for complex materials such as alloys, interfaces, and surface chemistry applications. In particular, we avoid the use of DFT MD calculations, which can be extremely time-consuming. We will demonstrate how we have successfully and efficiently trained ML force fields to perform detailed structural analysis of phase change materials, molecular adsorption on surfaces for ALD studies, and thermal simulations of 2D materials.

Moreover, we have recently developed an enhancement to the ML potential framework that makes it easier and more robust to fit and use potentials for systems involving many different elements. In the past, applications of ML force fields have been limited to relatively simple materials, but this extension has enabled us to e.g. generate a single potential to generate relaxed and defect-free geometries of high-k metal gate stacks consisting of multiple interfaces and amorphous regions, with a total of 5 elements (Si, O, Hf, Ti, N), and magnetic tunnel junctions (MTJ) with 6 elements (Mg, O, Ta, Fe, Co, W) with a low training error as 5 meV/atom. For these MTJs we show that the resulting magnetic properties are nearly identical compared to DFT-optimized geometries.

9:45 AM MD01.10.06
Towards Quantum Machine Learning via Tensor Network Architectures Kyriakos Flouris; ETH Zurich, Switzerland

Deep machine learning methods have already established their dominance is most automation tasks and Quantum computing is one of the most promising fundamentally alternative algorithmic structures of the century. Furthermore, tensor networks have been shown to create an equivalent description to quantum algorithms, as it would have been implemented traditionally with gates. Additionally, it is estimated that the fundamentally probabilistic nature of quantum algorithms implies that they can be suitable Bayesian estimators. We implement a simple tensor network as the latent space representation of a manifold learning flow. We explore its theoretical implications and the potential to be used as an efficient lattice model solver.

10:00 AM BREAK

10:30 AM MD01.10.07
Combinations of Machine Learning and Thermodynamic Integration Methods to Study Grain Boundary Segregation in Magnesium Alloys at Finite Temperatures Vaidehi Menon and Liang Qi; Univ of Michigan, United States

The segregation of solute elements to grain boundaries (GBs) can change the thermal and mechanical properties of metallic alloys. Atomistic simulations have been widely applied to investigate the thermodynamics and kinetics of GB segregation. However, these simulations are usually limited by the insufficient sampling of various GB sites and inaccuracy descriptions of free energy variations at finite temperatures. To solve these problems, we applied atomistic simulations and machine learning (ML) methods to investigate GB segregation in Mg alloys, which are promising lightweight structural materials. We present our studies of the segregation thermodynamics of solute elements (such as Y and Al) at Mg GBs using molecular dynamics (MD) simulations, thermodynamic integration (TI) methods, and ML.

We construct tens of symmetric tilt grain boundaries (STGBs) with different tilt axes and tilt angles as the GB structure sample set based on evolutionary algorithm [1]. The spectral segregation model [2], which uses a per-site distribution of zero-K segregation energies in the vicinity of each GB from the GB structure sample set, is employed to calculate the average GB segregation concentrations and the effective GB segregation energies at finite temperatures. The average GB segregation concentrations predicted by using the zero-K GB segregation energies show large deviations compared with experimental measurements. To reconcile these inconsistencies, our simulations also extend the current spectral model approach to carry out segregation free energy calculations at finite temperatures by using the TI method. We find that the finite-temperature Helmholtz free energy segregation spectra differ significantly from the segregation energy spectra obtained via 0 K simulations, which can change the GB solute concentration profile and effective segregation energy predictions at finite temperatures. However, a key bottleneck is that the direct TI calculations can only be applied to a small number of GB sites, which are insufficient for the spectral segregation model, due to the expensive computational costs of the TI method. Thus, ML methods are applied to accelerate the predictions of the accurate per-site distribution of GB-segregation free energies at finite temperatures by following steps.

First, we construct an ML surrogate model to predict the zero-K GB segregation energy as the function of local GB structural descriptors. Second, analyses of these descriptors determine the key structural descriptors for GB segregation energies, so the representative GB sites are chosen from the GB structure sample set based on the population distributions of these key structural descriptors. Third, the TI method is applied to calculate the finite-temperature segregation free energies for those representative GB sites. Fourth, ML methods were applied to construct the surrogate model to predict the difference between the zero-K segregation energy and finite-temperature segregation free energy for each GB site. The input descriptors of these surrogate models will be constructed based on both geometric factors and physics mechanisms, such as the estimation of the free energy variations based on the quasi-harmonic approximation. This free energy surrogate model is iteratively improved by including more representative GB sites in the training data sets based on adaptive learning methods. Finally, the free energy of solute segregation energy at each GB site in the GB sample set is predicated based on the surrogate model to get the accurate segregation free energy spectra, which are used for the accurate predictions of the GB segregation thermodynamics consistent with experimental measurements in Mg alloys.

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[2] M. Wagih, C. A. Schuh, Acta Materialia, 181 (2019) 228-237

10:45 AM MD01.10.08
Predicting Thermal Conductivity of Metal-Organic Frameworks using Graph Convolutional Neural Networks Meiirbek Islamov[1], Karl Krauth[2], Hasan Babaei[2], Michael Jordan[2] and Christopher E. Wilmer[1]; [1]University of Pittsburgh, United States; [2]University of California, Berkeley, United States

Metal-Organic Frameworks (MOFs) have gained prominence as revolutionary materials for gas storage and separation applications due to their high porosity, large surface areas, tunable pore geometry and chemistry. However, the practical usefulness of MOFs, especially in gas storage applications, depends on how rapidly they can disperse the tremendous amount of thermal energy generated during the typically exothermic adsorption process. Although adsorption-related properties of MOFs have been extensively investigated, comparatively limited studies have focused so far on understanding their thermal transport properties. To provide a data-driven perspective into this problem, we performed the first high-throughput computational screening of thermal transport properties in MOFs by performing classical molecular dynamics (MD) simulations on a diverse set of hypothetical MOFs. In addition to establishing universal structure-thermal conductivity relationships, we trained a crystal graph convolutional neural network on the thermal conductivities of 5353 hypothetical MOFs that were computationally generated with the ToBaCCo-3.0 code. Our model predicts the thermal conductivity of MOFs in a separate test set with a mean absolute error of 0.072 W m^{-1} K^{-1}. This model only requires MOF atomic and bonding information, which can help accelerate MOF discovery with tailored thermal transport properties by replacing expensive atomistic simulations that require interatomic potentials.

11:00 AM MD01.10.09
Efficient Sampling of Structural Configurations with A Universal Materials Graph Neutral Network Potential Ji Qi and Shyue Ping Ong; University of California, San Diego, United States

Training structure is one key component for fitting robust machine learning interatomic potentials (ML-IAPs). It is usually sampled by short trail runs of *ab initio* molecular dynamics together with manual selection by intervals. This traditional sampling method suffers from high computational cost and low diversity. The as-trained ML-IAPs are not reliable for severe temperatures at or above melting temperatures, thus prohibiting its accurate simulation for amorphous structures and calcination conditions. On the other hand, active learning (AL) strategy has been proposed and verified to effectively sample distinctive configurations in extreme and target scenarios, thus improving the reliability of ML-IAPs. However, AL still requires a good initial training set and intrinsically have to conduct *ab initio* calculations as well as ML-IAP fitting iteratively. In our study, we propose a method to broadly sample training configurations with a universal graph neutral network potential. Our strategy can achieve highly reliable ML-IAPs with one single iteration of optimization, and it is generally applicable to 89 elements in the period table.

11:15 AM MD01.10.10
ET-AL: Entropy-Targeted Active Learning for Bias Mitigation in Materials Data Hengrui Zhang, Wei Chen, James M. Rondinelli and Wei Chen; Northwestern University, United States

Growing materials data and data-centric informatics tools drastically promote the discovery and design of materials. While data-driven models, such as machine learning, have drawn much attention and observed significant progress, the quality of data resources is equally important but less studied. In this work, we focus on bias mitigation, an important aspect of materials data quality. Quantifying the diversity of stability in different crystal systems, we propose a metric for measuring structure–stability bias in materials data. To mitigate the bias, we develop an entropy-target active learning (ET-AL) framework, guiding the acquisition of new data so that diversities of underrepresented crystal systems are improved, thus mitigating the bias. With experiments on materials datasets, we demonstrate the capability of ET-AL and the improvement in machine learning models that mitigating bias offers through bias mitigation. The approach is applicable to data-centric informatics in other scientific domains.

11:30 AM MD01.10.11
Optimizing Thermodynamic Properties of High Entropy Alloys and Hydrides with Lattice Graph Neural Network Models Matthew Witman[1], Norman Bartelt[1], Sanliang Ling[2], Mark D. Allendorf[1] and Vitalie Stavila[1]; [1]Sandia National Laboratories, United States; [2]The University of Nottingham, United Kingdom

Efficient prediction of thermodynamic properties in both closed and open systems is needed to evaluate material performance and permit high-throughput materials discovery for a diverse array of technology applications, from rational design of low-density alloys, to optimizing battery cathodes, to modulating hydrogen absorption equilibria in complex metal alloys. Density functional theory (DFT) is typically needed to relax atomic configurations and predict energetics with sufficient accuracy in these systems. Yet it can be prohibitively expensive to achieve the necessary sampling required by statistical mechanics to converge thermodynamic predictions for even a single complex alloy due to the enormous phase space of possible configurations. Surrogate modeling strategies are therefore required, which critically must be able to predict energetics of these structural relaxations without knowing the relaxed structure, i.e., correctly predict relaxed energetics from an unrelaxed and trivial-to-generate structure representation. Cluster expansion methods can satisfy such requirements but can be very difficult to construct in systems with high compositional complexity. More recently, highly generalizable graph neural network models have been proposed that alleviate the difficulties associated with feature engineering for crystal structures. Therefore, it is now important to investigate their capacity to predict the energy of DFT-relaxed structures from an unrelaxed crystallographic representation, i.e., based on idealized lattice coordinates. Not only do they excel at this for systems investigated herein, but they accurately predict relaxed configurational energies well *outside* their training distribution. Thus, we can rapidly (minutes on a desktop computer) execute the large-scale sampling (hundreds of thousands of configurations) necessary for first-principles statistical mechanics methods to predict various thermodynamic properties, a task that would otherwise be intractable. Two exemplars, optimizing thermodynamic stability of low-density high entropy alloys and the modulating the plateau pressure of hydrogen in metal alloys, demonstrate the power of this approach. Its generalizability, which is limited in principle only by diversity of training data, has significant potential for future development and application to a multitude of materials discovery domains when sampling intensive routines are needed for thermodynamic predictions.

11:45 AM MD01.10.12
Discovering Novel Halide Perovskites using Multi-Fidelity Machine Learning and Graph Neural Networks Arun Kumar Mannodi Kanakkithodi; Purdue University, United States

The ABX_3 perovskite crystal structure is ubiquitous and the subject of extensive study owing to the sheer tunability of electronic and optical properties that can be achieved. Halide perovskites, in particular, are materials of great interest for solar absorption and many related optoelectronic applications such as LEDs, lasers, and UV or IR sensors. The discovery of novel perovskite compositions, including complex alloys with attractive properties, is hindered by the combinatorial nature of the chemical space and a general lack of quantification of systematic inaccuracies in simulations such as from first principles-based density functional theory (DFT). In this work, we generated large datasets of computed stability, electronic band gaps, theoretical photovoltaic efficiency derived from optical absorption spectra, and defect formation energies, of halide perovskite alloys from various DFT semi-local and hybrid functionals. This data is combined with smaller quantities of corresponding experimental measurements collected from the literature, and used for training multi-fidelity machine learning (ML) models to make property predictions at experimental accuracy. Such predictions, using state-of-the-art nonlinear regression techniques including random forests and Gaussian processes, are sequentially improved and coupled with a recommendation engine for new computations and experiments to gradually achieve new stable compositions with targeted band gap and absorption. Initial success if obtained using as inputs compositional information, known elemental properties of A, B, and X species, and one-hot encoding of perovskite phase and data fidelity. We extend these models to a much larger dataset of > 10,000 perovskite structures, wherein entire crystal structures are used as input via a variety of graph neural network-based approaches. This enables inclusion of lattice strain, octahedral distortions and rotations, and different kinds of alloy ordering as implicit inputs to the ML framework, ultimately resulting in general models applicable to any atom-composition-structure combination within the selected halide perovskite chemical space. Best DFT-ML surrogate models are coupled with optimization schemes using methods such as genetic algorithm, used to drive collaborative experiments and further DFT computations, and made available to the community via user-friendly tools on the NSF-funded online repository, nanoHUB.

References
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SESSION MD01.11: Machine Learning X
Session Chairs: N M Anoop Krishnan and Shingo Urata
Friday Afternoon, April 14, 2023
Marriott Marquis, Second Level, Foothill C

1:30 PM MD01.11.01
Efficient Implementation of Machine Learned Nonlocal Density Functionals for Molecules and Solids Kyle W. Bystrom and Boris Kozinsky; Harvard University, United States

Machine Learning (ML) has recently gained attention as a means to develop more accurate exchange-correlation (XC) functionals, and in particular could be used to improve XC functionals for solids without using the computationally expensive exact exchange energy. Feature design is one of the main challenges of this approach because the features must include enough nonlocality to capture the complex nonlocal nature of the exact XC functional while also allowing for computationally efficient and scalable implementations. To address this challenge, the CIDER model for designing nonlocal ML functionals is introduced and used to design a nonlocal exchange functional that obeys the uniform scaling rule for exchange. In addition, two efficient methods for evaluating CIDER features are implemented: A quadratic-scaling algorithm for all-electron, molecular density functional theory (DFT) and a quasi-linear-scaling algorithm for plane-wave DFT with the PAW method. Efficiency and accuracy benchmarks for molecular periodic systems are presented, and the importance of the kinetic energy as a feature for learning the exchange functional is discussed.

1:45 PM MD01.11.02
Materials Discovery for High-Temperature, Clean-Energy Applications Using Graph Neural Network Models of Vacancy Defects and Free-Energy Calculations Matthew Witman[1], Anuj Goyal[2], Tadashi Ogitsu[3], Anthony McDaniel[1] and Stephan Lany[2]; [1]Sandia National Laboratories, United States; [2]National Renewable Energy Laboratory, United States; [3]Lawrence Livermore National Laboratory, United States

High-temperature properties of oxides are often governed by O vacancy defect formation. To enable high-throughput screening of thermochemical materials for clean-energy applications, we developed a graph neural network modeling approach for defects. This model accelerates the screening of vacancy defects by many orders of magnitude by replacing the supercell relaxations in density functional theory (DFT) that are otherwise required for each symmetrically unique crystal site. It fully automates the prediction of the DFT-relaxed vacancy formation enthalpy of any crystallographic site based only on the primitive cell of the host crystal structure. It can thus be used off-the-shelf to rapidly screen 10,000s of crystal structures (which can contain millions of unique defects) from existing databases. This modeling approach therefore provides a significant screening and discovery capability for a plethora of applications in which vacancy defects are the primary driver of a material's utility. For example, by high-throughput screening the Materials Project's metal oxides, we rapidly "re-discover" and identify new high potential candidate materials for hydrogen generation via solar thermochemical water splitting and energy storage, for CO2 conversion via reverse water gas shift chemical looping, and for cathodes in solid oxide fuel cells. Thermodynamic modeling on the basis of the high-throughput screening results allows us to connect the predicted defect energies to high temperature process conditions relevant to the different application areas, and we extract the reduction entropies as an additional selection criterion for high-performance materials.

2:00 PM MD01.11.03
Unraveling the Structure-Spectrum Relationship Using Descriptor-Aware Adversarial Autoencoders Xiaohui Qu, Zhu Liang, Deyu Lu, Matthew Carbone, Fanchen Meng, Eli Stavitski and Mark S. Hybertsen; Brookhaven National Laboratory, United States

X-ray absorption near-edge structure (XANES) spectroscopy is a premier tool for materials characterization, which is sensitive to the local chemical environment of the absorber site. However, interpreting XANES is highly nontrivial and first-principles simulations are typically required for descriptor assignment (e.g., oxidation state and coordination number). Although some descriptors have been established with distinct spectral trends, it is much more challenging to systematically discover new descriptors with statistically salient trends in complex materials spaces. A promising approach is to identify spectral trends with dimensionality reduction methods, e.g., principal component analysis or autoencoder. However, the reduced representation, e.g., a latent space in an autoencoder, does not align with descriptors monotonically, and the interpretation of the latent space remains challenging. To achieve a direct mapping between the latent space and descriptor space, the latent space needs to be reorganized to align each dimension with a descriptor.

In this work, we developed a "rank constraint" which operates on top of the adversarial autoencoder (AAE) framework. It forces each latent dimension to "track" a specific structure descriptor monotonically while preserving latent space smoothness. Specifically, we use the Kendal rank correlation coefficient as a soft constraint in our loss functions, which enforces the monotonical dependence of each latent space variable with a chosen distinct physical descriptor. Our new method, the Rank constrained AAE (RankAAE), allows us to effectively reveal the spectral line shape variation for each individual descriptor. Descriptors of the material structure generally have intertwined contributions to the spectral line shape; however, our method is capable of systematically decoupling them. We demonstrated our method using diverse datasets across the eight transition metal oxide families which contain forty thousand simulated spectra of the K-edge XANES. RankAAE not only reproduces well-documented trends from the literature but also reveals three new structure descriptors: oxygen coordination number, the standard deviation in the nearest neighbor bond lengths, and the minimum oxygen-oxygen distance on the edges of the nearest neighbor polyhedron. Our method provides a general framework to enhance the interpretability of a dimension reduction algorithm, which is generally applicable to other spectroscopic data.

2:15 PM MD01.11.04
Predicting the Strain Field Evolution in 2D Digital Composites with Neural Operators Meer Mehran Rashid, Souvik Chakraborty and N M Anoop Krishnan; Indian Institute of Technology Delhi, India

The search for high-performance materials has led to advanced composite materials with hierarchical designs. However, designing a superior material with targeted properties and performance is challenging due to the vast design combinations and computational limitations imposed by conventional physics-based solvers. To solve this, we use deep learning methods to measure the material response for composite materials subjected to tensile loading. In this study, we attempt to benchmark the state of the art neural operators (SOTA) to predict the strain evolution in 2D composites. We employ (Fourier Neural Operator), DeepONet, Multi-wavelet based transform (MWT), Wavelet Neural Operator (WNO) and Conditional Generative Adversarial Networks (cGAN). By inputting the strain fields corresponding to first few time steps, the Neural Operators (NOs) predict subsequent strain fields until the onset of fracture. Besides, we evaluate the performance of various NO's for material and pixel-wise zero-shot super-resolution. Our results show the superior performance of the FNO with accurate predictions for different use cases.

2:30 PM MD01.11.05
Physics-Informed Machine Learning Prediction of the Composition and Load Dependence of Glass Hardness Sajid Mannan[1], Daniel Roberto Cassar[2], Mohd Zaki[1], Suresh Bishnoi[1], Johan Frederik Schou Christensen[3], Morten Mattrup Smedskjær[3], Edgar Dutra Zanotto[4], Nitya N. Gosvami[1] and N M Anoop Krishnan[1]; [1]Indian Institute of Technology Delhi, India; [2]Ilum School of Science, Brazil; [3]Aalborg University, Denmark; [4]Universidade Federal de São Paulo, Brazil

Oxide glass materials are crucial for a variety of applications in the automotive, aerospace, electronics, architectural, biomedical, and nuclear industries. However, their brittleness and low fracture toughness make them highly vulnerable to surface damage such as scratches, abrasion, and chipping during processing and application. Such damages can act as crack nucleation sites, leading to catastrophic brittle fracture upon tensile loading [1]. It is thus important to develop glasses with improved damage resistance, e.g., by improving their hardness. To address this problem, we have used a Physics-Informed Neural Network (PINN) to develop a model that can learn from existing data on the composition and load dependence of hardness. The data was extracted from the INTERGLAD database [2], and numerous scientific papers. Both purely data-driven and PINN models were trained. The purely data-driven model successfully predicted the composition dependence but failed to capture the load dependency. On the other hand, the PINN model performed reasonably well in predicting both the target variable and capturing the load dependency of hardness. Furthermore, we employed Shapley Additive Explanations (SHAP) techniques to understand the feature (chemical elements) dependency toward model prediction. The results indicate that nitrogen (N), silicon (Si), and lanthanum (La) contribute significantly to improving the hardness of oxide glasses. In contrast, sodium (Na), phosphorous (P), and tellurium (Te) are found to decrease the hardness of oxide glasses.
Additionally, the PINN model clearly demarcates the load dependency behavior of oxide glasses and indicates that hardness decreases significantly for a slight increase in load values. However, this behavior was observed only at relatively low loads, which we attribute to the Indentation Size Effect (ISE). The derived composition-property relationships can potentially aid in designing glasses with tuned hardness for a variety of applications.

2:45 PM MD01.11.06
Extracting Materials Compositions from Research Papers Using Natural Language Processing Mohd Zaki, Tanishq Gupta, Devanshi Khatsuriya, Kausik Hira, N M Anoop Krishnan and Mausam Mausam; Indian Institute of Technology Delhi, India

Machine learning and natural language processing tools have contributed to the development of materials science specific language models, named entity recognition systems, and classification systems for identifying relevant research papers. To accelerate material discovery, it is important to know about materials already reported in scientific literature. However, the manual curation of such information into both human and machine-understandable forms is quite cumbersome. In this work, we use a graph neural network pipeline powered by MatSciBERT - A materials domain language model, to extract compositions of glasses and alloys reported in research papers. We first discuss the challenges associated with composition extraction, which arise due to different ways of reporting followed by researchers. Further, we analyse the extracted compositions and discuss the potential applications of the generated datasets and the model.

3:00 PM BREAK

3:30 PM MD01.11.07
Extrapolative Discovery of Eco-Friendly Dielectric Gases Based on Machine Learning and Quantum Chemical Calculations Hajime Shimakawa, Akiko Kumada and Masahiro Sato; The University of Tokyo, Japan

Material discovery based on Materials Informatics (MI) generally aims to accurately predict material properties and to effectively explore unknown materials that are inaccessible by conventional methods. We have to tackle the fact in that machine learning is strong at interpolative prediction, but weak at extrapolative prediction. Because of the challenges of extrapolative performance of MI, there have been few studies that address this issue. Recently, some studies have reported network optimization methods [1] or flow-based generative model [2] that improve their extrapolative performance compared to conventional methods. However, we don’t have any MI model that has extrapolative performance sufficiently to discover unknown materials yet. We require an MI model that can obtain a correlation between material information and physical property, not as a stochastic distribution, but through physics-based analysis and machine learning. This study realizes the extrapolative prediction by learning linear correlations between quantum-chemical-based descriptors and material properties for each molecular cluster that is divided by quantum chemical information. As one of the successful applications, we design an extrapolative discovery model that can accurately predict boiling point, dielectric strength, and global warming potential (GWP) of gaseus molecules to explore for new eco-friendly dielectric gases beyond existing materials. Our results show that conventional graph-based deep learning and nonlinear machine learning models fail to extrapolative predictions, whereas our proposed model of quantum chemistry-based molecular cluster learning has a promising extrapolative performance. Using LSTM-based SMILES generation and molecular fragment reconstruction, a large number of novel molecular structures are generated and screened for low-boiling point, high-dielectric strength, and low-GWP molecules. As a result, we succeed to obtain new molecules that have powerful properties that overcome the trade-off weaknesses of existing materials and have a potential to contribute to realizing carbon neutrality. Our extrapolative discovery model extends the possibility of materials development with MI.
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3:45 PM MD01.11.08
Artificial Neural Network with Multi-Head Intermolecular Attention Predicts Chemical Reactivity of Organic-Battery Components Jaekyun Yoo and Kisuk Kang; Seoul National University, Korea (the Republic of)

Organic battery system gather lots of attention as post lithium ion battery becuase of its cost effectiveness and eco-friendliness. Organic electrodes, which consists of redox-active organic materials, are key components to implement organic batteries whose energy density and cycle performance is similar with conventional inorganic batteries. Selecting functional materials which are chemically compatible with each other is a prerequisite to discover high-performance organic materials and fabricate these multi-component systems and is especially crucial for their long-term system stability. In that, in the design of new organic-based batteries the exploration of organic compounds for the electrode and electrolyte should consider not only their intrinsic electrochemical activity/stability but also the compatibility among the constituting components. Herein, we report an extensive scheme of predicting the chemical reactivities of any combinations of two organic compounds by employing the so-called Intermolecular Reaction Rate Network (ImRRNet). This new artificial neural network (ANN) platform exploits the novel intermolecular multi-head attention method to predict the precise reaction rate constant between two organic chemicals from their molecular structure and was trained with a large chemical space of 175,987 datapoints on the nucleophilicity and electrophilicity. The intermolecular multi-head attention method successfully identified the local substructure that primarily determines the chemical reactivity of organic molecules by providing a greater attention score in the specific position. This means our new model catch hidden chemical information in the molecular structure even though we never instructed chemical information which belongs to molecular structure excpet reactivity between two molecules. The prediction accuracy of ImRRNet was observed to be remarkably higher (mean absolute error of 0.5760) than other previous ANN models (> 0.94), validating its efficacy for practical employment in the design of multi-component organic-based rechargeable batteries.

4:00 PM MD01.11.09
Novel Graph Imputation Method for Discovering Structure Property Relationships in Materials Vineeth Venugopal and Elsa Olivetti; Massachusetts Institute of Technology, United States

In this work, we present a novel method for materials discovery and property identification through node imputation in Knowledge Graphs (KG). The proposed method extracts a high dimensional embedding for entities in a KG using large language models from which a neural network is trained to generate the graph embedding representation. This allows us to add a node to a knowledge graph that was not present during the training of the graph embedding model and consequently allows for link prediction - thereby connecting the new node to other nodes in the graph. This approach for generating nodes in a knowledge graph is being demonstrated for the first time here.

Knowledge Graphs are an emerging tool for integrating data and relational ontologies through versatile graph databases. They have become the industrial standard for data retrieval and organization as demonstrated by KG use in Google Search, social media sites such as Facebook and LinkedIN, as well as companies with large data inventory such as Ikea and NASA. In the field of materials science as well, several domain specific ontologies and property graphs have been proposed, though the use of knowledge graphs as a relational database tool is not very common at present.

We recently presented MatKG: a knowledge graph in the field of materials science comprising over 80,000 unique entities and over 5 million statements, where each statement is an (entity, relation, entity) triple. The KG covers several topical fields such as inorganic oxides, functional materials, battery materials, metals and alloys, polymers, cements, high entropy alloys, biomaterials, and catalysts. The triples are generated autonomously through data driven natural language processing pipelines and extracted from a corpus of around 4 million published scientific articles. Several informational entities such as materials, properties, application areas, synthesis information, and characterization methods are integrated together with a hierarchical ontological schema, where the base relations are extracted through statistical correlations to which higher level ontologies are appended. Thus the KG is heterogeneous and contains multiple relations between entities. It is shown that a bipartite projection of the base KG leads to comprehensive relational graphs that link materials to their chief attributes and applications and help answer questions such as "what are key attributes of battery materials?" without human intervention. We use a graph neural network based representational learning method to learn embeddings for entities and their relations which translate the graph data structure to a high dimensional mathematical space in which semantic relations between entities can be formulated as algebraic operations.

However, these representation models cannot learn embeddings of entities that were not present during training. Consequently, we are not able to predict links to material or property nodes that are unseen/novel - a key requirement for materials discovery and development. While several node imputation models are currently available today, they require at least a few links to be known of the given node, which is inherently impossible for a newly developed material. The approach we have developed allows for a brand new node to be imputed into a graph by learning the representation from large language models. The neural network architecture used for training, the efficacy of the method, and the entities that are successfully/unsuccessfully imputed using this technique are described. Future directions of development are also discussed.

4:15 PM MD01.11.10
Machine Learning-Based Optimization of Segmented Thermoelectric Generators using Temperature-Dependent Performance Properties Wabi D. Diriba[1], Byungki Ryu[2] and Seunghwa Ryu[1]; [1]Korea Advanced Institute of Science & Technology (KAIST), Korea (the Republic of); [2]Korea Electrotechnology Research Institute (KERI), Korea (the Republic of)

Segmented thermoelectric generators (STEGs) offer an excellent platform for thermal energy harvesting devices because they enhance the performance of power generation for a wide range of operating temperatures. Despite its advantage of direct conversion of thermal energy into electricity, conventional optimization approaches of STEGs are not able to offer a systematic way of selecting the optimal multiple stacks of P-and-N-type thermoelectric materials (TEs) legs from a set of many TE materials. In this study, we propose a systematic machine learning-based optimization to find the optimal STEG for maximizing its performance. A deep neural network (DNN) is trained to learn the inherent nonlinear relationship between the temperature-dependent properties of P- and N-type TE materials, lengths of each segment, and external loads to predict performance outputs. The trained DNN model efficiently explores the design space via a genetic optimization algorithm and suggests new high-performance designs. To expand the DNN prediction accuracy in the new superior STEG designs, the DNN is iteratively updated by augmenting the new designs via active learning. We optimized STEG module with four stacked segments in each leg from 88 P- and 70 N-type TE materials database. The optimized STEG module design exhibits 1.91 and 1.5 times higher power and efficiency compared to the best designs chosen from the initial training dataset composed of 157,916 different STEGs, respectively.

4:30 PM MD01.11.11
Bayesian Optimization and Reinforcement Learning-Based Design of High-Performance Kirigami Piezo-Transmittance Strain Sensors Jimin Gu[1,2], Bowen Zheng[2], Grace Gu[2] and Inkyu Park[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]University of California, Berkeley, United States

Piezo-transmittance based strain sensors, which detect strains by mechanical deformation-induced optical transmittance change, have shown great promise in soft sensing applications due to their fast response, long-term stability, and negligible energy consumption. However, challenges lie in how to further improve their performances of interest such as sensitivity, working range, and deformability to adapt to tasks in extreme conditions like space and wearable device. Kirigami structures, an important subset of mechanical metamaterials, possess highly versatile mechanical properties due to their unique deformation behavior. Additionally, these structures can be highly parameterized, which favorably creates ample opportunities for optimization. In our study, we formulate the problem as a multi-objective optimization with respect to the sensing sensitivity, the linearity of the response, and the failure strain over a large design space of the kirigami structure. First, using finite element simulation results as training data, we develop a surrogate machine learning model that takes in geometric variables and outputs the performances of interest. This surrogate model is used to replace more expensive physical simulations to accelerate the optimization process. Next, we use both Bayesian optimization and reinforcement learning to search for high-performance kirigami designs for piezo-transmittance strain sensing. We show that the optimized kirigami sensors reliably outperform random geometrical configurations. We also conduct feature importance analysis to rank the contributions of individual features as well as feature combinations, which interprets the machine learning-based optimization results and gives insights to better parameterization for next design iterations. As a future step, we aim to conduct experiments to verify the high performance of the designed kirigami piezo-transmittance strain sensors.

SESSION MD01.12: Virtual Session: Machine Learning XI
Session Chairs: Ekin Dogus Cubuk and Daniel Lim
Tuesday Afternoon, April 25, 2023
MD01-virtual

9:00 PM MD01.12.02
Cost-Sensitive Bayesian Active Molecular Design with Auxiliary Properties Elliot Nelson[1] and Dmitry Zubarev[2]; [1]IBM T.J. Watson Research Center, United States; [2]IBM Almaden Research Center, United States

Given the costs of evaluating molecular properties, and the vast size of molecular search space, there is a need for data efficient algorithms which actively and strategically select candidate molecules for evaluation. While target properties are costly to compute or measure, in many cases auxiliary physical/chemical properties can be queried at a lower cost, and are known to be predictive of (and mechanistically related to) target properties. We introduce a Bayesian active learning algorithm which (i) maintains a graphical Gaussian Process based model of the dependencies between molecular structure, auxiliary physical/chemical properties, and target properties such as toxicity and biodegradability, and (ii) adaptively selects properties to evaluate depending on evaluation costs, model uncertainty, and expected task-relevant information gain. We discuss its ability to identify molecules with target property values in a cost-effective manner on a class of anionic photoacid generator (PAG) molecules, and study the dependence of learned molecule evaluation strategies on the relative query costs and mutual information between target and auxiliary properties.

9:05 PM MD01.12.04
An Ensemble Learning Approach for Efficient Crystalline Structure Classification in Atomistic Simulations Yanhao Deng[1], Yangyang Wang[1], Ke Xu[2] and Yanming Wang[1]; [1]Shanghai Jiaotong University, China; [2]Jilin University, China

In atomistic simulations, crystal structure identification could be crucial for many analyses. Traditional classification methods, typically relying on structure-specific formulas and empirical thresholds, may only be available for limited material types, occasionally with an unsatisfactory performance for complex systems. While emerging machine learning (ML) techniques have greatly helped improve the accuracy and applicability of atomic structure prediction, the large training data size requirement and expansive computational costs appear to be issues, especially when it is necessary to retrain the models considering new crystal structures. In order to tackle these problems, here we proposed a flexible ensemble learning framework, where several lightweight ML methods were assembled taking a series of carefully selected bond orientational order parameters as the input features. Our trained model can detect multiple common crystal structures including both pure substances and binary compounds, which exhibited an accuracy of 99.8% on our test dataset, outperforming several deep learning based methods. The model can also predict the relative probabilities of atoms in candidate structures, which may be useful for interpreting more complicated local environments such as the interfaces. In addition, given a completely unknown crystal structure, new knowledge can be more efficiently incorporated into our framework, with the help of generative sampled data from our current model. We believe that the versatility and extendibility of this framework make it a generally applicable tool for classifying crystal structures in atomistic simulations, promoting a deeper understanding in fundamental microscopic phenomena.

9:20 PM MD01.12.05
Predicting PV-PEC Promising Materials Based on Chemical Composition—Data-Driven Accelerated Machine Learning Study Chihun Kim, Seunghwan Jung and Young-Chae Chung; Hanyang University, Korea (the Republic of)

Artificial photosynthesis through solar cells (PV) and photoelectrochemical (PEC) devices utilizing solar energy will play a key role in the production of solar fuels for carbon neutrality. For the efficiency of time and cost in developing new materials for PV-PEC area, we modeled data driven supervised models. Learned classification and regression models can successfully predict electronic properties of materials only based on the chemical composition. Selected 373 features and 6353 experimental data are used for learning. For classification model, oversampling technique are adapted to overcome imbalance of data set. Through learned classification and regression model, materials can be classified by electronic properties only based on information of chemical composition. For regression model, prediction performance is revised by excluding outliers. Through regression model, band gap value can be predicted with low error 0.24 eV, in criteria of MAE. By investigating the features importance and the partial dependence plot, the relationship between target properties and features are unveiled. These models are expected to contribute developing new materials in PV-PEC research area and give guideline for surface engineering on purpose of band gap tuning.

9:35 PM MD01.12.06
Quantitative Evaluation of Fiber Mat in a Two-Dimensional Image with Deep Learning Hiroko Akiyama[1], Yoshihiro Takizawa[2] and Kyoichi Oshida[2]; [1]Ashikaga University, Japan; [2]National Institute of Technology(KOSEN), Nagano College, Japan

Fiber mats are utilized in a wide range of fields since they can be designed with functions such as flexibility, permeability, and adsorption. The functions and properties of fiber mats are related to mechanical properties, porosity, and the size/shape of the fibers and the interspaces among them. The evaluation and analysis of three-dimensional (3D) information is important for material development. While the interspaces can be observed with a microscope, the evaluation with this observation is qualitative. For quantitative evaluation, we analyze digital images taken with scanning electron microscopy.
In this research, we developed an algorithm that calculates the approximate volume of fibers in a two-dimensional scanning electron microscope (2D-SEM) image. Our goal is to generate 3D data from 2D image. Although 3D data can be obtained using 3D-SEM, 3D data construction requires a great amount of time, effort, techniques, and specific software as stereo imaging needs multiple 2D-SEM images taken from different angles. On the other hand, our method to calculate pseudo 3D data needs only a single 2D image. Hence, our method is useful to reduce the costs of evaluation for material development.
We calculated volume fraction of polyacrylonitrile nanofiber mats generated by electrospinning with image processing. First, the region of fibers in 2D-SEM image was extracted. The pixels of fibers were then manually selected, since the existing image processing software did not detect all fibers due to the conditions such as brightness and focus. Secondly, the volume and volume fraction of fibers were calculated by assuming that each fiber is cylindrical with a uniform diameter. For comparison, we experimentally measured the volume fraction of the sample mat as well. As a result, it was found that these values were comparable.
In addition, we have implemented deep learning algorithm in order to automatically extract fiber parts in the images. Selecting pixels of fibers manually is not practical to apply to various images since it takes numerous time and effort. We applied semantic segmentation algorithm, which is a deep learning method for clustering the pixels that represent the same object in an image. Since the pixels of fiber region are extracted with this algorithm, the volume is calculated with the number of the pixels. We used unsupervised learning algorithms among semantic segmentation. Thus it is not necessary to prepare a large amount of training data like supervised learning algorithms. Furthermore, pretrained models of semantic segmentation are available. We implemented several pretrained models specified to microscopic images. Volume fraction was calculated in the same procedure as the above, and we evaluated the results calculated by deep learning with experimental data.

9:40 PM MD01.12.07
Quantum Chemical Data Generation as Fill-In for Reliability Enhancement of Machine-Learning Reaction and Retrosynthesis Planning
Alessandra Toniato[1,2,3], Jan Unsleber[2,3], Alain Vaucher[1,3], Thomas Weymuth[2,3], Daniel Probst[1,3], Teodoro Laino[1,3] and Markus Reiher[2,3]; [1]IBM Research Zurich, Switzerland; [2]ETH Zürich, Switzerland; [3]National Center for Competence in Research-Catalysis, Switzerland

Data-driven synthesis planning has seen remarkable successes in recent years by virtue of modern approaches of artificial intelligence that efficiently exploit vast databases with experimental data on chemical reactions. However, this success story is intimately connected to the availability of existing experimental data. It may well occur in retrosynthetic and synthesis design tasks that predictions in individual steps of a reaction cascade are affected by large uncertainties. In such cases, it will, in general, not be easily possible to provide missing data from autonomously conducted experiments on demand. However, first-principles calculations can, in principle, provide missing data to enhance the confidence of an individual prediction or for model retraining. Here, we demonstrate the feasibility of such an ansatz and analyze resource requirements for conducting autonomous first-principles calculations on demand. We introduce our integrated AI-QC framework and discuss the challenges for the implementation and for the interface of the two technologies at play (IBM RXN platform for AI-based retrosynthesis and SCINE Chemoton for double-ended reaction network exploration). We present proof-of-concept results on two organic reactions (a Williamson ether synthesis and a more complex Friedel-Crafts reaction) and we discuss resource estimates and the scalability of our framework to a production environment.

Symposium Organizers
Soumendu Bagchi, Los Alamos National Laboratory
Huck Beng Chew, The University of Illinois at Urbana-Champaign
Haoran Wang, Utah State University
Jiaxin Zhang, Oak Ridge National Laboratory

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* Invited Paper
\+ Distinguished Invited

SESSION MD02.01: Mechanics of Materials I
Session Chairs: Soumendu Bagchi and Haoran Wang
Tuesday Morning, April 11, 2023
Marriott Marquis, Second Level, Foothill G1/G2

10:30 AM *MD02.01.01
Machine Learning Predictions for Microscale Strain Accumulation in Polycrystalline Metals Renato B. Vieira[1], William Noh[2], Huck Beng Chew[2] and John Lambros[2]; [1]Pontifícia Univer. Católica, Brazil; [2]Univ of Illinois at Urbana-Champaign, United States

Data-driven approaches based on machine learning (ML) have become increasingly popular for the study of the mechanical response of material behavior as both numerical and experimental novel methodologies have provided a wealth of big-data information for materials. On the experimental side, two dimensional (2D) and three dimensional (3D) full-field techniques such as digital image correlation (DIC) and digital volume correlation (DVC) provide datasets comparable in size and fidelity to numerical techniques such as finite elements (FEA) or molecular dynamics (MD). However, one criticism faced by data-driven approaches used to "fit" such big-data is that they often ignore or oversimplify the underlying physics and as such may not be suitable for predictively analyzing complex phenomena for which physics-based multiscale models are often developed. Failure event prediction in particular is especially challenging because failure is usually driven by local events though it is triggered by global loading, thus by its nature necessitating a multiscale approach. As a result, in this work we try to combine the ML "convenience" of bypassing explicitly modeling with the "physical accuracy" of a multiscale model by using ML within a physics-driven framework by combining experimental data as both training and constraints for the ML framework.

In particular, we wish to use microstructural strain accumulation in metals as a predictor of ultimate failure whether through plasticity, creep, fracture or fatigue loading. Depending on material, grain boundary vs. grain interior (i.e., "mantle vs. core", respectively) strain accumulation can serve as a driver for failure nucleation/initiation at the microscale. Experimental measurements based on high-resolution DIC (HiDIC) techniques which we have developed provide microscale strain fields with sub-grain level resolution that are then used to train artificial and/or convolution neural networks (ANNs and CNNs). Microstructural quantities such as grain misorientation, Schmid factor, and grain morphology, are used to identify strain hot-spot locations. Specifically, using a fitting neural network trained by experimental HiDIC we found that in an austenitic steel alloy the grain boundary inclination angle shows significant correlation with local stain accumulation in the mantle region. Considering the interior (core) strain build-up, we combined HiDIC measurements over large areas of a microstructure with crystal plasticity simulations to identify critical grains (or grain clusters–defined as neighboring grains similarly oriented) which would exhibit critical stain accumulation. Averaging the response, either within a grain or over several grains, allows for the development of an approach that can be more easily implemented at higher length scales to provide predictions of local failure using more global quantities (i.e., a reduced-order model of sorts) based on the knowledge gained through the multiscale ML efforts.

11:00 AM *MD02.01.02
Understanding Strain Hardening of Face-Centered Cubic Metals using Dislocation Dynamics Wei Cai[1], Sh. Akhondzadeh[1], Ryan Sills[2] and Nicolas Bertin[3]; [1]Stanford University, United States; [2]Rutgers, The State University of New Jersey, United States; [3]Lawrence Livermore National Laboratory, United States

Understanding plasticity and strength of crystalline materials in terms of the physics of microscopic defects has been a long-standing goal of materials research. Over the last two decades, much effort has been placed on the prediction of stress-strain curve of single crystals through large-scale dislocation dynamics (DD) simulations. If successful, DD can thus provide a quantitative link, which has been lacking to date, between dislocation physics at the atomistic scale and crystal plasticity at the continuum scale. Unfortunately, the progress in this direction has been limited by the very small strain that can be routinely reached (<1%) by existing DD simulations compared with the typical strain (up to 30%) in experiments. Because of this limitation, a direct comparison between DD predictions and experimental stress-strain curves has been impossible.

A series of advanced time integration algorithms have been developed to expand the strain range of DD simulations. In particular, the pairwise interaction forces between dislocation segments are separated into several groups, and each group is integrated with a different time step size. The resulting subcycling algorithm and implementation to GPU leads to an increase of computational efficiency by more than 1000 times. The new simulation capability enables the prediction of stress-strain curves for shear strains in excess of 1% routinely and repeatedly. As a result, a systematic investigation on the relation between the unit mechanisms and work hardening rate is now possible.

Here we report the latest findings from DD simulations of uniaxial deformation of single crystal Cu along more than 100 loading orientations. These DD simulations generate a large amount data on the dislocation microstructure evolution based on which physics-based constitutive relations can be constructed systematically. The dislocation networks are found to have a much more complex structure than previously expected, in the sense that most nodes (where three dislocation lines meet) are not recognizable from the conventional picture of binary junction formation. The dislocation link length on every slip system is found to obey a distribution describable by the sum of two exponentials. We also report the first direct comparison between DD simulations and Kolsky bar experiments for single crystal Cu under [001] and [011] orientations under identical loading conditions (strain rate ~ 10^4 s^{-1}).

Such a comparison is essential in establishing the fundamental premise of dislocation-based theory of crystal plasticity. We will present the insights gained from these comparisons.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-SC0010412 (W.C. and Sh.A.). Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. DE-AC52-07NA27344 (N.B.).

11:30 AM MD02.01.03
Dislocation Evolution in Iron during Nanoindentation Wurong Jian[1], Nicolas Bertin[2], Yifan Wang[1] and Wei Cai[1]; [1]Stanford University, United States; [2]Lawrence Livermore National Laboratory, United States

Nanoindentation has been applied widely to probe the local plastic behaviors of metals. However, the dislocation network under indenter and its evolution have not been fully understood. By comparing molecular dynamics (MD) and discrete dislocation dynamics (DDD) simulations in body-centered cubic (BCC) Fe single crystal in nano-scale volumes under nanoindentation, the DDD parameters can be calibrated and then used in micro-scale volumes. For most DDD simulations, cross slip and jog formation are ignored. Here, their effects on the evolution of dislocation network are studied, which explains why dislocation network evolves differently between the previous DDD and MD simulations.

11:45 AM MD02.01.04
Development of Data-Driven Interatomic Potential for Plasticity Analysis of Zinc Oxide Ceramics Shihao Zhang, Yan Li, Atsutomo Nakamura and Shigenobu Ogata; Osaka University, Japan

The dislocation toughening of ceramics has attracted considerable attention in recent years [1-3] since ceramics are inherently brittle and, thus, do not have a wide range of structural applications. However, understanding at the atomic scale is still lacking. We studied the dislocation-dominated deformation of wurtzite-type zinc oxide (ZnO) ceramic by nanoindentation simulation. ZnO ceramics has recently emerged as a leading semiconducting metal oxide ceramic. We developed data-driven interatomic potentials based on density functional theory (DFT) energy and force databases, yielding DFT accuracy and large-scale atomic simulation (millions of atoms). Large-scale indentation simulations were performed using the developed interatomic potentials to study indentation-induced dislocation nucleation and propagation in ZnO ceramics. An unprecedented phenomenon occurred in which identical rectangular dislocation loops were continuously nucleated from a single dislocation source under the indenter, induced by basal-to-prism dislocation cross-slip. The resulting dislocation loops pile-up, in good agreement with experiments. This study not only demonstrates the effectiveness of data-driven interatomic potentials in the analysis of plastic deformation of ceramic materials, but also provides new insights into the dislocation-dominated deformation behavior of ceramics. Authors acknowledge the JSPS Postdoctoral Fellowships for Research in Japan (Standard) and the Grant-in-Aid for JSPS Research Fellow Grant No. 22F22056.

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SESSION MD02.02: Mechanics of Materials II
Session Chairs: Soumendu Bagchi, Nithin Mathew and Haoran Wang
Tuesday Afternoon, April 11, 2023
Marriott Marquis, Second Level, Foothill G1/G2

1:30 PM *MD02.02.01
Using Data-Driven Methods to Learn the Properties of Extended Defects from Atomistic Simulations Nithin Mathew; Los Alamos National Laboratory, United States

Deformation and strength of polycrystalline metallic materials are dominated by motion and interaction of extended defects such as dislocations and grain boundaries. Molecular dynamics simulations have been used successfully for many decades to study the properties of these defects and unit mechanisms pertaining to physical processes involving these defects. In this talk, I will discuss the application of machine learning (ML) techniques on molecular dynamics simulation data to learn the properties of dislocations and grain boundaries in metals. I will demonstrate the utility of both supervised and unsupervised ML to extract physical insights into structure, mobility, and interaction between these defects. In some cases, we observe that the ML models are able to generalize well based on learning from a limited data set, provided that they are trained using a physically meaningful set of descriptors. Techniques to upscale the derived physical insights into mesoscale models for dislocation mechanics will also be discussed.

2:00 PM *MD02.02.02
Predicting Damage Initiation with Computer Vision Bruno Dobrovolski and Brandon Runnels; University of Colorado Colorado Springs, United States

Structural materials are designed to withstand mechanical loading, and are key to ensuring the safety of systems ranging from civil to military. Failure of structural materials can have catestrophic consequences, and so it is necessary to ensure that they perform reliably and predictably in all loading scenarios. In this work, we specifically focus on damage initiation in incipient spall experiments. Work by experimental collaborators at Los Alamos has produced extensive datasets showing void nucleation due to shock loading. Unsurprisingly, it has been observed that grain boundaries (GBs) seem to be preferential sites for void nucleation. Unexpectedly, however, there does not seem to be any definite trend observed in which GBs nucleate voids and which do not; that is, it appears that not all GBs fail equally. Initial analysis has shown that there appears to be no correlation between spall nucleation likelihood and typical GB properties such as energy or CSL ∑ value. Therefore, it is necessary to employ a more sophisticated method of analysis.
Convolutional neural networks (CNN) are a machine learning framework often used in computer vision applications such as image recognition. Multi-channel CNNs (MCCNN) are CNNs that incorporate non-visible channels as well as visible ones. In this work we apply MCCNNs to the problem of void identification in microstructure. Specifically, we train MCCNNs with reconstructed microstructure to resemble the pre-shock state, but categorized by whether the post-shock state contains a void. The channels for the MCCNN include visible channels (micrographs) as well as invisible channels such as

GB energy and CSL ∑. In some cases, these properties (such as the ∑ value) are readily available from EBSD analysis. In other cases, they must be computed using a surrogate model. Of particular interest is the GB energy. GB energy is computed automatically using the lattice-matching method, and then used retroactively to estimate the out-of-plane inclination of the boundary. Finally, the stress-state is etsimated automatically using quasi-static elastic simulations in Alamo. By incorporating all of these effects, the model is therefore able to conglomerate physical properties along with geometric properties in order to determine the subtle trends contributing to void nucleation. In this work, the processing and assembly of the training dataset are presented, along with training results from the MCCNN. This framework will eventually be used to rapidly screen, and perhaps even design, optimal damage-resistant microstructures for structural materials with enhanced safety.

2:30 PM MD02.02.03
Molecular Dynamics Study on the Mechanical Effects of V in FeCo Alloys Mario Hernandez, Joo T. Oh and Zhong Chen; Nanyang Technological University, Singapore

Interatomic potentials for the Fe-Co and Fe-V binary systems have been developed and merged to describe the Fe-Co-V ternary system based on the second nearest-neighbor modified embedded-atom method (2NN MEAM) formalism. Emphasis has been placed on the correct prediction of FeCo elastic properties and antiphase boundary (APB) energies to ensure proper description of the mechanical behaviors. The potentials are then used to analyze the crack nucleation and propagation mechanisms in polycrystalline FeCo and FeCo-2V alloys under different ordering degrees at grain boundaries (GB) and within the grains.
The results show that disordering inside grains has a larger impact on the ductility of the binary FeCo. The mobility of the antiphase domains (APD) inside the grains delays the ultimate tensile strength (UTS) and fracture point. The observed fracture procedure shows that triple junctions of GBs serve as the focal points of stresses concentration. The poor mobility at the triple GBs promotes crack nucleation and crack propagation, leading to an intergranular fracture in ordered and disordered binary alloys.
The effects of adding 2 at. % V to the FeCo alloy have also been investigated via molecular dynamics (MD) and hybrid grand canonical Monte Carlo-MD (GCMC-MD) simulations. It was shown that V prefers to migrate to (a) the GBs in an ordered state, and (b) GBs with some atoms to the APBs in a disordered state. The ordered FeCo-2V displays a decreased UTS and loss of ductility at room temperature. Introducing V exclusively to the APBs greatly increases the mobility of APD and migration of atoms to GBs boosting the ductility of the alloy.

2:45 PM MD02.02.04
Predictive Fracture Mechanics and Photochemical Reaction Kinetics Modeling of the Reliability of Photovoltaic Modules with Polymeric Encapsulants Undergoing Field Aging Alan Liu and Reinhold H. Dauskardt; Stanford University, United States

Solar photovoltaics (PV) is the fastest growing renewable energy sector, for which silicon-based solar modules comprise a market share of > 90% of the global photovoltaic market. However, reliability remains a pressing challenge. Reliability of solar modules over long lifetimes is crucial for their success as the U.S. and other countries aim to decarbonize power generation. PV modules are subject to environmental stressors (UV exposure, temperature, humidity) that cause degradation within the encapsulant and interfaces, limiting their lifetimes. This is especially problematic in modules with ethylene vinyl acetate (EVA) encapsulants, the dominant encapsulant used today. As the PV industry looks to extend module lifetimes beyond 30 years, more advanced predictive modeling with an emphasis on degradation pathways is critical for the development of next-generation resilient module materials. Previous work has experimentally characterized the adhesion energies of EVA-encapsulated modules over field aging time with well-established fracture testing metrology, and attempted to model the trends with analytical functions [1]. However, the development of an accurate multiscale reliability model that links the microscale chemical processes to macroscale adhesion properties remains elusive. Additionally, previous characterization efforts have shown that the EVA-cell adhesion is initially weaker at early aging times, but at long aging times the EVA-glass adhesion is weaker due to catalyzed hydrolysis reactions [2]. In this work, a novel time-dependent multiscale physics model is presented that connects interfacial bond densities to module adhesion energies, G_C, with detailed chemical kinetics and fracture mechanics calculations. The model addresses the rate and acceleration of degradation pathways at different materials interfaces, the plasticity generated at the interfaces during the delamination process, and changes in encapsulant mechanical properties over aging time. The model's initial conditions, such as the adhesion energy and encapsulant material properties at t=0, are informed by experimental data, while subsequent predictions are data-free and generated from a multi-scale physics model. Additionally, nanoindentation was done on EVA specimens at various stages of field aging to measure their mechanical properties variations over time.
The model predictions of module adhesion energies and mechanical properties, when compared with available experimental data, show a marked improvement from previously developed analytical models. Furthermore, the model can predict switches in fracture interfaces, such as the EVA-cell to EVA-glass fracture transition, while previous models could not. A sensitivity analysis study was conducted by varying the reaction rate constants for deacetylation, beta-scission, and crosslinking reactions to investigate their effects on predicted module adhesion energies. While the model was developed primarily for EVA-encapsulated modules, it is extendible to different encapsulation materials and interfaces by simple tuning of parameters such as the reaction rate constants and initial adhesion energy values. Finally, model extensions to polyolefin elastomer and silicone encapsulated modules are shown in this work to demonstrate its flexibility. This work provides a powerful framework for understanding how the rates of molecular degradation mechanisms can impact module adhesion properties and mechanical properties.

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[2] Thornton, P., Moffitt, S. L., Schelhas, L. T., & Dauskardt, R. H. (2022). Dependence of adhesion on degradation mechanisms of ethylene co-vinyl acetate encapsulants over the lifetime of photovoltaic modules. Solar Energy Materials and Solar Cells, 244 (Nov. 2021), 111818.

3:00 PM BREAK

3:30 PM *MD02.02.05
Towards High-Throughput, Small-Scale Fracture Investigations via Machine Learning Christos E. Athanasiou; Georgia Institute of Technology, United States

Investigating mechanical properties at small scales is a challenging endeavor. It requires sophisticated micro-/nano-scale experimental methods combined with laborious/time-intensive finite element computations. In this talk, a new framework for materials characterization at small scales using the latest developments in machine learning will be presented. This framework involves multi-fidelity deep learning and active learning methods limiting the need for finite element simulations. Its application for predicting the fracture toughness of microscale pentagonal cross-sectional ceramic cantilevers as well as micropillars will be showcased, demonstrating that it can significantly accelerate fracture toughness characterizations at small scales.

4:00 PM *MD02.02.06
Machine learning (ML)-Assisted Modeling of Composites Wenbin Yu[1] and Xin Liu[2]; [1]Purdue University, United States; [2]The University of Texas at Arlington, United States

Emerging artificial intelligence (AI) and machine learning (ML) techniques are changing the computational paradigm on the development of lightweight, high performance composite materials and structures. This presentation will introduce our recent works of ML-assisted modeling of composites. The presentation has two parts. The first part is the application of artificial neural network (ANN) models to reduce the computational costs of high-fidelity simulations. In this application, ANN models are trained to be efficient surrogate models for computationally intensive jobs such as multiscale modeling of textile composites, defect evaluation of non-crimp fabric (NCF) composites with fiber misalignment, and structural analysis of cylindrical shell buckling. Different physical constraints are imposed during the training to reduce the physically inconsistent predictions, minimize the required training data size, and customize the solutions with engineering practices. The second application is to learn unknown physics (e.g., constitutive model) with limited experimental data. A novel hybrid finite element-neural network computational framework is developed to enable training an ANN model with indirectly measurable data. This computational framework removes the requirements of training paired data and therefore many previously unlearnable physical laws can be learned within this computational framework. Moreover, the ANN models are fully constrained by known physics and therefore avoid physically inconsistent predictions. This computational framework has been applied to discover failure criteria of composites, nonlinear constitutive laws, and damage accumulation using limited measurable data.

4:30 PM MD02.02.07

Data-Driven Multiscale Modeling to Predict Full-Body Cutaneous Impact Injuries and to Design Protective Appliques Omar Elsafty, Christopher Berkey and Reinhold Dauskardt; Stanford University, United States

Assessing the behavior of skin damage from impacting debris is challenging due to the high input variability found in impacting projectile type and impact parameters, as well as in human skin anatomy and properties. Here we develop a multiscale approach to evaluate the damage mechanisms in human skin caused by high-speed fragmenting debris through the integration of physics-driven finite element modeling and data-driven machine learning algorithms. We use experimental studies to guide and validate our multiscale model and subsequently use our predictions to direct our topology optimization process for developing protective wearable appliques.

The first step of our multiscale approach involves developing a high-fidelity 3D finite element (FE) damage model of full-thickness human skin under highly dynamic impact conditions [1]. We use this model to quantitatively characterize the damage mechanisms that occur for single projectile impacts under different impact conditions, including a range of impact angles, impact energy, and projectile attributes, such as shape, size, and contact friction behavior with the skin. After validating the model using experimental data, it is then used to analyze the effect of epidermal and dermal layer thickness on injury severity. Two prominent damage mechanisms were derived from our model: epidermal tearing and dermal crushing.

Next, multiscale modeling was used to transition to a multi-projectile analysis, which is an integral part of analyzing multi-particle debris impact. As such, a machine learning (ML) pipeline composed of three multi-class classification algorithms was developed to assess injury severity, which is characterized by evaluating wound area, depth, and shape. After the training and optimization of the model using a 1000+ dataset composed of data generated from FE simulations and experimental results, accuracies of 71.8%, 79.4%, and 77.1% were obtained for the wound area, wound depth, and wound shape, respectively. The ML model was integrated with a multi-projectile full-body model that uses Newtonian physics-based equations to derive the projectile path for each fragment that could be in the vicinity of a human body placed a user-defined distance away from a blast source. This set up was used to investigate the frequency of injury severity and type for different body locations. It was found, for example, that 81.8% of severe injuries to the forearm were generated by epidermal tearing due to a high frequency of low-angled impacts.

The information derived from the multiscale analysis was then used to direct the topology optimization process for the design of protective appliques for the forearm. The optimization process was set up to resist in-plane deformation associated with epidermal tearing. Using periodic boundary conditions in the topology optimization simulations, a zero Poisson's ratio mechanical metamaterial structure with superior shock absorption properties was designed to reduce epidermal tearing-based injuries.

In this work, we demonstrate a multi-method approach to analyze cutaneous injuries caused by multi-projectile blast debris and use the results of the analysis to guide our topology optimization process for the design of a metamaterial protective applique structure for the forearm.

1. C. Berkey, O.Elsafty, and R.H. Dauskardt, "The Mechanics of Partial-Thickness Cutaneous Injury from Debris-Simulating Kinetic Projectiles" ***Communications Engineering****,* Oct 2022.

4:45 PM MD02.02.08

Interfacial Deformation Mechanism of {110} Hexagonal Dislocation Networks in BCC Iron Hadi Ghaffarian and Dongchan Jang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Deformation mechanism of BCC materials has still gained attention due to the unusual behavior of ½<111> screw dislocations at low-temperature regimes. One peculiar plasticity mechanism in BCC materials is the interfacial mobility of hexagonal dislocation networks (HDNs), which occurs under a very low-stress level. The HDN is usually formed as the evolution of the common {1-10} slip plane under martensitic transformation into the low angle twist grain boundary containing interfacial dislocation structure, known as lath boundary structure [1].

Although the mobility mechanism of HDN has already been investigated via atomistic simulations [2-3], they are confined to a few specific directions under strain-controlled shear deformation mode. Therefore, a rigorous and comprehensive understanding of HDNs is still required to recognize the gliding behavior of HDNs. Hence, this study aims to use the molecular dynamics (MD) simulation method to clarify the interfacial shear deformation behavior of HDN under stress-controlled deformation mode. The energy barrier analysis based on the nudged elastic band (NEB) method is used to address the contribution of geometrical and structural features to the in-plane shearing anisotropy of HDN.

For this goal, six bi-crystalline Fe samples containing HDN interface with $\theta=1-6°$ (misorientation angle) were constructed and subjected to in-plane stress-controlled simple shear deformation at 10 K. Our simulation results reveal the dependency of shear resistance on the direction of applied in-plane shear stress as well as the spatial configuration of the HDN structure. As the θ increases, the shear resistance along the [001] direction ($\tau_{c\text{-}0}$) decreases rapidly while the shear resistance along the [110] direction ($\tau_{c\text{-}90}$) increases gradually, implying that the different shearing mechanisms may exist under loading along the [001] and [110] directions. Our simulation results suggest that the mobility of [001] components serves as an important factor in controlling the HDN motion based on its core-structure energy. The core-structure energy per unit length of [001] dislocations ($E_{[001]}$) decreases as the θ increases with a significant jump from −5.917 eV/Å to −8.633 eV/Å between $\theta = 3°$ and 4°. Therefore, the plasticity mechanism of low-angle HDNs and their associated shear resistance anisotropy can be understood based on the core energy of [001] dislocation.

The interfacial mobility of HDN can be explained based on the kink's migration along the ½<111> dislocations with respect to the projection of applied shear stress along the ½<111> dislocation lines. Under shearing along the [001] direction (τ_0), the kinks move in opposite directions on ½[111] and ½[-1-11] dislocation lines. This migration behavior results in the accommodation of kinks on triple-junction nodes, which leads to extending of [001] segments to preserve the continuity of HDN. The new [001] segment possesses excess energy based on its length and core energy at the given θ. As θ decreases, the $E_{[001]}$ and $L_{[001]}$ (length of [001] segment) rise, developing higher required energy to distort the HDN. On the other hand, for the shearing along the [110] direction (τ_{90}), the kink's migration happens in the same direction on ½[111] and ½[-1-11] dislocation lines resulting in simultaneous extension and dissociation of [001] components at each triple junction pair, which preserves the length of [001] segments as well as the HDN shape. Therefore, the $\tau_{c\text{-}90}$ is lower than $\tau_{c\text{-}0}$ due to preserved HDN structure. The $\tau_{c\text{-}90}$ also shows less variation than $\tau_{c\text{-}0}$ as θ changes due to constant $L_{[001]}$ under shearing along the [110] direction.

References:
[1] L.L. Hsiung, Mater. Sci. Eng. A 528 (2010) 329–337.
[2] V. V. Bulatov, W. Cai, Phys. Rev. Lett. 89 (2002) 9–12.
[3] J.B. Yang, Y.N. Osetsky, R.E. Stoller, Y. Nagai, M. Hasegawa, Scr. Mater. 66 (2012) 761–764.

SESSION MD02.03: Scale Bridging I

Session Chairs: Soumendu Bagchi, Nithin Mathew, Danny Perez and Haoran Wang
Wednesday Morning, April 12, 2023
Marriott Marquis, Second Level, Foothill G1/G2

8:45 AM *MD02.03.01
Bridging Scales in Materials Science with Machine Learning and Data Science Shyue Ping Ong; University of California, San Diego, United States

Machine learning of the potential energy surface has emerged in recent years as an automatable, robust approach to bridging the quantum and atomistic scale in materials science. In this talk, I will focus on practical applications of machine learning interatomic potentials (ML-IAPs) in materials simulation and design. I will demonstrate that the ability to perform accurate simulations at much larger length and longer time scales can provide new insights into the ionic conduction in superionic conductors for all-solid-state batteries. I will also provide examples of how ML-IAPs have been applied in the study of short range chemical order, dislocation motion and mechanical behavior of refractory multiple principal element alloys.

9:15 AM *MD02.03.02
Automated Data-Driven Upscaling of Transport Properties in Materials Thomas Swinburne[1] and Danny Perez[2]; [1]Centre National de la Recherche Scientifique, France; [2]Los Alamos National Laboratory, United States

Transport properties of complex defects are crucial factors that control the performance of many material systems, e.g., the radiation tolerance of materials for nuclear fusion or fission applications. Characterizing the transport of complex defects is however notoriously tedious and time-consuming, especially as the defects grow, leading to a combinatorial explosion in the number of possible conformations and local transition pathways. We will present a large-scale data-driven approach to automatically obtain reduced-order models of defect evolution, transport coefficients, as well as effective continuum transport equations, from large number of short molecular dynamics (MD) simulations. The optimal MD simulations to carry out are identified on-the-fly using a Bayesian uncertainty quantification framework and automatically executed on a massively-parallel task-execution infrastructure. We show how this microscopic information can be systematically and efficiently upscaled into meso and macro-scale representations that can inform microstructure evolution models.

9:45 AM MD02.03.03
Universal Ion-Transport Descriptors and Classes of Inorganic Solid-State Electrolytes Claudio Cazorla and Cibrán López Álvarez; Universitat Politècnica de Catalunya, Spain

Solid-state electrolytes (SSE) with high ionic conductivities are pivotal for the development and large-scale adoption of green-energy conversion and storage technologies like fuel cells and electrochemical batteries. Yet, SSE are extremely complex materials for which general rational design principles remain indeterminate. Here, we unite materials modelling, computational power and modern data analysis techniques to advance towards the solution of such a fundamental and technologically pressing problem. Our data-driven survey reveals that the correlations between ionic diffusion and other materials descriptors in general are non-linear and largest when the latter are of vibrational nature and explicitly account for anharmonicity. Surprisingly, principal component and k-means clustering analysis show that elastic and vibrational descriptors, rather than the usual ones related to chemical composition and ionic mobility, are best suited for disentangling the high diversity of SSE. Our findings highlight the need of considering databases that incorporate temperature effects to improve our understanding of SSE, and point towards a generalized approach to the design of energy materials.

10:00 AM BREAK

10:30 AM *MD02.03.04
Machine Learning Potential to Study Phase Transition in 2D TMD material Wei Gao; Texas A&M University, United States

In Atomistic simulations, the interatomic potential that describes the interactions of atoms determines the fidelity of simulation results. The main disadvantage of the classical interatomic potentials is that they are limited by the fixed functional forms and small number of fitting parameters. As a result, they may not be able to provide reliable predictions. By contrast, machine learning potentials are not relying on a physical functional form, but must learn the physical shape of the energy surface from the training dataset. Therefore, if the training datasets (which usually come from first principle calculations) cover sufficient physics, a well-trained ML potential is able to provide accurate predictions that are comparable to first principle results.

In this talk, I will present a machine learning potential to study the phase transition in two-dimensional (2D) transition-metal dichalcogenides (TMDs) material, using $MoTe_2$ as a model system. 2D TMDs such as MoS_2, WS_2, $MoSe_2$, and WSe_2 present an unprecedented materials family. These materials promise to open up a new age of atomic-scale technology where devices can be scaled down to the truly atomic level and provide novel functionalities that cannot be obtained with conventional materials systems. One of the remarkable features of 2D TMDC is phase transition. Depending on the atom arrangements, 2D TMDC appears in two distinct stable phases: the 2H and 1T′ phases. These two phases exhibit completely different electronic structures, with the 2H phase being semiconducting and the 1T′ phase metallic. The dynamic control of transitions between these two phases can lead to revolutionary device applications.

11:00 AM MD02.03.05
Training Data Generation for Machine-Learning Interatomic Potentials Aparna P. A. Subramanyam and Danny Perez; Los Alamos National Laboratory, United States

Having flexible functional forms, machine-learning (ML) potentials make it feasible to aim for both accuracy and transferability, something that the earlier generations of potentials struggled to achieve. However, given their flexibility, these potentials often fail at extrapolating to properties beyond the training data, which makes the quality of the training set the determining factor in their performance. Training datasets typically consist of DFT energies and forces of relatively small systems, traditionally selected manually or randomly from subsets of the configuration space of interest. The need for human intervention in the curation of training sets makes their generation labor-intensive and time-consuming. Here, we present a generalization of a previously developed method based on the automated maximization of the information entropy of the descriptor distribution. The method is applied to train ML potentials for W and Be, primary candidates for divertor and first wall material applications in fusion reactors. The transferability of the potentials trained using the entropy-optimized training data is compared to that of traditional curation approaches, highlighting some desirable characteristics of optimal training data irrespective of the chemistry.

11:15 AM MD02.03.06
Application of Machine-Learned Potentials to Accurately Model Polymer Materials Mohammad Atif Faiz Afzal, Shaswat Mohanty, James Stevenson, Andrea Browning and Mathew Halls; Schrödinger Inc, United States

Polymers are widely and increasingly used in a variety of industries, for example, in aerospace, electronics, and automotive. This popularity is due to polymer materials being easy to process and able to make the devices lighter and flexible. Furthermore, we can obtain desirable mechanical and thermophysical properties for specific applications by changing and controlling polymer chemistry. However, the scope of chemical space exploration and testing in an experimental setup is limited. Modeling and simulation of polymer systems provide an accelerated means of characterization and design of new polymer materials. Designing new polymers requires a careful understanding of the interactions between polymers and also with other components in a formulated material. Polymer systems are typically modeled using molecular dynamics (MD) techniques, but using classical force fields in MD has several shortcomings, especially for properties dependent on the polymer chain dynamics. We built scalable and generalizable machine-learned (ML) potentials that accurately capture the dynamics of polymer chains. Using the ML potentials, we can precisely calculate the polymer properties, including dynamical, thermophysical, and mechanical properties. In this presentation, I will present several case studies demonstrating the key benefits of using ML potentials in modeling polymeric materials.

11:30 AM MD02.03.07
Scalable and Generalizable Neural Network Potential for Polymers: Application to Ethylene Glycol and its Oligomers Shaswat Mohanty[1], James Stevenson[2], Andrea Browning[2], Leif Jacobson[2], Karl Leswing[2], Mathew Halls[2] and Mohammad Atif Faiz Afzal[2]; [1]Stanford University, United States; [2]Schrodinger Inc., United States

Developing accurate force fields for studying polymer systems through molecular simulations is of growing interest and use across industries. Understanding and predicting their properties are vital in being able to develop tailored polymer molecules for desired applications. However, classical force fields fail to capture key properties such as the dynamics of a majority of polymer systems. As a potentially scalable solution, we present a charge recursive neural network (QRNN) model trained on DFT calculations made on smaller atomic clusters using the ωB97X-D3BJ/def2-TZVPD theory, that generalizes well to oligomers comprising larger atomic clusters or longer chains.

We demonstrate the validity of the polymer QRNN workflow by modeling the oligomers of ethylene glycol. We apply two levels of active learning and implement a novel model training approach that uses the initial partial charges from a semi-empirical method. Our developed QRNN model for polymers produces stable molecular dynamics (MD) simulation trajectory and captures the dynamics of polymer chains as indicated by the striking agreement with experimental values. The energy landscape predicted by the QRNN model is also demonstrated to be in closer agreement with the reference level theory than the classical MD force field. Our model allows working on significantly larger systems than allowed by DFT simulations, at the same time providing a more accurate force field than classical force fields which provides a promising avenue for large-scale molecular simulations of polymeric systems.

11:45 AM MD02.03.08
Dynamic Responses of Nanoparticle Heterogeneous Catalysts using Machine-Learned Force Fields Cameron J. Owen[1], Nicholas Marcella[2], Yu Xie[1], Anatoly I. Frenkel[3], Boris Kozinsky[1] and Ralph Nuzzo[2]; [1]Harvard University, United States; [2]University of Illinois at Urbana-Champaign, United States; [3]Stony Brook University, The State University of New York, United States

Quantitative understanding and control of interfacial reactions between the gas-phase and solid surfaces are crucial for improving numerous catalysis and energy conversion systems. Examples of these interfacial phenomena include H_2 exchange and CO adsorption on nanoparticles, both of which are important industrial processes and lead to markedly different particle behaviors.

While important for device performance in catalytic applications, these dynamic responses are not quantitatively understood from the atomistic level. Hence, this work demonstrates a collection of robust, Bayesian machine learned force fields (MLFFs) trained with an on-the-fly active learning framework implemented using Gaussian Process regression in the FLARE code to uncover these dynamic phenomena. Molecular dynamics (MD) simulations are used to sample atomic configurations and density functional theory is only called upon when the Bayesian uncertainty exceeds a threshold. The MLFFs retain first principles accuracy, are fast, and are uncertainty-aware. These MLFFs are then used to perform MD simulations for freestanding metal nanoparticle systems, as well as to study reaction mechanisms under gaseous exposure (e.g., H_2 and CO).

Particular emphasis is made on comparison of these simulations to experimental x-ray measurements (e.g., extended x-ray absorption fine structure (EXAFS)), from which the effect of gaseous exposure can be relatively compared across Pt-systems of various length-scales. The method is first benchmarked using bulk-Pt simulations and experimental EXAFS data, and applied to more complicated nanoparticle systems (e.g., Pt_{55}, Pt_{147}, and spanning to much larger particles (> 5nm)) afterwards, as well as extended surfaces. Ultimately, we uncover the atomistic mechanisms driving disparities in particle shape, and reactivity as a function of gaseous exposure, and correlate these dynamic observations to electronic effects inherent in the adsorption of these gasses on the particle surfaces.

SESSION MD02.04: Scale Bridging II
Session Chairs: Soumendu Bagchi, Andrew Rohskopf, Haoran Wang and Qian Yang
Wednesday Afternoon, April 12, 2023
Marriott Marquis, Second Level, Foothill G1/G2

1:30 PM MD02.04.02

Linear Versus Nonlinear Machine Learned Potentials for Transferability and Property Prediction Andrew Rohskopf, Aidan Thompson and Mitchell A. Wood; Sandia National Laboratories, United States

Machine learned potentials have proven useful in molecular modelling, but their construction and deconstruction remain a challenge for many researchers. We therefore created FitSNAP, an extension of the LAMMPS Python interface, to aid in the construction of potentials and then immediately deconstructing, or testing their viability in large-scale simulations, in LAMMPS. We generally approach the molecular machine learning problem by abstracting software components required for calculating descriptors, and then using these descriptors in machine learned models such as linear regression or neural networks. The modularity of these components allows convenient customization, and the various options allow users to find the best descriptor/model combinations for their systems of interest. Seamless integration to LAMMPS ensures a one-to-one agreement with the trained model and its end use in high-performance molecular dynamics simulations. The ability to easily and rapidly prototype different model and descriptor combinations allows for the study of how different models (e.g. linear regression or neural networks) influence accuracy and performance on any dataset.

This talk illustrates the usefulness of rapidly prototyping different machine learning models for interatomic potentials development. We overview linear regression models and the newer addition of rapid force training with general atom-centered neural networks. The latter feature makes use of automatic differentiation frameworks such as PyTorch and JAX to generally approach the atomistic machine learning problem in a performant manner. Finally, we overview the LAMMPS interface to show how we use the final models in LAMMPS simulations, to deconstruct our models and test their viability in their end use.

1:45 PM MD02.04.03
Anharmonic Thermo-Elasticity of Tungsten from Accelerated Bayesian Adaptive Biasing Force Calculations with Data-Driven Force Fields Manuel Athenes, Anruo Zhong, Clovis Lapointe, Mihai-Cosmin Marinica, Alexandra Goryaeva and Jacopo Baima; CEA, France

The elastic properties of tungsten, a ubiquitous material in future energy systems, are investigated up to its melting temperature by means of a data-driven approach. The proposed workflow combines machine learning of the force field and enhanced sampling of the crystalline structure. While the machine learning force field achieves the accuracy of {\it ab initio} calculations, its implementation in sampling methods is often limited due to its high computational cost, which is commonly a few orders of magnitude larger than that of traditional potentials. To overcome this limitation, we propose a fast and robust Bayesian sampling scheme aiming at estimating the fully anharmonic free energy of crystalline solids with the help of an improved adaptive biasing force method. This method performs a thermodynamic integration from a harmonic reference system, wherein zero frequencies associated with the periodic boundaries are screened off. The proposed sampling method drastically improves the speed of convergence and overall accuracy. We demonstrate the efficiency of the improved method by calculating the second order derivatives of the free energy, such as the elastic constants, which are performed almost 100 times faster than with the standard methods. The proposed method enables the prediction of the elastic properties of tungsten in the range of temperatures that cannot be investigated experimentally, from 2\,100 K to the melting temperature. Accuracy and numerical efficiency of the proposed strategy open up many avenues for the reliable predictions of finite-temperature properties of materials, like the relative stability of structural defects, elastic constants, etc.

2:00 PM MD02.04.04
Enabling Long Timescale Molecular Dynamics Simulation with *Ab Initio* Precision Jan Janssen and Danny Perez; Los Alamos National Laboratory, United States

Classical molecular dynamics (MD) is in principle an ideal tool to investigate the long-time evolution of materials, as ab initio-based MD simulations remain limited to very short time. While modern machine learning MD potentials report errors on the order 1 meV/atom, these errors are only typical of configurations that are similar to those found in the training set used to fit the potential, and transferability to genuinely new configurations remains limited. This poses a challenge to the accuracy of long-time MD simulations for two reasons: i) transition rates are exponentially sensitive to energy barriers, and ii) saddle configurations form a very small subset of the whole configuration space and so are very unlikely to appear in traditional hand-crafted datasets, or even as part of conventional active-learning approaches based on MD.

We propose a large-scale automated workflow to develop and validate transferable machine learning potentials for long-time simulations. Starting from an information-entropy optimized training set with over 7 million atomic environments, fitted potentials are benchmarked on a very large set of transition states to characterize their transferability. We also assess different practical strategies for enriching the training set so as to improve the accuracy for long-timescale simulations. The workflow is developed using the pyiron integrated development environment for computational materials science and executed with the Exaalt infrastructure.

2:15 PM MD02.04.05
A Multi-scale Percolation Model of Initial Passivation of FCC Binary Alloys John D. Cavin[1], Alex Tai[1], Ian McCue[1], Karl Sieradzki[2] and James M. Rondinelli[1]; [1]Northwestern University, United States; [2]Arizona State University, United States

Corrosion costs $2.5 trillion globally, which is equivalent to roughly 3.4% of the world's gross domestic product. The susceptibility of an alloy to corrosion depends on its ability to form a thin, protective layer, often an oxide, that prevents electrochemical degradation of the metal in its environment. In aqueous environments, for example, corrosion is primarily mediated by the electrochemical dissolution of metal ions at the anodic regions of local-action galvanic cells. Designing alloys that better protect against corrosion requires a deeper understanding of the interplay of oxidation and dissolution that occurs in the initial stages of passive oxide formation. Beyond the establishment of an initial oxide layer, these processes are also critical for the "self-healing" nature of corrosion resistant alloys that allow them to reform protective oxides if local abrasion exposes the underlying alloy. Recent work has shown that percolation theory can be used to gain a deeper understanding of the compositional dependence of corrosion resistance in BCC and FCC, Fe-Cr and Ni-Cr alloys [1]. Utilizing percolation theory to build predictive models, requires determining the connectivity of chromium oxide networks after selective dissolution of iron. In this work, we study the Cu-Rh system as a use case for FCC binary alloys, where Cu selectively dissolves. Using first-principles calculations of Cu-Rh supercells, we trained cluster expansion models that can be used to quickly determine the energies of large-scale alloy models. We then use to Monte Carlo methods with these cluster expansions to obtain thermodynamic ensembles to analyze short-range order in the Cu-Rh system and to study the connectivity of Rh oxide networks in the context of percolation theory. Additionally, preliminary results on training machine learning interatomic potentials to predict transition barriers to perform adaptive kinetic Monte Carlo simulations of the dissolution and oxidation process are discussed. We conclude by comparing our results in FCC binary alloys to available experiments.

[1] Y. Xie et al. A percolation theory for designing corrosion-resistant alloys. Nature Materials **20**, 789–793 (2021).

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3:00 PM *MD02.04.06
Regression-Based Projection for Learning Mori–Zwanzig Operators Yen Ting Lin, Yifeng Tian, Danny Perez and Daniel Livescu; Los Alamos National Laboratory, United States

More than half a century ago, Mori and Zwanzig (MZ) developed a mathematically rigorous formalism for constructing reduced-order models for dynamical systems using functional projection operators. Formally, a pre-specified projection operator is used to map any function which depends on both resolved and unresolved variables to a function that only depends on the resolved variables. As the latter does not depend on unresolved information, one can then prescribe a set of evolutionary equations for the resolved variables. Theoretically speaking, there are infinitely many choices of the projection operators. Several recent studies have established that with Mori's linear projection operator, it is possible to adopt a data-driven approach to learn the MZ operators using the time series of the resolved dynamics. We also showed in a recent study (Lin et al., SIAM Applied Dynamical Systems, 2021) that these methods provide higher-order and memory-dependent corrections to existing data-driven learning of the approximate Koopman operators.

In this talk, I will present our latest proposition of using regression analysis to define the projection operators, and a data-driven method for learning the associated MZ operators using time-series data. Interestingly, the resulting algorithm is very similar to statistical boosting, but with an intuitive structure prescribed by the MZ theory. We identified that the proposed learning is identical to our published method for Mori's linear projector, when the projector is defined by a linear regression. The newly proposed method can be considered as a generalization of the previously proposed one because it is not restricted to linear regressions. As we gradationally increased the complexity of the regression models (linear, polynomial, spline, to neural networks), we observed a consistent improvement of the learned reduced-order models on a few test examples. We still observed considerable improvements by including the MZ memory effect in these nonlinear projections, justifying the necessity of accounting for the past histories of under-resolved systems. We believe that the proposed method for learning MZ operators is promising because it is applicable to most data-driven methods (e.g., approximate Koopman and SINDy) for learning dynamical systems.

3:00 PM BREAK

3:30 PM MD02.04.07
Progress in Equivariant Deep Learning Interatomic Potentials—Allegro and NequIP Albert Musaelian[1], Simon Batzner[1], Anders Johansson[1], Lixin Sun[1], Nicola Molinari[1], Cameron J. Owen[1], Mordechai Kornbluth[2] and Boris Kozinsky[1,2]; [1]Harvard University, United States; [2]Robert Bosch LLC Research and Technology Center, United States

The utility of atomic-scale simulation of materials systems can be greatly expanded by machine learning interatomic potentials (MLIPs), which use small numbers of computationally expensive quantum chemistry calculations to enable simulating larger length- and time-scales than those quantum methods can achieve alone. A central challenge in such efforts is building model architectures that respect the symmetries of the underlying physics, namely permutation of atoms, rotation, translation, and inversion.

This talk discusses recent progress, both in methods and applications, with Allegro and NequIP, our "E(3)-equivariant" machine learning architectures for MLIPs. Most existing MLIPs respect the invariance of the true potential energy to symmetry transforms like rotations by operating only on already invariant scalar input encodings such as distances, angles, or even systematic basis expansions. Our models, in contrast, operate directly on 3D geometry: their inputs, internal latent representations, and predictions can contain not only scalars, which are invariant under symmetry transformations of the input, but also "equivariant" geometric vectors and higher-order tensors, which transform correspondingly when the input is transformed. This approach yields remarkable real-world improvements in accuracy, geometric and chemical extrapolation, simulation stability, and data efficiency as demonstrated in organic molecules, ionic liquids, catalysts, biomolecules, and other systems. Finally, the Allegro model further enables scaling these desirable traits to simulations at large very length-scales and high speeds.

3:45 PM MD02.04.08
Proper Orthogonal Descriptors for Complex Chemical Systems Ngoc-Cuong Nguyen[1], Andrew Rohskopf[2], Dionysios Sema[1] and Yeongsu Cho[1]; [1]Massachusetts Institute of Technology, United States; [2]Sandia National Laboratories, United States

We present the proper orthogonal descriptors for efficient and accurate interatomic potentials of multi-element chemical systems. The potential energy surface of a multi-element system is represented as a many-body expansion of parametrized potentials which are functions of atom positions, atom types, and parameters. Proper orthogonal decomposition is employed to decompose the parametrized potentials into a set of orthogonal basis functions. The orthogonal basis functions are used to construct proper orthogonal descriptors based on the elements of atoms, thus leading to multi-element descriptors. For a system of M elements, the number of multi-element proper orthogonal descriptors increases as M^3, while the computational cost is independent of M. We compose the multi-element proper orthogonal descriptors to develop two different interatomic potentials. The first potential expresses the energy of each atom as a linear combination of proper orthogonal descriptors, while the second potential expresses the energy as a linear and quadratic combination of the descriptors. The second potential is shown to provide a significant increase in accuracy relative to the first potential, while having the same computational complexity as the first potential. The POD potentials are demonstrated on a wide variety of materials including InP, GaN, TiO2, HfB2, and HfO2, and compared with the spectral neighbor analysis potential (SNAP), atomic cluster expansion (ACE), Allegro potentials, as well as DFT calculations and experiments.

4:00 PM MD02.04.09
Uncertainty Aware Active Learning of Coarse Grained Free Energy Models Blake Duschatko, Jonathan Vandermause, Nicola Molinari and Boris Kozinsky; Harvard University, United States

Coarse graining techniques play an essential role in accelerating molecular simulations of systems with large length and time scales. Theoretically grounded bottom-up models are appealing due to their thermodynamic consistency with the underlying all-atom models. In this direction, machine learning approaches hold great promise to fitting complex many-body data. However, training models may require collection of large amounts of expensive data. Moreover, quantifying trained model accuracy is challenging, especially in cases of non-trivial free energy configurations, where training data may be sparse. We demonstrate a path towards uncertainty-aware models of coarse grained free energy surfaces. Specifically, we show that principled Bayesian model uncertainty allows for efficient data collection through an on-the-fly active learning framework and open the possibility of adaptive transfer of models across different chemical systems. Uncertainties also characterize models' accuracy of free energy predictions, even when training is performed only on forces. This work helps pave the way towards efficient autonomous training of reliable and uncertainty aware many-body machine learned coarse grain models.

4:15 PM MD02.04.10
A First Principles Approach to Spectral Phonon Transport in Heterostructures Jackson R. Harter[1], Cameron Chevalier[2] and Alex Greaney[2]; [1]Idaho National Laboratory, United States; [2]University of California -- Riverside, United States

Understanding thermal transport across interfaces which give rise to a thermal resistance (also known as Kapitza resistance) is a critical issue affecting the development of nanotechnologies. Much modern and emergent nanotechnology consist of adjacent materials, and phonon mediated heat transfer governs thermal behavior across internal interfaces in these devices. The physics of thermal transport in solids are governed both by phenomena occurring at the atomic scale and interactions with the material's microstructure. The forecasting of fundamental quantities such as temperature, heat flux and thermal conductivity typically employs the semi-classical Boltzmann transport equation to predict the macroscopic behavior of materials in terms of the microscopic dynamics of its heat carriers.

Kapitza resistance was first discovered in liquid helium experiments and has led to a fundamental research thrust in micro and nano-scale heat transport, the behavior of thermal carriers across internal interfaces. Thermal interfacial resistance (TIR) is a widely studied phenomenon, first engaged by Swartz and Pohl through their development of the acoustic and diffuse mismatch methods, then continued through myriad efforts with varying methods and approaches in an attempt to resolve carrier behavior at thermal interfaces.

Many of the fundamental approaches to TIR have been at the nanoscale, and research is conducted with molecular dynamics (MD) and density functional theory (DFT) methods. The limitations of these methods is system size; atomistic methods tend to be limited to system sizes of 100,000 atoms or less. Larger length-scale methods have also been pursued, based on the principles of acoustic or diffuse mismatch, but not all include simulation of TIR using a full phonon band spectrum, or temperature dependent methods.

Our approach to enabling phonon transport in layered materials draws upon our previous work of demonstrating spectrally coupled phonon transport in homogeneous and heterogeneous materials. We use a semi-analytical approach in which the Bose-Einstein (B-E) statistics set the strength of the phonon radiance in a frequency group, but the B-E statistics are informed with information from the transport system. The B-E statistics in a single frequency group feels the influence of all the groups through the spatial temperature. We also include a new field term which is an indicator of the amount of non-equilibrium behavior of the phonon spectrum---this is added to the phonon source term in all groups to ensure closure and conservation of energy, as the phonon groups in the transport system and the analytical systems are coupled.

This work builds upon our previous approach by adding a phonon coupling term at an internal interface, using the principles of the DMM through transmission and reflection coefficients. In this work, the coefficients are determined through computing a common temperature at the interface, influenced by the phonon band structure of both materials, in effect, providing mixing between the two material systems and using the common temperature to set the strength of the phonon radiance at the boundaries on either side of the interface. Our approach uses material properties computed along various crystallographic orientations, and while some isotropy is built into the interface condition, the material properties weight the phonon distributions in the proper crystalline direction. Geater resolution of phonon behavior in proximity to an interface, and more accurate predictions of TIR are obtained. While it is true the assumption of diffuse mismatch can yield inconsistent results compared to experiment especially at low temperatures, this work focuses on room temperature and beyond effects, for future applications in nuclear fuel, or thermoelectric devices; a modified mismatch approach may be feasible if applied properly. Additionally, our methods focus on bridging mesoscale to engineering scale.

SESSION MD02.05: Materials Design I
Session Chairs: Soumendu Bagchi, Victor Fung, Jan Janssen and Haoran Wang
Thursday Morning, April 13, 2023
Marriott Marquis, Second Level, Foothill G1/G2

8:30 AM *MD02.05.01
Graph Neural Networks for Materials Chemistry Victor Fung; Georgia Institute of Technology, United States

Graph neural networks (GNNs) are a rapidly expanding class of machine learning models with exceptional potential for materials chemistry problems across a wide range of spatial and time scales. A key strength in GNNs lies in their high expressivity and capacity for learning from large datasets over traditional feature engineering approaches in the materials sciences. Here, we develop a GNN-based software platform, MatDeepLearn, which offers broad customizability in data processing, model construction, hyperparameter selection and post-processing for materials informatics applications. In particular, we show the importance of the large hyperparameter space offered by the MatDeepLearn framework towards obtaining high performance in materials property predictions. We also demonstrate the viability of GNNs for the prediction of atomistic to macroscopic quantities, and across a large range of applications, including in catalysis, gas capture, and for molecular dynamics.

9:00 AM MD02.05.02
Artificial Intelligence Assisted Gas Diffusion Electrode Development for Carbon Dioxide Reduction Sang-Won Lee[1,2], Bjørt Joensen[1,3], Joel Jenny[1,4], Dong Un Lee[1] and Thomas Jaramillo[1,2]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States; [3]Technical University of Denmark, Denmark; [4]Swiss Federal Institute of Technology Zurich, Switzerland

Intergovernmental panel on climate change (IPCC) presented the 6th IPCC report that the temperature of Earth is likely to exceed the 1.5 °C rise. The IPCC forecasts 2025 will be the tipping point at which greenhouse gas emissions must turn to a decreasing trend, otherwise preventing global warming after 2030 below the 2 °C limit will be difficult. We are coming to the point where we must not only switch to renewable energy, but also remove already emitted greenhouse gases.[1]
Electrochemical carbon dioxide (CO_2) reduction has been investigated since 1980s-1990s as a promising greenhouse gas elimination method. The activity of CO_2 reduction in aqueous electrolytes is far lower than economically viable minimum. The low solubility (< 30 mM) and diffusivity of CO_2 in aqueous electrolyte limits reduction current approximately to 30 mA in ambient condition. The fact that the majority of feedstocks in the real world of greenhouse gases are in the gaseous state has also fueled technological innovation. [2]
The gas diffusion electrode (GDE) emerged to address this problem and enable current densities a few orders of magnitude higher than planar electrode.

The development of GDEs has been investigated by applying materials with various properties, such as porosity, hydrophobicity, mechanical strength, and conductivity. However, the complex GDE structures and various roles of each layer in GDEs cause difficulties in theory-based development of the optimal GDE.
In order to overcome the aforementioned complexities of developing the optimal GDE, this study focuses on utilizing a structure data-based machine learning to optimize the structures in the GDEs. Imaging of GDEs can be performed using characterization techniques such as scanning electron microscopy and commutated tomography to obtain the structural information.[3] Relationship between CO_2 reduction performance and structural characteristics of GDEs are used as training data for 3D convolutional neural network. AI unsupervised learning, such as Affinity Propagation and MiniBatch k-Means cluttering, are utilized to reveal unknown GDE design parameters.
We provided method for dealing with complexities involved in the GDE development through 3D structure information measurements, segmentation, learning and clustering. The method presented in this study can be applied not only to the development of GDEs for electrochemical CO2 reduction but also to many other applications in the energy fields.

[1] IPCC, 2022: Summary for Policy Makers. In: Climate Change: Mitigation of Climate Change of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change (2022, April)
[2] Nitopi, Stephanie, et al. "Progress and perspectives of electrochemical CO2 reduction on copper in aqueous electrolyte." Chemical reviews 119.12 (2019): 7610-7672.
[3] Primakov, Sergey P., et al. "Automated detection and segmentation of non-small cell lung cancer computed tomography images." Nature communications 13.1 (2022): 1-12.

9:15 AM MD02.05.03
Data Science-Driven Bulk Electronic Structures Descriptors in Cubic Perovskite Oxides for Oxygen Evolution Reaction Activity Oguzcan Dedeci, Cigdem Toparli and Irmak Sargin; Middle East Technical University, Turkey

The discovery of new materials has been accelerated using machine learning in electrocatalysts in which the main performance criterion is the work function of oxides. It is possible to predict the work function and reveal quantitative information regarding its dependence on the structure by machine learning models. However, the experiments and calculations required to obtain the work function are costly and challenging. As a result, many descriptors based on geometry and bulk electronic structure have been offered for predicting the work function of new compositional candidates, especially for the perovskite oxide family. Among many alternatives to replace noble metals in electrocatalytic applications, perovskite oxides have been extensively studied, and promising candidates have been suggested from this class of materials for better performance. However, due to their complex electronic and crystal structure, a generally applicable descriptor to cover all possible compositional candidates is still lacking. The compositional dependence of the relationship between the most frequently used bulk electronic structure descriptor, O2p band center, and work function limits its use, verifying the need for a new descriptor. Consequently, the lack of such a descriptor is the barrier to the accelerated discovery of new simple and complex compositions by machine learning. In this study, we have investigated the potential of new bulk electronic structure descriptors for characterizing the work function of the BO_2-terminated surfaces in cubic perovskite oxides using a dataset from the scientific literature, including 583 different simple perovskite compositions with 26 different A-site and 23 different B-site elements. We have first identified the bonding-related reasons that cause the composition dependence of the relationship between the O2p band center and work function by univariant exploratory data analysis. The bonding-related features that cause the compositional dependency are electronegativity, ionicity, covalency, ionization energy, valence orbital energy, orbital radii, band-filling, bond hybridization, and charge distribution. We have generated several new descriptors by combining these features with the O2p band center in varying mathematical forms. A new descriptor that is a function of O2p band center, valence orbital energy, d-orbital radii, bond hybridization, and charge distribution has been found to have a Pearson correlation coefficient of 0.82 with the work function that is 30% higher than the previously suggested and widely used bulk electronic structure descriptor O2p band center. The strategy suggested here is exemplified for the cubic perovskite oxides with a definite surface termination; however, it is general enough for application to other crystals and surface terminations as well as other materials and application areas showing the strength of combining data science with domain knowledge.

9:30 AM MD02.05.04
Deep Learning of Multi-Component Cathode Electrochemistry from Experiments Peichen Zhong[1,2], Bowen Deng[1,2] and Gerbrand Ceder[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Disordered rocksalt materials are the most promising earth-abundant cathode materials for Li-ion batteries, and as such can enable scaling of Li-ion energy storage to many TWh/year production. However, the computational modeling for DRX is difficult as such modern battery materials can contain a large number of elements with substantial site disorder.

Instead of approaching from *ab-initio* modeling, we will demonstrate a novel approach to the modeling and prediction of electrochemistry (discharge voltage profile) of DRX materials. We applied a deep neural network (DNN) trained directly on a large amount of experimental results. The DNN is trained with an end-to-end learning scheme, that includes the redox information appropriately regularized. The DNN can interpolate and make predictions for compounds that have not yet been tested, which can accelerate the exploration of DRX and other electrode materials.

9:45 AM MD02.05.05
Ternary Oxides of Pre- and Post-Transition Metals for Photocatalytic Solar-to-Hydrogen Conversion Simon Gelin[1], Nicole Kirchner-Hall[1], Rowan Katzbaer[1], Monica Theibault[2], Yihuang Xiong[1], Matteo Cococcioni[3], Iurii Timrov[4], Quinn Campbell[5], Hector Abruna[2], Raymond Schaak[1] and Ismaila Dabo[1]; [1]The Pennsylvania State University, United States; [2]Cornell University, United States; [3]University of Pavia, Italy; [4]Ecole Polytechnique Federale de Lausanne, Switzerland; [5]Sandia National Laboratories, United States

Green hydrogen produced via photocatalysis is a promising sustainable energy source. However, many of the known water-splitting photoactive semiconductors are costly or of low efficiency due to their high electronegativity which impedes the transfer of electrons from the catalyst to chemisorbed/hydrated protons. To address this issue and expand the list of known water-splitting photocatalysts, we build on previous studies [1,2] which showed via data-intensive screening that inserting pre-transition (s-block) metals in binary metal oxides can lower electronegativity while maintaining appealing light absorption properties. Starting from a family of post-transition (p-block) metal oxides used in optoelectronics, we analyze how adding pre-transition metals in these materials impacts the electronic couplings between their constituents and may improve their photocatalytic properties. Then, we screen 109 of these ternary metal oxides using band gaps and band edges predicted at both the semilocal DFT and DFT+U levels of theory. Pourbaix diagrams are also used to assess the stability of the materials in water. Based on the screening protocol, we identify seven ternary oxides among which two appear to not have been previously proposed as water-splitting photocatalysts.

[1] Xiong et al., *Energy Environ. Sci.* (2021) 14, 2335-2348
[2] Katz et al., *Adv. Energy Mater.* (2022) 2201869

10:00 AM BREAK

10:30 AM MD02.05.06
Design of High-Entropy Hydrides for Reversible Hydrogen Storage Vitalie Stavila, Matthew Witman, Sapan Agarwal and Mark Allendorf; Sandia National Laboratories, United States

Hydrogen is a promising energy carrier that can be produced with zero-carbon emissions and is expected to play a key role in future energy systems. However, storage and transportation of hydrogen in a safe and cost-effective way is challenging. One promising method is to store hydrogen in a solid metal hydride; compared to high-pressure hydrogen storage, the metal hydride technology offers potential safety advantages (due to low pressure operation), with the additional benefit of higher volumetric density. We developed a machine learning approach to design high entropy alloys (HEAs) with a high hydrogen-to-metal ratio and tunable equilibrium plateau pressures. We used a gradient boosting tree approach combined with SHapely Additive Predictions (SHAP) to elucidate simple physics-based design rules that dictate the thermodynamic properties of metal hydrides, then employed these models to screen HEA hydrides across a large compositional space (>21,000 distinct candidate compositions). We demonstrated how feature importance uncovers the strong dependence of the metal hydride equilibrium H_2 pressure on a volume-based descriptor that can be computed from just the elemental composition of the alloy material. This in turn permitted rational targeting of high-hydrogen capacity HEAs by their descriptor values. We used high-energy ball milling and arc melting approaches to synthesize dozens of HEA materials which cover a wide range of pressure and temperature regimes for reversible hydrogen uptake and release. The HEA materials were characterized by X-ray diffraction, scanning and transmission electron microscopy, and X-ray photoelectron spectroscopy. Hydrogen storage properties were measured using the Sieverts techniques, and Pressure-Composition-Temperature measurements were used to determine the enthalpy and entropy of hydrogen uptake and release in the case of most promising HEAs. We show that frustrated chemical environments found in HEA materials composed of 4-, 5-, or 6- different atom types lead to important changes in the thermodynamics and kinetics of chemical processes, which can be leveraged for sustainable hydrogen storage applications..

10:45 AM MD02.05.07
Data-Driven Learning and Interpretable Model Reduction of Chemical Reaction Networks Qian Yang[1], Carlos A. Sing-Long[2], Enze Chen[3] and Evan Reed[4]; [1]University of Connecticut, United States; [2]Pontificia Universidad Católica de Chile, Chile; [3]University of California, Berkeley, United States; [4]Stanford University, United States

Complex reactive chemistry such as that occurring in catalytic systems and energetic materials are complicated nonlinear dynamical systems that are difficult to model and interpret. While *ab initio* molecular dynamics (MD) is a key computational method that can be used to interrogate reactive chemistry, many challenges remain due to its computational limitations in time and length scales. In this talk, we will first discuss how it is possible to use the wealth of data generated by a few expensive MD simulations to statistically learn fast kinetic Monte Carlo (KMC) models of chemical reaction networks. Our KMC models can not only extrapolate the behavior of the chemical system by as much as an order of magnitude in time, but can also be used to predict the dynamics of entirely different chemical trajectories. With this framework, one can imagine a future where MD data will be routinely archived to form a "chemical genome" that can be used to quickly simulate new chemical systems. Second, we will consider the question of how to build reduced models of these chemical reaction networks, both to build understanding and to accelerate simulations. We have developed a data-driven method utilizing L_1-regularization for model reduction of nonlinear dynamical systems, which can handle large-scale systems with as many as thousands of reactions in a matter of minutes. Our method uses minimal parameterization and produces a family of reduced models that exhibit a trade-off between model complexity and estimation error. Finally, we will conclude with a discussion of how machine learning can be used to adaptively reduce the reaction network under different initial conditions and enable long-time scale extrapolation of reduced-order models. Our methods can be easily interfaced with existing simulation software to enable automatic, interpretable reduced-order modeling of complex reactive chemistry.

11:00 AM MD02.05.08
Informing Experiments Through Machine-learned Representations of Text-mined Synthesis Conditions to Rationalize Impurity Phase Formation in Sol-gel-directed $BiFeO_3$ Thin Film Synthesis Kevin J. Cruse[1,2], Viktoriia Baibakova[1,2], Maged Abdelsamie[2], Kootak Hong[2,3], Christopher Bartel[2,4], Amalie Trewartha[2,5], Anubhav Jain[2], Carolin M. Sutter-Fella[2] and Gerbrand Ceder[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Chonnam National University, Korea (the Republic of); [4]University of Minnesota, United States; [5]Toyota Research Institute, United States

Understanding the reaction pathways in complex oxide synthesis is an ongoing goal in materials science. Clues to understanding these pathways can be gathered by monitoring the persistence of intermediate phases as impurity phases in the final sample. With the goal of better understanding the formation of impurity phases in $BiFeO_3$ thin film synthesis through the sol-gel technique, we have constructed a high-quality dataset of 340 synthesis procedures and outcomes extracted manually from 178 scientific articles. From this dataset, we built a decision tree model that reinforces important experimental heuristics for the avoidance of phase impurities, but ultimately shows limited predictive capability. Under the assumption that this limited performance is due to hidden variables and the need for more data, we used the text-mined dataset to inform several experiments aimed at reproducing results from the literature as well as proposing new syntheses to explore under-represented regions of the synthesis condition space. In our investigation, we identify important features in controlling phase purity that are corroborated by known heuristics in the field, such as annealing temperature and Bi:Fe metal ratio, as well as other less frequently studied indicators, such as solution stirring temperature and precursor solution concentration. We also highlight the limitations of building predictive models for complex synthesis tasks based on text-mined data alone, which may often be due to the incompleteness of synthesis descriptions in the literature. Nevertheless, we show how such a dataset can be made useful by informing new controlled experiments and forming a better understanding for impurity phase formation in this complex oxide system.

11:15 AM MD02.07.25
A Predictive Approach to Quantify the Role of Entropy in Metal Plasticity from Atomistic Simulations Soumendu Bagchi and Danny Perez; Los Alamos National Laboratory, United States

Thermally activated dislocation events significantly govern yield characteristics, especially temperature and strain-rate dependence of yield strength in metal plasticity. Generally being difficult to quantify directly, the entropic contributions are often approximated with empirical compensation rules to inform the activation energetics associated with a wide-range of dislocation driven plastic events, e.g. slip nucleation, cross-slips, kink-pair nucleation/migration and twinning, to name a few. Despite their popular use in crystal plasticity models, several recent investigations demonstrate significant anomaly with both empirical as well as harmonic approximations when entropic effects dominate defect pathways. In this talk, I will introduce a computationally simple predictive approach to quantify the rates of dislocation mediated events aided by atomistic simulation data. To exhibit the significance of entropic contributions and the approach's potential impact, we discuss a key scenario concerning crystal plasticity i.e., the nucleation of dislocations from surface steps, where currently existing approximations dramatically fails to reproduce the nucleation rates observed in direct MD. By accurately quantifying the change in vibrational entropy along the minimum energy pathway, we elucidate the non-trivial effects of anharmonic kinetics which is otherwise intractable with the existing empirical and harmonic approaches ubiquitous in modeling materials.

11:30 AM MD02.05.10
Navigating Phase Diagram Complexity to Design More Efficient Solid-State Synthesis Recipes Jiadong Chen[1], Sam Cross[2], Lincoln Miara[2], Yan Eric Wang[2] and Wenhao Sun[1]; [1]University of Michigan, United States; [2]Samsung Research America, United States

An emerging goal in the *ab initio* materials design community is to predict efficient synthesis recipes to novel functional materials. Precursor selection plays a major role in designing effective recipes, as there are many examples where a reaction can work from one set of precursors but not another. Here, we present a conceptual strategy to navigate high-dimensional convex hulls in the search of reactive precursors for more-efficient materials syntheses. The overarching strategy is to determine pairs of precursors where the reaction to a target material has large driving force and few competing phases. Using a high-throughput robotic synthesis laboratory, we design novel precursors for a diverse set of 32 quaternary oxide materials, and show that our DFT-guided precursors are substantially better at synthesizing the target oxides than naïve traditional precursors. This enables us to guide precursor selection for solid-state synthesis using information that is largely-available in high-throughput materials databases like the Materials Project.

11:45 AM MD02.05.11
Fully Automated Nanoscale to Atomistic Structure from Theory and Spectroscopy Experiments Davis G. Unruh, Venkata Surya Chaitanya Kolluru and Maria K. Chan; Argonne National Laboratory, United States

Computational investigation into the structural and electronic properties of a material begins with knowledge of the underlying atomistic structure. When investigating novel or non-stoichiometric materials, various experimental spectroscopic techniques can be used to probe the material. However, moving from the spectra to the oxidation state and atomic configuration requires searching a vast structural space, where it is critical to not only match the experimental data but to also minimize quantities such as the energy to ensure structures are physically plausible and realizable. To address this need, we have previously developed the FANTASTX code, a multi-objective evolutionary algorithm which performs structure search for a variety of spectroscopies using genetic algorithm and basin-hopping methods. While FANTASTX has demonstrated success with few-atom systems, a significant challenge in extrapolating to more complex large-scale systems is the presence of near-duplicates within the search space and the significant computational expense of first-principles calculations on large-scale systems. To address these issues, we have extended FANTASTX to automatically incorporate on-the-fly machine learning methods, including both structural fingerprinting and graph neural network methods, to both identify and eliminate structural duplicates prior to processing and replace the use of density functional theory as the geometric relaxation and energy prediction mechanism.

SESSION MD02.06: Materials Design II
Session Chairs: Soumendu Bagchi, Grace Gu, Rishi Gurnani and Haoran Wang
Thursday Afternoon, April 13, 2023
Marriott Marquis, Second Level, Foothill G1/G2

1:30 PM *MD02.06.01
Automatic Discovery of High-Performance Quantum Dot Thermoset Nanocomposites Ozgur Keles, Birsen Sirkeci and Folarin Erogbogbo; San Jose State University, United States

More than 65 million tons of thermosets are used annually. Ten percent of this is used for fiber reinforced composites. Thermosets have higher stiffness, strength, and fire resistance than thermoplastics, which make them suitable for transportation, defense, electronics, construction, consumer product, piping, adhesive, and other applications. In addition, fiber reinforced thermoset composites dominate structural applications that demand high strength-stiffness and low density. However, thermosets are brittle. For example, the common thermoset epoxy is as brittle as window glass. Many different fillers–graphene, clay, rubber–have been used to enhance the toughness of epoxies. Yet, poor bonding, agglomeration, voids, misalignment, and waviness limit their effectiveness. An alternative filler without these problems is the two-dimensional (2D) quantum dots (QDs), such as graphene QDs. In this talk, I will explain potential origins of enhanced toughness and thermal conductivity in QD thermosets. I will discuss how the unique properties of QDs, such as photoluminescence, can be used for future applications, such as structural carbon fiber composite batteries. Furthermore, concepts on artificially intelligent high-throughput automatic processing-structure-property exploration towards faster discovery of sustainable nanocomposites will be introduced.

2:00 PM MD02.06.02
Discovering All-Organic Flexible High-Temperature Polymer Dielectrics with Virtual Synthesis and Machine Learning Rishi Gurnani[1], Stuti Shukla[2], Deepak Kamal[1], Chao Wu[2], Chris Kuenneth[1], Yang Cao[2], Gregory Sotzing[2] and Rampi Ramprasad[1]; [1]Georgia Institute of Technology, United States; [2]University of Connecticut, United States

A record-setting new polymer dielectric that displays the highest-ever electrostatic energy density (8.9 J/cc) at 200 C has been designed using advanced AI algorithms, and subsequently validated through synthesis and breakdown testing. This new flexible, all-organic polymer, polyoxanorbornene-1 (PONB1), beats the current industry standard for high energy density capacitors--biaxially oriented polypropylene (which degrades rapidly above 25 C)--by a significant margin of 3.5 J/cc. Concurrent developments, also by us, in polymer informatics played a key role in the discovery of PONB1. These developments include an advanced deep learning framework that reduces the time required for polymer screening by more than 50 times compared to traditional approaches, and two algorithms for generating realistic but never-before-synthesized polymers. Our progress, especially in the development of algorithms for polymer generation and in the real-world validation of PONB1, was made possible by lively collaboration and iteration with experimental colleagues. Looking forward, the polyoxanorbornene family--which includes PONB1--expands the scope and effectiveness of capacitor-based energy storage, a technology that may ultimately power the world's electrification. Given the results of our work, it is likely that other valuable candidates exist in our massive data set of never-before-synthesized polymers for many applications. We offer this data set to the community, as well as the open source code for our advanced deep learning framework.

2:15 PM MD02.06.03
Improving Deep Neural Network in Predicting Electron Ionization Mass Spectra by Molecular Similarity-wise Sampling Ryohei Yamaguchi, Shigenori Takeda, Toshifumi Kakiuchi and Yutaka Imamura; AGC Co., Japan

Mass spectrometry is an indispensable analytical tool to identify molecular species. A target molecule is often determined by comparing the mass spectrum with known spectra stored in a database. This approach is useful for detecting known molecules, but not applicable for novel molecules. To solve this issue, a recent study proposed to add machine-learning predicted spectra into the database in order to increase chemical space covered by the database. This method is expected to extend applicability of the knowledge-based searching system, but the coverage of the system would be still restricted by the predictability of the machine-leaning model. In this study, we therefore modified the machine-learning model by training our own dataset in addition to the original open data of mass spectroscopy.

First, we tried to extend the novel approach by adding our own dataset of fluorinated molecules to the open database composed of more than 200 thousand molecules; however, the limited additional dataset much less than the huge original datasets was not enough to improve the predictability of the machine-learning model for fluorinated molecules. We therefore applied a simple but powerful dataset sampling scheme that downsamples the molecular datasets in terms of molecular similarity. The molecular similarity between molecules in own and open datasets was evaluated by Tanimoto method with Morgan fingerprints, then the datasets with reduced data with low similarity were used for training the machine-learning model as the downsampled dataset. Additionally, the datasets exhibiting bit collision due to the limitation of Extended-Connectivity-Fingerprints (ECFP4) in representing molecular structures were eliminated to improve the training performance. Consequently, the model trained with the reduced dataset was found to overperform the original model for predicting mass spectra of extra fluorinated molecules, which demonstrated that the strategic learning with appropriate downsampling can improve the performance of deep learning models, even though additional data is limited.

2:30 PM BREAK

3:30 PM MD02.06.04
Computer Vision and Artificial Intelligence for Smart Additive Manufacturing Grace Gu; University of California, Berkeley, United States

Additive manufacturing (AM) has made huge strides in the past decades, enabling the fabrication of multiscale and multi-material designs previously deemed infeasible. As AM spreads to the fields of aerospace, automotive, and medical fields, part quality and reliability become increasingly important. Improper settings of process parameters can lead to imperfections in the part; small imperfections in one layer can propagate into the rest of the build. In this work, we present a real-time monitoring and autonomous correction system enabled by computer vision and machine learning to diagnose the quality of parts and modify 3D-printing parameters iteratively and adaptively in real-time. Sensor technologies embedded in our platform are used to capture images during the printing process to train a machine learning model. Precise localization and semantic segmentation detection algorithms are implemented to shed light on the evolution of defects during real-time printing, specifying a quality profile at each layer of the print. This advanced detection system is capable of providing defect information for quality assessment and has the potential for further automated control as well as correction of AM systems.

3:45 PM MD02.06.05
Understanding Alloy Microstructure During Additive Manufacturing Through Meso-Scale Modeling Indranil Roy[1], Ying Yang[1], Alex J. Plotkowski[1] and Shuanglin Chen[2]; [1]Oak Ridge National Laboratory, United States; [2]CompuTherm, United States

In the recent years, as the additively manufactured alloys are gaining popularity in vehicle technology, space sector, and manufacturing industry, the effect of fast cooling rate (compared to conventional casting) on the microstructure evolution of alloys require detailed study. The mechanical properties of alloys depend on the final microstructure and elemental segregation. Although the dendritic growth of the primary phase is well studied, the eutectic microstructure modeling, especially lamella type is not well established. As Aluminum based alloys is a promising candidate for commercial vehicle application, we have selected them as our prototype material. The lamella eutectic structure in Al-based alloys, e.g., Al-Ce, Al-Mg is also often observed. Therefore, we developed a cellular automaton (CA) based modeling tool that simulates dendritic-eutectic combined solidification of Al-based alloys. CALPHAD approach is used to initialize the input material property parameters for the solidification model. The modeled microstructure is compared to experimental micrographs obtained from controlled additively manufactured samples that show significant similarity. Using this approach, multiple Al alloys with varying element and composition are studied which provides important insight into the precipitation behaviors of such alloys that ultimately results in better understanding of mechanical properties.

4:00 PM MD02.06.06
AI-Powered *In Situ* X-Ray Characterization for Laser Metal Additive Manufacturing Process Sen Liu, Vivek Thampy, Peiyu Quan and Christopher Tassone; Stanford/SLAC, United States

Energy materials research, development, and production are facing huge challenges as the world's energy infrastructure is changing in favor of renewable energy. Additive manufacturing (AM) has shown its promise to change the way how future energy materials and systems can be designed and delivered, such as producing 3D functional energy structures, saving materials waste and energy, reducing production cycle and cost, and achieving extraordinary mechanical system compactness. In recent years, laser AM has been applied for metal-ceramic composite, turbine molds and cores, advanced battery electrode architectures, GE LEAP engine parts, aerospace brackets, lattice heat exchangers, and power electronics. However, manufacturing "printable" high-quality parts are inherently difficult due to the fast cooling rate of laser-induced melt-pool and multi-physics effects are poorly understood. Excessive costs and lengthy certification cycles have hindered the application of AM in many industrial sectors.
The recent explosion of artificial intelligence (AI) and machine learning (ML) shows great potential in the breakthrough of laser AM process modeling. The AI-based approaches are an indispensable step to derive the complex metal alloy composition-process-structure-property relationships. In this study, it will present the results of artificial intelligence (AI)-based methods to process real-time X-ray diffraction and radiography of Aluminum alloy printing during the laser AM process at synchrotron radiation lightsource. Aluminum alloys are key materials in additive manufacturing (AM) technologies due to their low density and high strength-weight ratio for structural function. However, printing densified and defects-free Al alloy faces many challenges because of their low laser absorption, high thermal conductivity and AM fast cooling rate; they are characterized as highly crack sensitive or poor printability. Inoculation treatment offers a chance to solve this problem, where the grain refining inoculants are mixed into molten metals and act as heterogeneous nucleation catalysts during crystallization. Grain refinement was achieved by the contribution of Al3Ti nuclei and their coherent interfaces. Equiaxed grains accommodate the solidification shrinkage allowing the production of crack-free samples. The high-speed X-ray diffraction extracts subsurface phase transition and cooling rates from melted to solidified track. The X-ray radiography reveals the pore formation mechanism and fluid dynamics during laser melting. The effects of processing parameters and constituted composition on the phase transition and molten pool characteristics are analyzed. The electron microscopy characterization shows pore defects reduction and fine equiaxed grains for nanoparticle-reinforced Al alloy.

4:15 PM MD02.06.07
Machine Learning of Borophene-Boride Hetero-Structures for Borophene Synthesis Luqing Wang[1,2], Qunfei Zhou[1,2], Qiucheng Li[1], Joshua Paul[1,2], Mark C. Hersam[1], Pierre T. Darancet[2] and Maria K. Chan[2]; [1]Northwestern University, United States; [2]Argonne National Laboratory, United States

Borophene, two-dimensional (2D) boron, exhibits versatile properties which may lead to a variety of environmental and energy applications, such as CO_2 reduction, hydrogen and oxygen evolution reactions, nitrogen fixation, superconductivity, and so on. Also as a synthesized 2D material without a bulk layered counterpart, borophene structure cannot be predicted from bulk boron, and has polymorphic phases. These structural characteristics not only enrich the diversity of available materials properties, but also are informative for the fundamental understanding of 2D crystal structures and boron chemistry. However, a big challenge in borophene field is synthesis. Though borophene has been synthesized on several metal substrates, the strong interaction between borophene and substrates limit the achievement of free-standing borophene. Recently, it was found that boride is formed through the reconstruction of the top metal layer mixed with boron during borophene synthesis on Al(111). Metal borides have the potential to be superior substrates, compared to metals, for borophene synthesis and separation. Here to search for good substrates for borophene synthesis, we firstly generate a dataset of approximately 100 borophene-boride hetero-structures by density functional theory (DFT) calculations, then perform machine learning (ML) to analyze the interaction in the hetero-structures based on binding energy and charge transfer. For ML, random forest algorithm is used and features are initially imported from Matminer. Furthermore, we use the ML model in a larger dataset of hypothetical borides structures to predict good substrates. This work allows us to explore alternative routes of borophene synthesis. Also it will advance the understanding of the bindings with boron and explain the mechanism of determinants for borophene synthesis. What is more, this work is promising to solve the major challenge in borophene field which is the isolation of borophene from the substrates.

4:30 PM MD02.06.08
AI/ML Guided Exploration of Electronic Polymer Thin Films for Manufacturing Henry Chan[1], Jie Xu[1], Chengshi Wang[1,2], Aikaterini Vriza[1] and Rohit Batra[1,3]; [1]Argonne National Laboratory, United States; [2]The MathWorks, Inc., United States; [3]IIT Madras, India

Electronic polymers are emerging as the materials for novel electronics that are flexible, wearable, and printable. To realize these applications, it is crucial to understand the processing-structure-property relationships of these polymers and derive suitable processes to manufacture them into high quality thin films at scale. This task is challenging due to the complex interplay between thin film processing steps such as solution formulation, rheology, and post-processing, and the many tunable parameters associated with these steps. With the advancements in data-driven approaches and experimental instrumentations, autonomous materials acceleration platforms driven by AI/ML is beginning to revolutionize the discovery of materials. Here, we introduce an example of such platforms developed at our facility and demonstrate its success in simultaneously handling many experimental processing parameters and optimizing the conductivity and processibility of electronic polymer thin films. We will also outline various challenges and prospects related to small data and digital twins that facilitates the integration across physics-based simulations, ML models, and experiments.

4:45 PM MD02.06.09
A Sensitivity Analysis for an Electron Transport System with Uncertainty in the Underlying the Material Parameters—A General Approach Applied to the Specific Case of Wurtzite Gallium Nitride Yanyan He[1], John Chilleri[2], Michael Shur[3], Robert Kirby[4] and Stephen K. O'Leary[5]; [1]University of North Texas, United States; [2]New Mexico Institute of Mining and Technology, United States; [3]Rensselaer Polytechnic Institute, United States; [4]The University of Utah, United States; [5]University of British Columbia, Canada

The electron transport that occurs within semiconductors is often studied through the use of Monte Carlo simulations. The results of such a simulation are critically dependent upon the underlying material parameters associated with the specific material being examined. For a compound semiconductor, the critical material parameters are the effective masses, the non-parabolicity constants, the deformation potential, the phonon energies, and the elastic constants. It is often the case that many of these material parameters are not very well known or have a range of different reported values. In this study, we employ an uncertainty quantification technique that allows us to determine the effect of the uncertainty of the underlying material parameter values on the computed transport properties through the use of a Monte Carlo simulation approach. In order to make matters concrete, this technique is applied to the specific case of wurtzite gallium nitride, a material whose material properties remain less well known than that of the more traditional compound semiconductors, such as gallium arsenide. The broader consequences of this approach, for the constellation of compound semiconductor materials, is considered.

SESSION MD02.07: Poster Session
Session Chairs: Soumendu Bagchi and Haoran Wang
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM MD02.07.01
Automated Defect Analysis of CdSe Nanoparticles through Supervised Learning with Large Simulated Databases Corey H. Williams, Luis E. Rangel DaCosta, Mary Scott and Tofunmi Ogunfunmi; UC Berkeley, United States

In the development of advanced functional nanomaterials, knowledge of the precise atomic structure and its relationship to functional characteristics of a material can rapidly accelerate the design of new material systems. Transmission electron microscopy (TEM), in conjunction with machine learning tools for automated analysis, is a powerful platform for providing atomic-scale characterization of next-generation materials like nanoparticles for large sample populations. CdSe nanoparticles, a highly tunable quantum dot system, are attractive functional nanoparticles due to their broad range of photoemission over a small range of sizes and established synthesis protocols. However, it is yet unclear as to the precise role planar defects, like stacking faults, play in quantum dot synthesis, growth, and functional performance.

In this work, we reveal the relationship between defect density and functional performance in CdSe quantum dot systems with high-resolution transmission electron microscopy (HRTEM) and machine learning. We use large, simulated HRTEM image databases of CdSe to train high-accuracy neural networks with supervised learning techniques to measure the morphology and defect statistics of CdSe nanoparticles at the atomic- scale, providing a direct measurement of the joint distribution between quantum dot morphology and defect characteristics. Through supervised learning techniques with ground-truth simulated databases, we can automatically detect and count stacking faults in CdSe quantum dots. Access to ground-truth data also allows us to develop methods for predicting and measuring sources of uncertainty and error related to systematic sources of error such as nanoparticle misorientation. Atomic structure measurements are linked back to population-wide functional behavior through UV-Vis spectroscopy. Our techniques point towards robust workflows for high-throughput, atomic-scale characterization of advanced nanomaterial systems using HRTEM via neural network analysis and provide a route for high-accuracy defect analysis in nanoparticle systems.

5:00 PM MD02.07.02
STEM Image Analysis Based on Deep Learning—Identification of Vacancy of Defects and Polymorphs of MoS_2 Kihyun Lee, Jinsub Park, Soyeon Choi and Kwanpyo Kim; Yonsei University, Korea (the Republic of)

Identifying structural features in scanning transmission electron microscope (STEM) images of crystalline materials is important in studying structure-property correlations, but traditional methods for identification are often time-consuming and require expertise. Recent advances in deep learning for computer vision, in particular the use of convolutional neural networks (CNNs), holds promise for efficient high-throughput STEM image analysis. Here we investigate the generalizability of CNNs in identifying point defects and polymorphs in STEM images of transition metal dichalcogenides (TMDCs) in the presence of different levels of noise and aberrations. We focus on the application of ResUNet, a type of fully convolutional neural network, in identifying sulfur vacancies and different polymorphs of molybdenum disulfide(MoS_2). Based on these results, we provide a guideline on best practices to train a deep learning model to identify structural features of interest in STEM images.

5:00 PM MD02.07.03
Beyond Single Molecules: Intermolecular Interference Effects Louise Hyllested and Gemma C. Solomon; University of Copehagen, Denmark

Molecular electronics is a field that has been widely investigated over the last 25 years. Previously molecules have been found to function as rectifiers, diodes, and switches.[1][2][3] These have been observed in single molecules and self-assembled monolayers of molecules. One other interesting feature of some organic molecules is destructive quantum interference (DQI).[4] When DQI is present, a molecule will suppress the current across the junction, acting as an insulator. One challenge here is that the most common indication of DQI in experiments is low current, but this is also an indication of e.g., a weak connection to the electrodes. Therefore, we are interested in observing a more direct signatures, for example a sharp dip in the differential conductance, but this has of now only been observed for monolayers. Since the indirect indication of DQI has been observed for single molecules, while the direct signature (the sharp dip) has not – it must be that the step from single molecules to monolayers is not destroying DQI but for some reason making it more readily observable.

We have investigated the influence intermolecular interactions have on DQI effects for a group of conjugated and cross-conjugated molecules using density functional theory. We observe that intermolecular interactions can shift the energy of interference features. In the cases we considered, transitioning from a single molecule to a monolayer the interference feature is moved closer to the Fermi energy, thus making the DQI more pronounced and easier to observe for monolayers compared with single molecules.

If we can understand how and when DQI effects occur in monolayers, we take a step towards designing molecular materials with DQI effects for electronics applications such as large on/off switching, highly insulating materials, or dielectric materials.

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[2] Y. Ai et al. *Nano Letters 18,* (2018), 7552–7559.
[3] M. Del Valle et al., *Nature Nanotechnology 2,* (2007), 176-179.
[4] C. M. Guedon et al., *Nature Nanotechnology 7(5),* (2012), 304-308.

5:00 PM MD02.07.04
Insight into the Reactivity of Electrocatalytic Glycerol Oxidation—The Strength of the Hydroxyl Group Bonding on Surface Minseon Park[1], Jeemin Hwang[2], Song Jin[3,4], Daehee Jang[1], Hyung Ju Kim[5], Won Bae Kim[1] and Min Ho Seo[6]; [1]Postech, Korea (the Republic of); [2]Korea Instutitute of Energy Research, Korea (the Republic of); [3]Gwangju Institute of Science and Technology, Korea (the Republic of); [4]Korea Institute of Materials Science, Korea (the Republic of); [5]Korea institute of Chemical Technology, Korea (the Republic of); [6]Pukyong National University, Korea (the Republic of)

Glycerol is a main byproduct originating from the transesterification process of vegetable oils and animal fat into biodiesel. The production of glycerol byproduct has become greater than the demand as the biodiesel production has increased. Its oversupply has significantly lowered the market price. Therefore, research on electrocatalytic glycerol oxidation reaction (EGOR) has been highlighted recently since it can generate both electricity and valuable chemicals. Glycerol can be used not only as fuel in direct alcohol fuel cells but also as reactants to produce valuable chemicals like dihydroxyacetone, glyceric acid, glycolic acid, and formic acid. However, it is not fully unknown for the reaction pathway on various catalysts due to the complexity of reaction intermediates. Most of the research focused on finding the mechanism for which desired target substance is produced. However, this work is done to comprehend a key mechanism that not only determines glycerol oxidation having various pathways but also might relate to the selectivity of each intermediate in oxidizing process. What to find the main descriptor that affects the glycerol electro-oxidation would be worthy for further design of the electrocatalyst. Combination studies of *ab-initio* computations and experiments to find the represent descriptor that affect the glycerol electro-oxidation was performed. The adsorption energies of OH and hydroxyl group in the glycerol at the catalyst surface were compared with calculating binding energies and a crystal orbital Hamilton population (COHP) analysis. As a result, the binding energy of OH and that between the hydroxyl group in glycerol and the catalyst surface were proposed as key descriptors to control the glycerol oxidation reaction in PtCu surface model. Both OH and hydroxyl group of the glycerol molecule were most strongly bound on the $PtCu_3$ surface. The alloy catalyst of Pt and Cu supported on porous carbon was used to support this data. (Pt/PC, Pt_3Cu/PC, PtCu/PC, and $PtCu_3$/PC) The mass activity of the glycerol oxidation experiment showed the same tendency as the result of the calculation, that the $PtCu_3$/PC sample showed the highest mass activity among other catalysts. Therefore, the stronger OH binds on the surface, the higher the reactivity of the glycerol oxidation. This study identified that the binding energy of OH on the catalyst surface is the key descriptor in the glycerol oxidation reaction. This is expected to be helpful in predicting and analyzing the reactivity of glycerol as well as various alcohol-based molecules. This research will pave the way for the design and development of future catalysts to produce value-added chemicals for electrocatalytic glycerol conversion reactions.

5:00 PM MD02.07.05
Ripplocation Boundaries and Kink Boundaries in Layered Solids Kaustubh Sudhakar and Michel Barsoum; Drexel University, United States

Ripplocations - best defined as an atomic scale ripple and characterized by oppositely signed ripplocation boundaries (RBs) – have recently been shown to be the underlying mechanism responsible for buckling in layered crystalline solids (LCS) such as graphite, mica, and the MAX phases. The malefactor for the deformation of LCS for more than half a century has been basal dislocations (BDs) which manifest themselves into kink boundaries (KBs) at high stresses. Since the inception of ripplocations, much work has gone into deciphering the fundamental deformation mechanism of LCS, and other layered systems such as steel sheets and playing cards. To develop a thorough understanding of the phenomena, we collected data via retrospective analysis of the literature on RBs and KBs that was carried out to date. Furthermore, to support this study we also provide new molecular dynamics (MD) data to analyze the deformation behavior in graphite through bending tests to substantiate our hypothesis. Based on this work, it is evident that KBs and RBs are distinctive in many ways; i) RBs are reversible in nature in that the system can return to its original state after deformation while KB formation only occurs when the material has been plastically deformed, ii) Atomical observations show that RBs have rounded edges as opposed to the sharp, pointy edges seen in KBs, iii) RBs are associated with high stresses at their surface which is absent in the case of KBs, and lastly iv) At extreme strains, RBs transform into KBs. By employing several - mostly past – and present investigations we intend to fundamentally unravel the differences between these atomic boundaries occurring in layered systems. The consequences of this study will help elucidate the deformation mechanics of layered systems in tens of orders of magnitudes, from the nanoscale to the geological scale.

5:00 PM MD02.07.06
Data-Driven Electrode Optimization for Vanadium Redox Flow Battery by Reduced Order Model Chao Zeng, Soowhan Kim, Edwin Thomsen, Yucheng Fu, Yunxiang Chen, Jie Bao and Zhijie Xu; Pacific Northwest National Lab, United States

The vanadium redox flow batteries are a promising energy storage technology for stationary applications (e.g., renewables integration) that offer a pathway to cost-effectiveness through independent scaling of power and energy as well as longevity. However, the flow non-uniformity and high pumping loss in cell reduce system efficiency and increase resistance. Many current research efforts are devoted to optimizing electrode configuration and screening electrode materials for flow uniformity and higher system efficiency. Current high-throughput laboratory-scale testing is time and material intensive for this purpose. An integrated experimental and numerical method are proposed to accelerate the optimization of electrode material and structure. Current state-of-art 780 cm2 interdigitated flow cell is paradigm for further optimization. Reduced order model is developed based on equivalent circuit model to represent full 3D model and is validated with experimental results. The reduced 2D model can significantly reduce computational cost and create large datasets for optimization. Based on the large datasets, statistical optimization is used to search for optimal combination of electrode dimension and properties. This date-driven method and statistical framework may serve as a general guideline for structure optimization and material screening for redox flow battery stacks.

5:00 PM MD02.07.07
Application of Baysian Super Resolution to Spectroscopic Data Analysis Shunta Harada[1], Kota Tsujimori[1] and Jun Hirotani[2]; [1]Nagoya Univ, Japan; [2]Kyoto University, Japan

The number of data points of digitally recorded spectra have been limited by the number of multi-channel detectors employed, which sometimes inhibits the precise characterization of spectral peak shape. Here we describe a methodology to increase the number of data points as well as the signal-to-noise (S/N) ratio by applying Bayesian super-resolution in the analysis of spectroscopic data. In our present method, first the hyperparameters for the Bayesian super-resolution are determined by a virtual experiment imitating actual experimental data, and the precision of the super-resolution reconstruction is confirmed by the calculation of errors from the ideal values. For validation of the super-resolution reconstruction of spectroscopic data, we applied this method to the analysis of Raman spectra. From 200 Raman spectra of a reference Si substrate with a data interval of about 0.8 cm^{-1}, superresolution reconstruction with a data interval of 0.01 cm^{-1} was successfully achieved with the promised precision. From the super-resolution spectrum, the Raman scattering peak of the reference Si substrate was estimated as 520.55 (+0.12, -0.09) cm^{-1}, which is comparable to the precisely determined value reported in previous works. The present methodology can be applied to various kinds of spectroscopic analysis, leading to increased precision in the analysis of spectroscopic data and the ability to detect slight differences in spectral peak positions and shapes. So far, we have already confirmed that the present method is effective not only to Raman spectroscopy but also to electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy and the electric signals.

5:00 PM MD02.07.08
A Workflow to Track Time-Resolved Dislocation Behavior in High Temperature Aluminum Holland Stacey, Naomi G. Mo, Lichao Fang and Leora E. Dresselhaus-Marais; Stanford University, United States

Studying dislocation behavior furthers our understanding of their effects on the mechanical, thermal, and electronic properties of materials. Previous observation-based research on dislocation motion has primarily been conducted with TEM and thus typically concerns dislocations near or at the surface (< 2 µm thick foils). While models for subsurface dislocation movement exist, many of these models have yet to be validated by experiments with comparable samples. Dark-Field X-Ray Microscopy (DFXM) is a new technique developed in the last decade to study subsurface dislocations. We use DFXM to track deep subsurface dislocations approximately 200 µm beneath the surface of single crystalline FCC aluminum at 96% of the melting temperature. In this work, we present a 5-step workflow to automatically track time-resolved dislocation movement in DFXM scans, including a Stationary Wavelet Transform (SWT) approach, convolution kernels, adaptive thresholding, structuring elements, and an image segmentation tool. This workflow allows us to identify and quantify the position of dislocations in DFXM images over time, paving the way to discovering more about dislocation dynamics at tri-junctions.

5:00 PM MD02.07.09
Investigation of Solidification in Supercooled Water Drops using Large Data Sets of Synchronized Optical Images and X-ray Diffraction Patterns Claudiu A. Stan[1,2], Armin Kalita[1], Maximillian Mrozek-McCourt[1], Thomas Kaldawi[1], Philip Willmott[3,2], N. Duane Loh[2], Sebastian Marte[1], Raymond Sierra[2], Hartawan Laksmono[2], Jason Koglin[2], Matt Hayes[2], Robert Paul[2], Serge Guillet[2], Andrew Aquila[2], Mengning Liang[2] and Sébastien Boutet[2]; [1]Rutgers, The State University of New Jersey, United States; [2]SLAC National Accelerator Laboratory, United States; [3]Paul Scherrer Institute, Switzerland

The freezing of supercooled water drops is a complex example of rapid nonequilibrium solidification that includes dendritic crystal growth, changes in volume leading to mechanical deformation and fracture, and the formation of metastable crystal phases. It is also an important natural phenomenon that occurs in clouds and can trigger precipitation.

We investigated the freezing of water drops cooled by evaporation in vacuum. We imaged optically the freezing drops at high magnification with short light exposures, and we probed them simultaneously with ultrashort X-ray laser pulses. This approach provided a snapshot of a drop's state at both the micron scale and at the molecular scale, and had the temporal resolution needed to resolve a freezing process that is completed in approximately one millisecond. Since the X-ray lasers are pulsed and have sufficient energy to damage the drops, only one multiscale data point can be collected from a drop.

A major challenge in investigating a spontaneously freezing system with high resolution is the randomness of nucleation. Our experiment reduced greatly the range of nucleation times by using very rapid cooling, but even so the spread of nucleation times was comparable with the duration of solidification, and the nucleation statistics averaged the details of the freezing dynamics. We therefore collected large data sets of drops freezing at several average time delays, which each set containing a distribution of drops at different elapsed times after ice nucleation. The data contains more than 10000 simultaneous optical and X-ray measurements from single drops, and additional optical data from more than 40000 drops. At each average time delay, we had available thousands of data points to measure the distribution of the stages of freezing that could be observed experimentally.

Seven distinct stages of freezing were identifiable from the optical images, from supercooled liquid drops to drops that shattered due to the strain accumulated during solidification. We developed a kinetic model of freezing based on these stages, and we determined all the model properties (nucleation rate, stage durations, probability of shattering, etc.) though a complex fitting procedure that used the experimental distributions of freezing stages.

Using the optical images and the seven-stage freezing model, we sorted the X-ray diffraction data by the time elapsed from nucleation. Sorting improved substantially the temporal resolution of diffraction, and the resolution was sufficient to observe the increase in the intensity of high-index diffraction peaks, which indicated that long-range crystalline order in ice was largely formed in approximately one millisecond. The diffraction patterns also showed that during the first millisecond after freezing the ice had a hexagonal crystal structure with inhomogeneous strain and a grain size on the order of 100 nm.

5:00 PM MD02.07.10
Characterizing Dislocations by formulating the Invisibility Criterion for DFXM Dayeeta Pal and Leora E. Dresselhaus-Marais; Stanford University, United States

The motion and long-range interactions of dislocations are essential to understand the mechanical, electronic and thermal properties of materials, but their dynamics are difficult to measure. While transmission electron microscopy (TEM) has imaged dislocations for half a century, its limited field of view and sample thickness requirements may not be representative of bulk phenomena. To understand the “stochastic” dislocation dynamics in bulk crystals that govern their properties and dynamics, Dark Field X-ray Microscope (DFXM) has been developed to image deep subsurface dislocations. By imaging along an X-ray diffracted beam with an objective lens, DFXM images lattice distortions hundreds of micrometers beneath the surface of crystalline materials – mapping hierarchical structures of dislocations. While today’s DFXM can effectively map the line vector of dislocations, it still cannot quantify the Burgers vector required to understand dislocation interactions, structures, and energies. Our study formulates a theoretical model to establish the theory behind how DFXM images map information to deduce the Burgers vector of dislocations. By revisiting the “invisibility criteria” from TEM theory, we re-solve this formalism and extend it to the ray-optics models developed for DFXM in order to evaluate how the images acquired from different scans about a single {hkl} diffraction peak encode the Burgers vector within them. This work advances our understanding of DFXM to establish its capabilities to connect *bulk* experiments to dislocation theory and mechanics.

5:00 PM MD02.07.11
Optical Property Database of Inorganic Phosphor Seunghun Jang, Gyoung S. Na and Hyunju Chang; Korea Research Institute of Chemical Technology, Korea (the Republic of)

Developing inorganic phosphor with desired properties has relied on time-consuming and labor-intensive material development processes. Moreover, the results of material development experiments depend significantly on the intuitions and experiences of each researcher. For efficient and reliable materials discovery, machine learning has been widely applied to various scientific applications in materials science. However, the prediction capabilities of machine learning methods fundamentally depend on the quality of the training datasets. In this work, we constructed a high-quality and reliable database that contains experimentally validated inorganic phosphors and their optical properties for data-driven research on inorganic phosphors. Our database includes 3,432 combinations of 27 dopant elements in 2,231 host materials. The database provides material information, optical properties, measurement conditions for inorganic phosphors, and metainformation. For the validation of the collected database, we preliminarily performed machine learning on the database and evaluated the prediction results.

5:00 PM MD02.07.12
Numerical Investigation of Using Mechanical Metamaterial as a Broadband Microwave Absorber Daniel D. Lim[1], Sangryun Lee[2], Jeong-ho Lee[1], Wonjoon Choi[3] and Grace Gu[1]; [1]University of California, Berkeley, United States; [2]Ewha Womans University, Korea (the Republic of); [3]Korea University, Korea (the Republic of)

A porous structure composed of lossy materials enables advanced microwave absorption compared with non-porous material owing to its improved impedance matching and multiple internal reflection. Optimizing the internal geometry of lossy material-based porous structures leads to the active control of microwave absorption for desired target operating ranges while the mechanical strength and stiffness can be secured for practical applications. It has been shown that introducing porous, strong, and stiff mechanical metamaterial with a low density as a microwave absorber has a high potential to create a new kind of broadband absorber satisfying both the electromagnetic and mechanical requirements. So far, empirical approaches were employed to investigate the wave absorption characteristic of materials.There is currently a lack of understanding of the underlying physics of geometric features such as lattice structure, volume fraction, or unit cell length. Furthermore, there are challenges in exploring myriad input variables and visualizing the electromagnetic fields interacting with the structure.
Here, we investigate the effect of the geometric feature of the mechanical metamaterial on microwave absorption, using the microwave simulation using finite element analysis. By varying geometric features such as volume fraction, unit cell length, and lattice type of different mechanical metamaterials (octet-truss, body-centered cubic, cubic foam, and octet foam), we define different absorption mechanisms depending on the structural adjustments. The central finding is that low-density unit-cell (5-20% relative density) absorbs microwaves better than high-density structure, because microwaves going through more porous material enables impedance matching and improved internal multiple scattering effects. When the thickness of the whole structures is varied by changing the unit cell length of the mechanical metamaterial, different lattice structures show a similar response regardless of the lattice types at the subwavelength scale. Meanwhile, when the size of the total thickness of the structure is larger than the incident wavelength, it results in major variance in absorbance with different mechanisms based on the lattice type. Lastly, broadband microwave response (4-18 GHz) under the fixed unit cell length is examined to elucidate different microwave absorption mechanisms depending on lattice structures such as strut-based and facet-based geometries. This work can pave the way for expanding mechanical metamaterial as a broadband microwave absorber by defining the correlation between the geometric feature to the microwave absorption.

5:00 PM MD02.07.13
Determination of Contact Models for AFM Nanoindentation Without Tip Shape Knowledge by Machine Learning Linh T. Nguyen and Bernard H. Liu; National Cheng Kung University, Taiwan

Atomic force microscopy (AFM)-based nanoindentation provides local nanomechanical measurements of materials by acquisition and analysis of force-displacement (FZ) curves. However, the calculated nanomechanical properties usually contain uncertainty due to the use of contact model corresponding to the AFM tip shape and the nature of the tip-sample interactions. Therefore, the present study proposes a machine learning (ML) classification framework to suggest the appropriate contact model based on features of the FZ curves, and the information of tip shape is not required. The ML framework is performed using multiple ML classifiers and contact models; both balanced and imbalanced datasets are applied.
The testing results indicates that the quadratic discriminant analysis (QDA) classifier trained using both balanced and imbalanced datasets, provides the best predictive quality. In the balanced learning task, the ML classifier is trained and tested using more than 5000 sets of FZ curves of homogeneous materials, i.e., polydimethylsiloxane (PDMS), polymethyl methacrylate (PMMA), polyvinyl alcohol (PVA), and gold (Au). The practical feasibility of the proposed ML framework is examined by processing more than 200 sets of unseen FZ curves of a heterogeneous material, i.e., *Staphylococcus aureus* (*S. aureus*) bacteria. The QDA classifier outputs the use of the SND contact model with a testing accuracy of above 95.0%. In the imbalanced learning task, the ML classifier is trained and tested using several thousands of FZ curves of PDMS, PMMA, PVA, Au, *S. aureus*, and methyl-ammonium lead iodide perovskite ($MAPbI_3$). The QDA classifier suggests the use of the SND contact model with a testing accuracy of above 90.0% for each set of unseen FZ curves (~700 curves/set) of *S. aureus* and $MAPbI_3$, respectively. The results show that ML is an efficient approach to not only reduce the uncertainty

remain in the AFM measurements, but also speed up AFM data analysis.

5:00 PM MD02.07.14
Predicting Elastic Modulus of Materials without AFM Tip Shape Parameters and Contact Model Fitting Linh T. Nguyen and Bernard H. Liu; National Cheng Kung University, Taiwan

Atomic force microscopy is a commonly used technique to characterize the nanomechanical properties of materials. In this technique, the elastic modulus of a material is calculated by fitting an appropriate contact model into the force curve. However, the contact model fitting is a challenging task since such practical paramtertes of AFM tip are difficult to determine. Hence, the present study develops a machine learning (ML) regression framework to determine the elastic modulus of materials based on the force-displacement (FZ) features, without the need for both knowledges of tip parameters and process of contact-model fitting.
In the ML framework, FZ features are extracted and implemented into the ML regressor, which learns the relationship between these features and the corresponding elastic modulus values, and then outputs the modulus values for the unseen data based on the these FZ features. The robustness of the ML framework is examined using two groups of materials with elastic modulus spanning several orders of magnitude (from kPa to GPa): (1) homogeneous materials including polydimethylsiloxane, polymethyl methacrylate, and polyvinyl alcohol and (2) heterogeneous materials including *Staphylococcus aureus* and methylammonium lead iodide. The results show that, for all considered materials, Gaussian process regression (GPR) outperforms other ML regressors, i.e., random forest, support vector regression, and multiple linear regression (MLR). Specifically, the GPR model achieves a high testing coefficient of determination value, R^2, above 90% and 80.0% for homogeneous and heterogeneous materials, respectively. By contrast, the MLR model shows the worst prediction performance with an R^2 value of up to 50.0% and 35.0%, respectively. Overall, ML is a promising approach for calculating the nanomechanical properties of materials based solely on FZ features.

5:00 PM MD02.07.15
Optimization of Atmospheric Plasma Treatment Parameters for Hydrophilic Surface Functionalization of Non-Woven Fabrics Through Design of Experiment MiJeong Park[1], Hee Yeon Jeon[1], Jeong Hyun Kim[1], Dong Hoon Lee[1] and Young-In Lee[1,2]; [1]Seoul National University of Science and Technology, Korea (the Republic of); [2]The Institute of Powder Technology, Korea (the Republic of)

The use of hydrophilic polymers is a promising technology in various application fields such as filters and oil-water separation membranes, but it is difficult to directly utilize them due to problems such as a very small number and low mechanical properties. Accordingly, various attempts have been made to modify the surface of the non-hydrophilic material to be hydrophilic. The plasma treatment method in which activated ions collide with the surface to be modified by supplying energy to the gas has the advantage of being able to modify the surface easily and simply without major damage to the surface of the polymer. Among them, atmospheric pressure plasma is attracting attention in that it can perform surface modification with only a plasma source and a substrate without a special device such as a vacuum system or solvent treatment. It is well known that the surface of the non-hydrophilic polymer is modified to be hydrophilic when plasma treatment is performed using a specific gas on the polymer surface, but the effect of each process variable and the optimized conditions are not discussed in detail.
Although the nonwoven fabric treated with atmospheric pressure plasma parameters as described above has many advantages, it has a problem, named the aging effect, in that the hydrophilic effect rapidly decreases over time. The aging effect is a phenomenon that occurs due to the characteristic that the reactors formed by plasma treatment return to their original state over time. Many studies have introduced various physicochemical methods in the plasma treatment process to solve this problem, when optimizing for improved conditions, a large problem arises in that a lot of time is additionally required because the effect over time for each condition must be reflected. Therefore, we propose a post-treatment method that uses the "design of experiment" to find the factor that has the greatest influence on the aging effect and reduces the decrease in the hydrophilic performance of the nonwoven fabric while maintaining the first optimized condition.
Design of Experiments (DoE) is a statistical technique for quickly optimizing the performance of experimental results using input process variables. By analyzing the results of the DoE experiment, it is possible to find out which factors have a statistically significant effect on the results, how and which factors are interdependent, and finally, the experimental conditions can be optimized for the purpose of the experiment. A process capability index is a tool for determining whether the results of a set of process results meet a specific quality. Experimental results conducted with optimized process variables can be statistically verified by confirming process consistency and process yield through process capability analysis.
In this study, a chain of experimental procedures based on various parameter combinations was performed using the DoE method, and the main factors that had the largest influence were found by quantifying the effect of each process variable of plasma treatment. In addition, based on the results, multiple regression analysis was used to optimize the experimental parameters under the conditions of maximizing the hydrophilicity of the polymer surface, and the excellence of the optimized conditions was shown statistically and physicochemically through process capability analysis and surface analysis. Finally, to evaluate the effect of reducing the effect over time, the estimation of hydrophilicity ability over time was also conducted. A series of experiments and analysis procedures were characterized by Minitab 20 software, X-ray photoelectron spectroscopy (XPS), Atomic Force Microscope (AFM), and contact angle analyzer.

5:00 PM MD02.07.16
Machine-Learning Interatomic Potential for Silicon Carbide: A Molecular Dynamics Study of Mechanical Properties Kenji Nishimura[1] and Ken-ichi Saitoh[2]; [1]National Institute of Advanced Industrial Science and Technology, Japan; [2]Kansai University, Japan

Silicon carbide (SiC) is a promising candidate for next-generation power electronics materials because of its superior electrical properties. However, SiC is a brittle material at low temperatures and is known to be a hard-to-work material. Thus, ductile mode machining, which yields a highly efficient and smooth machined surface, has been developed over several decades. To grind brittle materials in ductile mode, a basic understanding of the material's mechanical properties is necessary, that is, mechanisms of plastic deformation, phase transformation, and crystal defect formation. Specifically, since electronic materials require precise processing, mechanical phenomena occurring at the nanoscale should be focused on.
Quantum electronic structure calculations are highly accurate, but due to its high calculation cost, the computational scale is often limited to hundreds of atoms. That is why it is difficult to elucidate the mechanical properties including nanoscale phenomena at an atomistic point of view by means of first-principles calculations. Recently, some types of machine-learning interatomic potentials (ML-IAPs) have been proposed, which can reproduce the results of the first-principles calculations adequately without any empirical information or data, and have been applied to molecular dynamics (MD) simulations. It is expected for ML-IAPs to analyze crystalline defects in large systems with the same accuracy as the first-principles calculations.
In this study, we attempt to create a spectral neighbor analysis potential (SNAP) for SiC from reference data obtained by the first-principles calculations. The SNAP proposed by Thompson et al as one of ML-IAPs adopts bispectrum components as descriptors to express the energy of the atomic system. Then the SNAP potential for SiC we built is applied to MD simulations to examine its reproducibility. As a result, the SNAP potential developed in this study reproduces a lattice constant, elastic modulus, and bulk modulus with higher accuracy than any other empirical ones. We confirm that stable edge dislocation cores are generated as a dislocation dipole in crystalline 3C-SiC and they properly glide in a predicted slip plane. Additionally, the Peierls stress estimated by our MD simulations agrees well with that of the previous study.

5:00 PM MD02.07.18
Machine Learning for Predicting Emulsion Stability in Agrichemical Formulations Ryan Marson, Chris Roth, Wanglin Yu and Michael Tate; Dow, United States

Crop protection is a multi-million-dollar industry requiring complex formulations of multiple surfactants in a solvent, which must form stable emulsions prior to being dispersed. We outline a joint computational and experimental study undertaken within Dow to predict the stability of a given formulation. Data from thousands of high-throughput formulation experiments were compiled and analyzed for emulsion stability. This experimental data set was then used in combination with physical and chemical descriptors of the formulation components to train an ensemble of cluster-based machine learning models (e.g., Decision Trees, k-means, etc.) to predict whether a given formulation would be stable, some of which demonstrated cross-validation accuracies as high as 75%. We outline the details of this effort and discuss opportunities for continuous improvement of the models.

5:00 PM MD02.07.20
In-Situ Analysis of Convoluted Data at Large-Scale Facilitates Trygve M. Ræder; Technical University of Denmark, Denmark

Advances to electron microscopes and X-ray facilities have enabled tremendous leaps in the quality of experimental data over the past decades. This has lead to the development of experimental configurations and techniques that were not possible even five or ten years ago. Simultaneously, improvements in informatics and detectors have dramatically increased the rate of data acquisition. Data processing has in many cases become more challenging due to increased experimental complexity and data throughput despite advances to data quality. In particular, the challenge arises when using novel experimental configurations, as is often the case at X-ray free electron lasers. Successful execution and optimization of the experiment is frequently contingent on in-situ data analysis, and data-processing often becomes a bottleneck for the experiment as a whole. Most critically, as the number of collaborators grows with experimental complexity, the programming knowledge often does not scale in a similar fashion.

This poster will detail our approach to automating data analysis in-situ during an ongoing experiment. We have found that automatic and semi-automatic data processing have enabled faster feedback to guide experiments during an ongoing beamtime at X-ray free electron facilities, and empowered more team members to access convoluted results in an approachable manner. Automated data analysis also reduces the overall workload of the beamtime, allowing for more rest between shifts and less exhaustion. We believe our approach is generally applicable to electron microscopes and scanning probe microscopy in addition to X-ray science.

5:00 PM MD02.07.21
Towards Automatic Characterization of Nano-Energetic Material Response to Directed Energy Camden I. Boyle[1], Timothy Gaines[1], Alex Hurt[1], James Keller[1], Grant Scott[1], Stanton R. Price[2] and Matthew I. Maschmann[1]; [1]University of Missouri–Columbia, United States; [2]U.S. Army Research and Development Center, United States

Aluminum nanoparticles (Al-NPs) have garnered interest from researchers due to their low cost, naturally occurring passivating aluminum-oxide shell, and high energy density. The passivating oxide shell limits the achievable rate of reaction, thus restricting the possible applications for this material. Various proposed reaction mechanisms describe the escape of aluminum from the passivation shell. The first and most common is thermally driven diffusion which describes when a cluster of particles is irradiated, the temperature increase causes particles near sinter together. The melt dispersion mechanism proposes that volumetric expansion during rapid heating overcomes the yield stress of the shell, leading to shell rupture and spallation of the particle. Melt dispersion remains largely unobserved experimentally, and therefore not fully understood. However, if this mechanism was well understood and triggerable, the application space for aluminum nanoparticles would expand significantly.
To better understand these reaction mechanisms, single particle experimentation has been performed using targeted photothermal heating with a custom optical microscope setup equipped with a microscope camera, piezoelectric nano positioner, and diode laser. Experiments have been performed by irradiating particles or particle clusters while capturing optical and SEM images before and after irradiation. However, because particle composition, particle diameter, heating rate, and packing density are all contributing factors to reaction outcomes, the parameter space has become overwhelmingly large to explore using traditional experimental techniques. To combat this, automation has been employed to accelerate the experimental throughput allowing for more efficient and effective exploration of this parameter space. Automation was achieved by coordinating the microscope setup using a control computer and API calls to carry out experimentation without the need for human intervention. Likewise, computer vision techniques have been used to measure distinctive features from images captured before and after directed energy excitation of nanoenergetic particles. These features are used to describe the reactions in the pursuit of creating an automated nanoenergetic material reaction characterization model. Combined, these endeavors can autonomously collect and analyze experimental data to better inform researchers and physical models.

5:00 PM MD02.07.23
Optimizing Biomimetic Cellular Structures Inspired by the Sea Glass Sponge Using a Surrogate Model and Multi-Jet Fusion Printing Ailin Chen, Sangryun Lee and Grace Gu; University of California, Berkeley, United States

Architected cellular structures have great significance in the biomedical industry because, when compared to completely dense metallic implants, orthopedic prostheses with a porous structure can provide better stress shielding and osseointegration. The considerable skeletal structure observed in the sea glass sponge demonstrates great yield strength and buckling resistibility during compressive testing. This structure's biomimetization gives cutting-edge inspiration for lightweight constructions with superior compression characteristics. However, finding, fabricating, and testing the best design in conventional ways, on the other hand, is both costly and inefficient. In our study, we trained a neural network using massive datasets produced from finite element analysis (FEA) and achieved a coefficient of determination over 94% on relative density and von mise stress prediction. The FEA model is validated by experiments, and the specimens are printed using the Multi-jet Fusion (MJF). It is a novel additive manufacturing process for the powder bed fusion of thermoplastic polymers. Next, an active deep learning-based optimization technique is used to investigate the best spacing between the diagonal lines and the frames in the sponge structure. Later, the optimized structure will be applied to the close cellular structure and tested for its mechanical properties improvement. This study takes advantage of the performance and power of computer algorithms and additive manufacturing processes to discover optimal biological designs in structural applications and broaden the spectrum of materials available.

5:00 PM MD02.07.24
Multiscale Mechanisms of Twisted Carbon Nanotube Yarns Probed *In Situ* by Soft X-Rays During Tensile Loading Philip M. Jean-Remy[1], Daniel Malone[1], Adam Golder[2], Alexander Schwartz[1], Cheng Wang[2], Eric R. Meshot[1] and Xavier Lepro Chavez[1]; [1]Lawrence Livermore National Laboratory, United States; [2]Advanced Light Source, United States

Resonant soft x-ray scattering (R-SoXS) can help realize the promise of data driven research in hierarchical materials whose structure spans multiple length-scales, such as carbon nanotube (CNT) assemblies. Our prior work demonstrated the wealth of high-resolution and statistical data R-SoXS provides about chemical and structural morphologies across different length scales in CNT materials.[1] CNTs are known as the strongest 1D material due to their covalent *sp*^{2} carbon bonds, hexagonal lattice, and cylindrical shape. However, piecing together CNTs into assemblies has proven to be so far a failed strategy to achieve the same elite performance metrics as individual CNTs. This highlights a critical deficiency in understanding the effects that the processing of individual nanostructures has on the performance of their derived macroscale assemblies, thereby hindering the development of a process-structure-performance map for these materials.

In this work, we propose a new method to decouple the distribution orientation of nanoscale tortuosity and the macroscale twist of CNT dry-spun yarns under applied loads via *in-situ* R-SoXS probing at high energy (1300 eV) and low energy (280 eV), respectively. With this decoupling enabled by *in-situ* R-SoXS, we gain new insights on the deformation mechanisms of these yarns which have been structurally reinforced with a novel vapor-phase polymer that is subsequently self-crosslinking.[2] Further, we examine how both the distribution orientation of the nanoscale tortuosity of CNT bundles and the macroscale twist of the yarns evolve as a function of applied load for different processing conditions, including yarns with plasma-enhanced surface reactivity prior to the polymer reinforcement. Better understanding of the multiscale structural behavior of CNT yarns as a function of processing will allow advances for the manufacture at large scale of products based on ultra-strong, flexible, conductive fibers for aerospace, defense, communications, wearables, and biomedical industries.

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5:00 PM MD02.07.26

Using Machine-Learning and Deep-Learning to Discover Relationships in Intercalation Compounds Joseph S. Fenton[1], Ryan Aguilar[1], Iman Ellahie[1], Heidi G. Paisley[1], Jordyn A. VanOrman[1], Jack R. Vitek[1], Kaci L. Kuntz[2] and Natascha Knowlton[1,2]; [1]Rowland Hall, United States; [2]The University of Utah, United States

Intercalation refers to the insertion of guest species into the interlayer space of a host material. This can create drastically different properties in the resulting compound and therefore, intercalation can be used to tune the properties of a material. Layered materials such as graphite are common host structures because of their large van der Waals gap between layers; this allows for the insertion of guest species, resulting in graphite intercalated compounds (GICs). As guest species insert, the interlayer space may expand or contract, the guest may donate electrons (n-doped) or accept electrons (p-doped) from the host--resulting in an increased conductivity of the GIC, and may insert with different staging--where a stage I intercalation compound has molecules inserted in between each host layer while a stage II is every other layer, and so on. Thusly, intercalation is a powerful tool, as it provides a unique avenue to tune and engineer the properties of a material.

However, because of the vast combinations of guest and host compounds as well as the variations in staging, understanding the relationships between guest, host, and GIC properties are incredibly complex and challenging. However, machine learning (ML) and deep learning (DL) provide a route to elucidate the complex relationships between the properties of guest species, graphite host, and intercalated compounds. Here, we successfully employ these techniques to elucidate structure-property relationships in GICs. This work has application toward improving efforts in engineering materials without needing to test every possible combination; thereby, materials can be strategically selected to synthesize for specific applications, including medical, optoelectronic, and energy storage (*Inorg. Chem. Front*., 2016, 3, 452; *Adv. Mater*., 2019, 1808213).

Example: Strategies for Synthesis of GICs
By training on input parameters (donor/acceptor of the intercalant, stage, in-plane conductivity, and interlayer spacing of the GIC), we predicted thermodynamic values for the enthalpy of formation, $\Delta H_f \pm 5\%^{,}$ with 40% accuracy and entropy, $\Delta S \pm 5\%$, with 80% accuracy. These results allow for the calculation of Gibbs Free Energy, ΔG_f, for the formation of a GIC. Furthermore, because of the dependance of on temperature, we can determine the conditions which a GIC will form—including temperature, pressure, and applied voltage. This is significant for the broader materials community, since these ML- and DL-discovered relationships provide a new tool to guide the parameters for the synthesis of GICs. Furthermore, these relationships create the possibility of predicting and discovering new GICs.

In summary, with this work, we successfully used ML to elucidate structure-property relationships between intercalants, graphite host, and GICs, including thermodynamic values, which could be relevent to efficiently synthesizing GICs. With DL, we utilized the individual properties of guest species, graphite, and GICs to predict composite characteristics of GICs. More broadly, this research can lead to facilitating more sustainable efforts in material design for intercalation compound

5:00 PM MD02.07.28

Origin of the Onset Temperature in Solid-State Ceramic Synthesis Shibo Tan[1], Gabrielle Kamm[2], Karena Chapman[2] and Wenhao Sun[1]; [1]University of Michigan, United States; [2]Stony Brook University, The State University of New York, United States

Temperature plays a crucial role in solid-state synthesis, but there are currently no mechanistic theories to predict the optimal temperature to carry out a solid-state reaction. A variety of recent observations suggest that transient liquid intermediates provide a diffusion media for solid-state reactions at subsolidus temperatures. Here, we hypothesize that in a solid-state reaction $A + B \text{->} AB$, the precursors A and B first melt into a metastable liquid phase before transformation into the solid AB product phase. In this theory, the onset temperature of a solid-state reaction derives from the extension of liquidus curves into the metastable eutectic region of a Temperature-Composition phase diagram. We validate this theory by combining *in situ* XRD synchrotron observations with a thermal gradient heater, which produces temperature-time-transformation curves for a solid-state reaction that largely agree with the theory of a metastable liquid intermediate. To more readily predict the reaction onset temperature, we present with a strategy to combine DFT convex hulls with CALPHAD approaches to rapidly estimate the high-temperature liquidus curves of phase diagrams at minimal computational cost.

5:00 PM MD02.07.29

Clinical and Forensic Characterization of Exhaled Breath—Multiscale Computational Studies for the Metrics of Aerosol Particle Capture Veruska Malavé, Kavita Jeerage, Edward J. Garboczi and Tara Lovestead; National Institute of Standards and Technology, United States

Exhaled breath research consists of the study of gases, water vapor, volatile organic compounds, as well as aerosol particles. This research field typically involves the implementation of state-of-art methodologies for both novel technology and metric test analysis. This is particularly the case when collecting, detecting, and measuring exhaled submicrometer aerosol particles. Particle matter is produced in the lungs due to mechanical disruption of the airway lining fluid, which consists of water, lipids, proteins, and non-volatile compounds. Drugs of abuse, for instance: amphetamines, cocaine, and tetrahydrocannabinol (THC), have been detected in exhaled aerosol particles in conjunction with potential biomarkers of health or disease. Particles can be deposited in surgical masks, electret filter devices, and impaction filter devices; however, the absorptive properties of masks and some filters can hinder recovery for instrumental laboratory analysis. *Future development and adoption of exhaled breath sample tests and aerosol particle collection based on the particle fraction of breath require a deeper understanding of how human factors interact with device design, as a collector method, to influence particle deposition*. Robust multiscale computational methods, such as computational fluid dynamics (CFD) in conjunction with computational fluid particle dynamics (CFPD) numerical models, can support the design, optimization, and prototype development of these breath devices while aiding the interpretation of human subject exhaled breath studies that are not yet fully comprehended. In this work, the development and application of a three dimensional (3D) multiscale CFD-CFPD model of a single impact filter is carried out to aid *understanding of the complexity phenomena of the dynamics, transport, and deposition of submicrometer particles in exhaled breath*, the macroscale domain. The focus is on numerical simulations informing about the exhaled breath velocity profile as well as the local transportation, deposition, and distribution of submicrometer polydisperse particles in exhaled flow in a single-impact filter of a commercial breath aerosol capture device. This fluid dynamics and discrete phase computational approach is novel in terms of how depicting (a) exhaled breath and particle deposition within an aerosol collection device and (b) fluid breath dynamics of submicrometer polydisperse particles deposited in a filter by means of impaction. This study highlights needed decoupling strategies to characterize the influence of the size of particle as well as their concentration distribution and human (e.g.: flowrate and breath volume) and device factors. The goal of this study is to aid reproducibility and laboratory analysis of particle collection when human subject breath analysis is involved. This work will contribute to developing crucial standardized metrics that will promote pathways to advance public health and safety while offering a mean for a deeper comprehension of exhaled breath particle research.

5:00 PM MD02.07.30

Exploring the Reaction Mechanisms in Sol-Gel Synthesis of BiFeO3 Thin Films Using Chemical Reaction Networks Viktoriia Baibakova, Kevin J. Cruse, Carolin M. Sutter-Fella, Anubhav Jain and Samuel M. Blau; Lawrence Berkeley National Laboratory, United States

BiFeO3 thin films have potential applications in memory devices and photovoltaics due to their multiferroic properties [1]. They can be synthesized through spin-coating of a sol-gel [2], but this process is complex and can result in impurity phases that negatively impact physical and device properties. In this study, we aim to improve our understanding of the mechanisms involved in sol-gel synthesis of BiFeO3 by using chemical reaction networks [3]. We also seek to propose a different method for managing precursor materials in synthesis recipe databases that can produce defining features effectively processed by machine learning models. We present preliminary results obtained from constructing and analyzing the reaction network for the reaction between bismuth(III) nitrate pentahydrate and 2-methoxyethanol. For instance, our study suggests that replacing the nitrites and water in the outer layer of bismuth with 2-methoxyethanol may be hindered by kinetics, but becomes easier once hydrogen bonds are weakened. This finding may help explain why the reaction does not occur at room temperature in experiments [4]. We also report our efforts to explore preferred chemical routes based on energy gain using high-throughput computations with xTB [5] and QChem [6]. Additionally, we discuss alternative representations of materials that can be used to improve the success of chemical reaction networks and contribute to a data-driven understanding of the effects of different chemical components on the outcome. Our findings contribute to a more predictive and mechanistic understanding of the sol-gel synthesis process, which could lead to the production of high-quality BiFeO3 thin films.

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5:00 PM MD02.07.31

The Study on Intelligentization of Heat Treatment Conditions for Alloy Steel Using Artificial Intelligence Kyeonghun Kim[1], Uro Heo[1], Jeong Hyeon Kwon[1], Seongtak Kim[2] and Hae Woong Yang[1]; [1]Pohang Institute of Metal Industry Advancement, Korea (the Republic of); [2]Korea Institute of Industrial Technology,, Korea (the Republic of)

The cold forging heat treatment process is known to be a decisive factor in the mechanical properties of products. In the case of alloy steel used in cold forging, coarsening and refinement of crystal grains occur according to changes in alloy composition and heat treatment conditions, which directly affect mechanical properties, so proper heat treatment conditions according to the material are very important. However, most of the processes, such as changing the heat treatment pattern and inspecting and confirming before input, are currently performed manually, which takes a lot of time and has a disadvantage in that productivity is low. Also, depending on the experience, know-how and proficiency of the operator, some deviations in the process occur. In this study, atypical data collected in the heat treatment process (quenching and tempering) was preprocessed after removing invalid columns by setting optimal variables. Random Forest Regressor, Gradient Boosting Regressor, Extra Trees Regressor, and Bayesian Ridge were used as experimental models for preprocessing results, and heat treatment calculation results were derived through data such as alloy components and external environment. In order to evaluate the consistency of these calculation results, as a result of conducting a regression analysis (comparative verification) with the actual heat treatment material, the result value within the error range was confirmed.

5:00 PM MD02.07.33

Vanadium Dioxide-Containing Formulations for Smart Windows Applications, Synthesized and Characterised via Automation for Multi-Objective Optimisation Mohammed F. Amin[1,2], Yee Fun Lim[1] and Ivan P. Parkin[2]; [1]Agency for Science, Technology and Research (A*STAR), Singapore; [2]University College London, United Kingdom

Smart windows have been proposed as a solution to improve the energy efficiency of buildings. VO_2 is a phase change material that has shown promises because it stable during synthesis and allows EM waves to penetrate the building at cold temperature or reflect at high temperatures [1].
To fully optimise a smart window: the phase change should occur at 27°C (transition temperature), be transparent and uniform. Typical synthesis and characterisation routes are time consuming because finding an optimum requires extensive exploration of large search spaces, including but not limited to reagents, stoichiometry, reaction, and conditions analysis methods [2]. In this work, we aim to minimise manual experimentation and optimise VO_2

properties by combining automated experimentation and ML to converge to the three objectives.
We first utilized an automated machine chemical synthesis tool (Zinsser), which has robotic tools to mix reagents, dopants, coat the substrate, and anneal 15 samples in approximately 8 hours. Additionally, the Zinsser measures the UV-vis spectra for transparency data. Transition temperature data is then measured using a custom-built, robust, automated measurement set-up which consists of a 4-point probe, thermal camera, and a heating bed. Finally, the uniformity, is measured in high throughput with HPS. Consequently, we have collected a large dataset that can be used in multi-Objective optimisation processes.
Results obtained are in line with an operational smart window, both functionally and compositionally (XRD). Over 90% of the entire process yielded target material and was completed without human interaction, allowing us to generate a large and varied dataset which will drive ML-based optimisation.
Bayesian optimisation has been tested with synthetic a dataset by varying parameters and implement different regression algorithms to achieve the best RMSE and R^2 scores, as well as minimise the number of iterations. The experimental results obtained will undergo pre-processing and scaling before optimisation using open-source Python library, scikit-optimize (*skopt*) [3].

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5:00 PM MD02.07.36
Database of Computed Properties for Color Center Defects in Silicon Vsevolod Ivanov[1], Alexander Ivanov[2], Jacopo Simoni[1], Prabin Parajuli[1], Thomas Schenkel[1] and Liang Z. Tan[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]Brown University, United States

Color center defects in silicon are emerging as a promising platform for realizing a number of applications in quantum information science (QIS), including quantum sensing, single-photon sources, and integrated quantum communication between quantum computer nodes. Several well-studied defects such as the G-center, W-center, and T-center, possess some of the necessary attributes for these applications, including narrow linewidths, emission in the telecommunications band, long electron spin coherence times, and coupling between spin and optical degrees of freedom. Despite this, no known defect is perfectly suitable for QIS applications, and in fact different devices can require defects with expressly distinct sets of properties. We report the publication of a searchable online quantum defect database containing the computed properties of over 5000 distinct silicon defect structures. Formation energies, defect energy levels, ground and excited spin states, zero phonon lines, and electric dipole matrix elements are provided for each defect, which are then used to screen for candidate defects with emission within the telecommunications band, non-trivial spin state, and strong optical coupling. Additionally, a machine learning approach is applied to predict defect properties directly from structural data.

This work was supported by the Office of Fusion Energy Sciences and the Molecular Foundry, a DOE Office of Science User Facility, supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

5:00 PM MD02.07.39
Steps Towards Convergence Informatics—Enriching the Groundwater Chemical Composition Data Alexey Gulyuk[1,2], Akhlak-ul Mahmood[1], Paul Westerhoff[3] and Yaroslava G. Yingling[1]; [1]North Carolina State University, United States; [2]STEPS research center, United States; [3]Arizona State University, United States

The problem of reusing available natural resources and, particularly, removing various chemical pollutants from water sources is a topic that currently receives a lot of attention. Utilization of various agents (nanoparticles, hydrogels, or solvents) opens new paths to recovery the dangerous wastewater pollutants like hydrogen, phosphorus, or heavy metals.

The very first step for developing water cleaning strategies requires assessing full chemical composition of a target water source. In practice, extensive water quality analysis involves analyzing enormous amounts of data and requires rigorous data preparation and several preprocessing steps.

Here we want to present our vision of how the combination of experimental and ML- derived data can help to facilitate the increased accuracy of data analysis for further advances in clean water sustainability. Particularly, we focus on assembly, analysis, and completion of the water chemical composition dataset, which became one of cornerstones of the project. Data enrichment tools utilized in this work rely on Machine Learning algorithms and enable elements of Convergence Informatics, thus advancing data-driven research with the end goal of finding the most effective water treatment compounds and agents.

5:00 PM MD02.07.40
Evaluating Extended Length Scale Structures in Aqueous Solutions of Sodium Nitrate and Sodium Nitrite Yihui Wei[1], Emily Nienhuis[2], Sebastian T. Mergelsberg[2], Trent Graham[2], Gregory K. Schenter[2], Carolyn Pearce[2,3] and Aurora Clark[1,2]; [1]The University of Utah, United States; [2]Pacific Northwest National Laboratory, United States; [3]Washington State University, United States

Relating electrolyte solution structure, from local solvation to that of the extended ion networks, to the solubility and reactivity is of interest due to its relevance in the processing of industrial wastes. X-ray total scattering, for pair distribution function analysis, is one key method to access structures across multiple length scales in these materials, while readily allowing for complementary experimental and computational efforts. In this work we used computation methods to unravel the molecular origin of multiscale correlations observed in the experimentally obtained X-ray pair distribution functions of dilute to concentrated $NaNO_2$ and $NaNO_3$ aqueous solutions. Two graph theory approaches, polyhedra identification and geodesic pathway analysis, combined with Molecular Dynamics simulations were utilized to identify the organizational motifs composed of intermolecular networks and their concentration-dependent evolution. The growing population of extended ion networks is found to be responsible for the change of atom pair correlations while bulk water structure remains unperturbed.

5:00 PM MD02.07.41
Voxelized Atomic Structure Potentials for Molecular Dynamics—Determining Mass Diffusion Coefficient in Ti-Al Alloys Mayur P. Singh, Matthew C. Barry and Satish Kumar; Georgia Institute of Technology, United States

Prediction of dynamical properties of materials through Molecular Dynamics (MD) simulations comes with the established problems such as exponential increasing computational cost with increasing size, limited time scale, and inaccuracy of results from using empirically derived interatomic potentials compared to first principles Density Functional Theory (DFT) simulations. Neural Network Interatomic Potentials (NNIPs) have lower computational cost and comparable accuracy to the first principles calculations. However, one problem faced by NNIPs is the creation of mostly simplified or expert-guided *ad hoc* selection of the salient material structure descriptors to describe interatomic forces, when in actuality these interactions happen on complex 3D atomic structures. In this work, we introduce the Voxelized Atomic Structure (VASt) potential for Molecular Dynamics. VASt is a framework for creating interatomic potentials through the voxelization of the atoms in an atomic structure. This creates a 3D representation of the structure, which can be trained in a Convolutional Neural Network with 3D convolutions. We use the VASt potential in MD simulations to calculate the mass diffusion coefficient of two-component systems. Performance of many metallic alloys are highly dependent on the mass diffusion coefficient of the components, notably Ti-Al alloys. We consider a 2-component system of Al and -Ti and study the diffusion of Al into -Ti in a wide range of temperature, i.e., 300-1500 K. Overall, our approach has great potential to predict diffusive, mechanical and thermal properties of multi-component systems.

5:00 PM MD02.07.42
EGBO: Evolutionary-Guided Bayesian Optimization for Materials Discovery Kai Yuan Andre Low[1,2], Yang Bai[2], Khoo Zi Hui Jonathan[2], Made Riko I[2], Eleonore Vissol-Gaudin[1], Huiqing Xie[2], Albertus D. Handoko[2], Vijila Chellappan[2], Jianwei Jayce Cheng[2], Fengxia Wei[2], Yee Fun Lim[2] and Kedar Hippalgaonkar[1,2]; [1]Nanyang Technological University, Singapore; [2]Institute of Materials Research and Engineering, Singapore

The development of Materials Acceleration Platforms has enabled High-Throughput (HT) materials experimentation towards solving materials grand challenges with large decision spaces, multiple conflicting objectives and complex constraints. The implementation of existing state-of-the-art Bayesian Optimization called q-Noisy Expected Hypervolume Improvement (qNEHVI) is able to solve noisy constrained multi-objective problems with batch evaluations, appropriate for HT experimentation. However, the stochastic sampling approach used to generate candidates leads to inefficient exploration of the search space and inability to fully resolve the Pareto Front, reducing the number of good solutions that can be tested experimentally. In this work, we develop a new algorithm specifically designed for materials discovery using a hybrid framework called Evolution-Guided Bayesian Optimization (EGBO) that introduces selection pressure via evolution to rapidly navigate the exploration-exploitation trade-off. We demonstrate this on multiple multi-objective benchmark problems, both synthetic and real-world, and show that EGBO is able to efficiently resolve the Pareto Front [1]. Asides from hypervolume, we present other metrics that are specifically relevant to assessing optimization for material science problems such as scalability, consistency and feasibility. We demonstrate this on a closed-loop experimental workflow that explores Cu-Sb-S compositional space to optimise its photoelectrocatalytic hydrogen evolution from water,. The multiple-objective optimization model discovered optimum experimental conditions after only nine cycles of integrated experiments-machine learning loop. Photocurrent testing at 0 V *vs.* reversible hydrogen electrode (RHE) confirmed the expected correlation between the materials properties and photocurrent. An optimum photocurrent was observed on $Cu_9Sb_{45}S_{46}$ in the form of single layer coating on F-doped SnO_2 (FTO) glass with corresponding bandgap of 1.85 eV and 63.2% Cu^{1+} species content [2].

[1] EGBO: Evolution-guided Bayesian Optimization for Efficient Pareto Front Exploitation for Materials Discovery, submitted to Nature Computational Science (2022)
[2] Multi-Objective Optimization for Photoelectrocatalytic Materials Discovery via High-throughput Experiments Combined with Machine Learning, submitted to Advanced Materials (2022)

SESSION MD02.08: Materials Characterization
Session Chairs: Soumendu Bagchi, Nathan Szymanski and Haoran Wang
Friday Morning, April 14, 2023
Marriott Marquis, Second Level, Foothill G1/G2

8:30 AM MD02.08.01
Adaptive X-Ray Diffraction with Automated Phase Identification Nathan Szymanski[1,2], Christopher Bartel[1,2], Yan Zeng[2], Mouhamad Diallo[1,2], Haegyeom Kim[2] and Gerbrand Ceder[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

The speed by which machine learning models can be evaluated creates novel opportunities to integrate them directly with experiments. In this presentation, we will demonstrate how the effectiveness of X-ray diffraction (XRD) can be improved by using machine learning to analyze data on the fly so that the diffractometer can be autonomously steered toward features that accelerate phase detection. This is accomplished by training a neural network to propose which phases best match a given XRD pattern, quantify the uncertainty related to each proposed phase, and pinpoint the features in the pattern where these phases differ most. By leveraging early experimental data from a rapid XRD scan on an unknown sample, the neural network can effectively narrow down the list of possible phases from thousands to only a handful. To distinguish between these few phases, the neural network controls the diffractometer in real time such that high-resolution measurements are focused on regions containing features that are unique to each phase. Scans are performed adaptively until all phases can be identified with high confidence. We show that this method significantly boosts the accuracy of impurity detection on multi-phase samples while cutting their measurement time in half. Because adaptive XRD scans are fast but accurate, they can be used to characterize chemical reactions where short-lived intermediates appear. As a proof of concept, we demonstrate that all phases can be successfully identified by adaptive XRD during the synthesis of a common solid electrolyte. These findings showcase the advantages of in-line machine learning for materials characterization and point to the possibility of more general approaches for adaptive experimentation.

8:45 AM MD02.08.02
Characterizing 2D Materials with Semi-Supervised Learning and Convolutional Neural Networks Chengyin Wu, Isaiah A. Moses and Wesley Reinhart; The Pennsylvania State University, United States

The unique and fascinating properties exhibited by 2D materials have triggered tremendous interest in their research. Characterization of 2D materials is often performed using Atomic Force Microscopy (AFM) which generates topographic images of synthesized samples. However, the height maps from AFM are usually processed by manual analysis with specialized software such as ImageJ to extract information like thin film coverage, thickness, or descriptions of morphology. This process is inefficient since each image generated by AFM must be analyzed one by one in a time-consuming postprocessing step. Therefore, developing a method to automatically process the AFM images by Machine Learning (ML) can improve workflow efficiency. Meanwhile, utilizing computational metrics can provide some useful information other than numerical data, such as correlating thin film patterns with experimental parameters or overall thin film coverage by different vapor deposition methods for further physical properties investigation.
In this study, we explored the use of statistical learning models and Convolutional Neural Networks (CNN) to automate the AFM postprocessing workflow for samples of WSe2 grown by Metal-Organic Chemical Vapor Deposition. We first developed a semi-supervised ML scheme to propagate the sparse labels of thin film coverage to the rest of the dataset. In this step, we also learn abstract representations of the unlabeled data and identify qualitative features of AFM height maps that are not obtained in the conventional workflow. In the next step, we evaluated different CNN architectures to design

optimized models for our image processing workflow. After training, we achieve significantly better performance than using statistical learning alone. The automated workflow can also augment the traditional image analysis by providing searchable abstract representations. We anticipate this approach can be applied to all kinds of 2D materials for high-throughput characterization.

9:00 AM MD02.08.03
Machine Learning for Predicting Structure- and Environment-Dependent Degradation Behavior of Biopolymers Jessica N. Lalonde[1,2], Babetta Marrone[2], Stefan Zauscher[1] and Ghanshyam Pilania[2]; [1]Duke University, United States; [2]Los Alamos National Laboratory, United States

Plastics derived from fossil fuel feedstocks have become essential to modern life around the world, but the detriment to the environment and human health throughout their entire materials life cycle continues to be a significant challenge. Materials design of bio-based alternatives to conventional plastics are often limited by time- and resource-intensive experimental screening for optimum degradation rates, thermal processing ranges, and durability. In this work, we employ machine learning (ML) as a powerful data-enabled technique to explore the structure-property-processing relationships of a diverse family of bio-derived polyesters, poly(hydroxyalkanoates) (PHAs), in a quantitative and efficient way. We conduct a thorough literature review of varying PHA structures and compositions, degradation environments, and experimental conditions to explore a broad suite of variables affecting the overall degradation rate of the PHA biopolymers. Individual data entries, including over 1,700 unique data points from more than 200 different sources were collected from peer-reviewed journal articles, published book chapters, and other open-source formats to create a ML dataset unique to PHAs to predict the degradation rate in a variety of real-world environments. We demonstrate how this curated database of PHA samples can be used to employ a robust ML approach that is capable of both: (1) regression for prediction of the degradation rate of the PHA samples, and (2) classification of samples into different categories of degradation profiles at specific timepoints. A random forest (RF) decision tree algorithm was used for semi-quantitative predictions of two degradation parameters which capture the key features of the database to predict the weight loss over time for each sample. We show this novel approach to parameterization of the features to develop a degradation profile for each sample can be used to compare PHA samples with vastly different degradation timescales. Using this approach, we achieve a highly accurate and physically meaingful model. By demonstrating the potential of ML-informed experimental materials design process for PHAs, we present a generalizable framework for biopolymer materials design for other types of biopolymers in addition to PHAs, with potential impacts of helping to push the biopolymer materials design process forward.

9:15 AM MD02.08.04
Experimental Design for High Fidelity Polymer Solubility Data to Improve Machine Learning Capabilities Mona Amrihesari, Joseph D. Kern, Amari Murry, Ramamurthy Ramprasad and Blair K. Brettmann; Georgia Institute of Technology, United States

Recently developed machine learning approaches to understanding material properties provide new opportunities for studying and developing new knowledge about polymers. The vast application of polymers and their sensitivity to many parameters like molecular weight, temperature, morphology, etc. requires developing high throughput experimentation methods that lead to accurate results. This will be vital for developing any prediction model in data science analysis. Although polymer informatics has significantly improved in recent years, using artificial intelligence and machine learning techniques, a significant hurdle in the polymer informatics area is the lack of complete and sufficiently detailed databases. One example where this is a challenge is in developing a dataset for polymer solubility and dissolution, where the classification of “soluble” or “insoluble” is sensitive to molecular weight, concentration, temperature, heating/cooling rate, and other factors that are not always reported or well-controlled. To overcome the challenges with the current dataset on polymer solubility, in this work, we apply turbidity measurements with precise temperature control using a Crystal16 parallel crystallizer and develop an experimental design to maximize usable data from a single sample, while still controlling for the factors that impact the kinetics of polymer dissolution. With this method, the experiments are possible to do in reproducible and time-effective ways while also collecting time-resolved dissolution data continuously throughout the experiment. This approach produces detailed results in a controllable manner allowing us to develop a more information-rich data set for predicting the polymer solubility using machine learning techniques.

9:30 AM MD02.08.06
Developing Robust Neural Networks for High-Resolution TEM Image Analysis Katherine Sytwu[1], Luis E. Rangel DaCosta[2] and Mary Scott[2,1]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

Neural networks are promising tools for high-throughput and accurate transmission electron microscopy (TEM) analysis of nanomaterials. However, these powerful analysis techniques have yet to move past proof-of-concept into wider adoption. Notably, neural networks perform poorly on data that is “out-of-distribution” from its training data. Given the wide variety of microscope conditions and potential samples yet limited types of local features typically seen in TEM images, it is unclear what sort of images would be classified as different, or "out-of-distribution," from others. Without an idea of what training protocols are needed for a robust network, one would need to either retrain neural networks for every dataset one wants to analyze, or acquire/label a large dataset of TEM images that spans every sample/imaging condition, both of which prohibit wider usage of neural networks for analysis of TEM images.

Here, we investigate how the choice of training dataset influences neural network performance in the context of an automated characterization pipeline. We curate and label high-resolution TEM image datasets of nanoparticles under controlled imaging and material parameters, including magnification, dosage, nanoparticle size, and nanoparticle material. By training and cross-validating neural networks with these curated datasets, we not only identify under what conditions these neural networks generalize, but also uncover the biases that arise when test data differs from training data. As an example task, we focus on segmentation, or pixel-wise classification, of atomically-resolved crystalline nanoparticles against an amorphous TEM substrate background. We find that neural networks generalize well across images of different nanoparticle sizes, but are sensitive to images taken with different electron dosages. Networks tested on images taken with a higher electron dosage than the training set underestimate nanoparticle size, and vice versa. Synthetic image augmentation can help with small perturbations in microscope and sample conditions, but is not a viable strategy to cover a wide variety of conditions. In general, images taken with different microscope conditions are more likely to be flagged as out-of-distribution, implying that neural-network-aided analysis may be more feasible for in situ datasets whose microscope conditions are heavily controlled. Our results point towards the need for additional testing of data-driven algorithms to account for generalizability across multiple datasets.

[1] This research was supported by an appointment to the Intelligence Community Postdoctoral Research Fellowship Program at Lawrence Berkeley National Laboratory, administered by Oak Ridge Institute for Science and Education (ORISE) through an interagency agreement between the U.S. Department of Energy and the Office of the Director of National Intelligence (ODNI).

9:45 AM BREAK

10:15 AM MD02.08.07
Toward Automated Characterization of Disordered Materials by Integrating Atomistic Simulations, Machine Learning and X-ray Absorption Spectroscopy Wonseok Jeong, Wenyu Sun, Yu-Ting Hsu, Fikret Aydin, Xiao Chen, Michael Bagge-Hansen, Liwen Wan, Michael Nielsen and Tuan Anh Pham; Lawrence Livermore National Laboratory, United States

Optimizing material performance requires accurate knowledge of local composition and structure at atomic scale. Spectroscopic techniques such as X-ray Absorption Near-Edge Structure (XANES) have been widely used for material characterization. However, extracting chemical information from experimental probes can be intractable in heterogeneous systems. In this work, we discuss how atomic simulation is integrated with machine learning techniques and XANES calculations to understand chemical speciation of amorphous carbon nitride systems as a case study. We discuss the development of machine learning (ML) potentials that can efficiently explore a large configurational space of amorphous carbon nitrides. The ML potentials are then combined with statistical methods to elucidate the most representative local structures, such as carbon and nitrogen hybridization, and how they evolve with chemical compositions and density. Our simulations indicate that structure of amorphous carbon nitrides is highly complex, exhibiting non-linear and unexpected behavior at medium density and nitrogen concentration. Structural analysis is then combined with XANES simulations to establish a relationship between local structure and spectroscopic signatures, which in turn, is used to provide high-fidelity interpretation of experimental measurements. Development of ML models, including a transformer model, for describing structure-spectrum relationship will also be discussed.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Funding was provided by LLNL Laboratory Directed Research and Development (LDRD) Program Tracking No. 22-ERD-014.

10:30 AM MD02.08.08

Robustly Describing Atomically Dispersed Catalysts Using Deep Learning Assisted Microscopy Analysis Haoyang Ni[1,2], Jacob Smith[3,2] and Miaofang Chi[2]; [1]University of Illinois at Urbana-Champaign, United States; [2]Oak Ridge National Laboratory, United States; [3]North Carolina State University, United States

Atomically dispersed catalysts (ADCs) are a recently emerging category of catalysts where metal atoms are anchored on substrates in a mononuclear or monomolecular form[1]. Due to the size reduction, better catalytic performance is expected from the higher specific activity and utilization of atoms[2]. However, heterogeneous atomic configurations, such as dimers, trimers, and clusters, can form during synthesis[3] or catalytic reactions[4]. These different atomic configurations can contribute differently to the overall catalytic performance. Therefore, it is necessary to characterize the local structure of adsorbed metal atoms in ADCs to understand the origin of the observed catalytic performance.

Annular dark field (ADF) scanning transmission electron microscopy (STEM) has been used to characterize the local structure of ADCs and identify the presence of different atomic configurations[5]. ADF STEM allows metal atoms to be intuitively distinguished via image contrast against the background contrast of bulk support. The continued development of STEM instruments permits the automatic acquisition of many ADF images to allow researchers to build statistics of ADCs dispersions and capture their structural evolution in different operant environments[5]. However, the identification and counting of different atomic configurations are normally performed through either manual labeling or conventional thresholding methods, which become a bottleneck for data analysis.

Here, we present a deep-learning-based algorithm for atom configuration identification and categorizing in ADCs. We propose a convolutional neural network structure – AtomNet- consisting of four consecutive residual neural networks as the backbone. A pipeline of automatic generation of synthetic datasets that can mimic different imaging conditions, such as magnification, dwell time and resolution, is designed to train the neural network. Applying trained AtomNet to synthetic and real STEM images shows the high accuracy of atom identification under different imaging conditions and different materials systems. On a desktop with GPU support, an image with size 1024*1024 only needs milliseconds to process, which outruns most in-situ STEM image acquisition time. Therefore, live feedback on atom positions and configurations can be achieved and applied to time-of-flight analysis.

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9. The microscopy work was supported by an Early Career project supported by DOE Office of Science FWP #ERKCZ55–KC040304. All microscopy technique development was performed and supported by Oak Ridge National Laboratory’s (ORNL) Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility.

10:45 AM MD02.08.09

Data-Driven Modeling and Adaptive Optimization of Floating Zone Crystal Growth Process Applying Gaussian Mixture Model and Reinforcement Learning Shunta Harada[1], Yusuke Tosa[2], Ryo Omae[2], Ryohei Matsumoto[2] and Shogo Sumitani[2]; [1]Nagoya Univ, Japan; [2]Anamorphosis Networks, Japan

Materials process has been upgraded, automated, and efficiently optimized by applying various kinds of informatics algorithms and the field of “process informatics” were emerging. Although parameters for most materials processes are time-independently given, which means that a set of input parameters gives a single output, some materials processes are manually controlled according to the information obtained during operation. For example, in crystal growth by the optical floating zone (FZ) method, an operator monitors the status of the melt in a furnace with a camera and changes the inputs to maintain suitable conditions for single-crystal growth. In the present study, we predicted the dynamics of crystal growth by the optical FZ method using Gaussian mixture model (GMM) and optimized the operation trajectory by reinforcement learning for automated operation.
There are two characteristics in the operation data of the material manufacturing process which requires adaptive control according to the process states including FZ crystal growth process. One is that the amount of data for learning is limited, and so-called "big data" cannot be collected. It is unrealistic to run thousands of experiments for automation. The other is that the operation trajectories are not identical, but they are all similar trajectories. An operation is carried out according to the process states, and it is natural to control refering to the similar operations which once succeeded. Therefore, it is necessary to construct a prediction model in a limited parameter space with a limited amount of data. Considering these characteristics of the operation data, we selected to apply for the prediction of the dynamics by GMM in the present study. GMM is a model that can predict nonlinear dynamics near the training trajectories with high sample efficiency. In order to validate the predication of the dynamics by GMM, we created an emulator of FZ crystal growth process and generated virtual operation trajectories. As a result, from only five training trajectories, we successfully predicted the operating dynamics using GMM with better precision than one obtained by using linear regression or neural networks.
<!--StartFragment -->Once the prediction model for the dynamics of the operation trajectory with high accuracy is constructed, it is possible to generate an

ideal operation trajectory by reinforcement learning. In the present study, the control model was trained using proximal policy optimization (PPO). In reinforcement learning, it is generally important to appropriately define a reward function that quantifies whether state is good or bad. In order to accurately control the operation of the FZ crystal growth by reinforcement learning from the dynamics predicted by GMM, the reward function should be properly designed. As a result, we have reveald that not only the error from the ideal shape of grown crystal considering the necking process but also the error from the training trajectories should be minimized in the reward.
Finally, by applying GMM and PPO, we succeeded in achieving an operation trajectory that is closer to the ideal one than one manually controlled.<!--EndFragment -->

11:00 AM MD02.08.10
S/TEMfit—A Tool for Real-Space Analysis of Large-Scale S/TEM Images Ewout van der Veer, Ruben Hamming-Green, Beatriz Noheda, Majid Ahmadi and Bart J. Kooi; University of Groningen, Netherlands

The analysis of atomic resolution (scanning) transmission electron microscopy images has been a topic of much research interest in recent years due to its ability to locally determine material properties such as elastic strain, electric polarization, phase distributions, etc. Real-space techniques, in particular, have taken flight to circumvent the limitations of traditional methods like geometric phase analysis. In this context, several software packages have been developed, including Atomap, STATstem and mpfit. Although these tools have shown great utility in the analysis of highly idealized images containing relatively few atoms, they tend to fall short on larger images and those with defects like out-of-zone or amorphous regions. This precludes the accurate analysis of, for example, highly strained epitaxial thin films.
We demonstrate the analysis of such strained films consisting of $BaTiO_3$ grown on a $SrTiO_3$ substrate using a Sn-doped $SrTiO_3$ buffer layer with tunable lattice parameter using an in-house developed software package—called S/TEMfit. The package is designed for the *a posteriori* analysis of as wide a range of S/TEM images as possible in a performant and automated manner. It is fundamentally based on principal component analysis for image filtering, a thresholding procedure for atom detection and 2D Gaussian fitting.
We show that S/TEMfit allows us to visualize continuous strain relaxation in our film and resolve inter-layer lattice parameter differences down to at least 2 pm, despite the presence of significantly defective regions in the images. It further allows us to image electric polarization and identify different structural phases in the image.

11:15 AM MD02.08.11
Transfer-Learning Strategies for using Simulated and Experimental Datasets in Machine Learning for Automated HRTEM Characterization Luis E. Rangel DaCosta[1], Katherine Sytwu[2], Catherine Groschner[1] and Mary Scott[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Supervised machine learning techniques offer the potential for high-accuracy, automated analysis of high-resolution transmission electron microscopy (HRTEM) data, providing precise atomic scale characterization of next-generation nanomaterials. However, it can be difficult and expensive to train accurate neural network models which are generally applicable and robust to a wide variety of experimental conditions. Curating sufficient high-quality experimental data to train and develop models with supervised learning techniques is prohibitively expensive and prone to human error and biases. Alternatively, simulated datasets are cheaper to produce and can compete with and even outperform the use of experimental data in neural network training, despite not capturing all fine details of experiment with a given forward model. When both synthetic and experimental data streams are available, it can be advantageous to use all aggregated data for training neural network models, but it is still unclear how to best incorporate multiple datastreams arising from distinct sources when training models.

In this work, we address the challenges of developing experimentally robust and general neural network models to analyze HRTEM data at atomic resolution by using mixed simulated and experimental data streams. Models trained in multiple phases with multiple datastreams can accrue the benefits of each: robust performance and generalization given by large simulated datasets covering a variety of experimental conditions, and well-tuned high-performance on target datasets given by experimental data. We isolate strategies for curating a mix of simulated and experimental HRTEM datasets for training neural networks with good generalization behavior in data-efficient manners through a comparative study of various fine tuning and transfer learning strategies for training neural networks. We observe that, with sufficient experimental data, fine-tuning/transfer learning after pre-training on simulated data can improve the performance of a model beyond what is achievable by training solely with experimental data. The final performance ability is not necessarily tied to how well a model performs after the pre-training stage. In other scenarios, fine-tuning a model on a specific experimental dataset offers only marginal gains in performance at a significant sacrifice to its ability to generalize well to other experimental datasets. Common data augmentation strategies, like sampling non-orthogonal rotations of a training image, further improve performance but again at a sacrifice to generalization. These results point towards pragmatic lessons for producing and deploying machine-learning-based automated characterization tools at low cost and with stronger guarantees on measurement accuracy in scientific environments.

SESSION MD02.09: Virtual Session
Session Chairs: Soumendu Bagchi and Haoran Wang
Tuesday Morning, April 25, 2023
MD02-virtual

8:00 AM MD02.09.01
Data-Driven Characterisation of Materials for Fins and Surfboards Pawel Kryzanowski and Marc In het Panhuis; University of Wollongong, Australia

Surfing waves with surfboards for sport of leasure is practiced in many coastal areas around the world. Surfboards consisting of balsa wood started to spread from Hawaii to mainland USA and Australia. Modern surfboards with a foam core were introduced at the end of the 1950’s.

The mechanical characteristics of surfboards (and fins) most valued by surfers is mechanical stiffness and is generally referred to as flex. During characteristic surfing manoeuvres (bottom turns) a surfboard (and its fins) will bend either due to the shape of wave or the force exerted on the board by the surfer or a combination of both effects.

However, development of new materials for surfboards and fins are almost entirely based on subjective experiences (feedback from surfers) rather than scientific data.

In this presentation we show that data-driven approaches (using sensors) can be used to develop new materials for fins and surfboards that improve performance for surfers. We present the development and field-testing of a working prototype of a surfboard with inbuilt electronics and a set of instrumented fins. We demonstrate that data collected in real-time via telemetry during surfing waves can be used as a research tool for developing new materials for surfboards and/or fins.

8:05 AM *MD02.09.02
Autonomous Workflows for an Accelerated Design of Battery Electrodes and Interfaces Ivano Eligio Castelli; Technical University of Denmark, Denmark

The development of automated computational tools is required to accelerate the discovery of new functional materials, to speed up the transition to a sustainable future. Here, I address this topic by designing new battery electrodes for different intercalation battery chemistries. These workflows are implemented in the framework of Density Functional Theory, using MyQueue and the Atomistic Simulation Environment (ASE). In the first part, I describe a fully autonomous workflow, which identifies materials to be used as intercalation electrodes in batteries, based on thermodynamic and kinetic descriptors like adsorption energies and diffusion barriers [1]. A substantial acceleration for the calculations of the kinetic properties has been obtained due to a recent implementation of the Nudged Elastic Bands (NEB) method, which takes into consideration the symmetries of the system to reduce the number of images to calculate. Moreover, we have established a surrogate model to identify the transition states, which can further reduce the computational cost to at least one order of magnitude [2, 3]. We have applied this workflow to discover new cathode materials for Mg batteries as well as solid state electrolytes for Li, Na, and Mg all-solid-state batteries [1, 3]. In the second part of my talk, I discuss how nanostructured materials can positively impact the Li-ion battery solid/electrolyte interface towards a controlled formation of the Solid Electrolyte Interface (SEI) [4, 5] and to adjust the volume expansion in Si-anodes during battery cycling [6].

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8:35 AM MD02.09.03
Unifying Molecular and Textual Representations via Multi-task Language Modelling Dimitrios Christofidellis, Giorgio Giannone, Jannis Born, Teodoro Laino and Matteo Manica; IBM Research Europe, Switzerland

Neural language models have achieved impressive results in various natural language understanding and generation tasks.
Recently, advances in language models have been successfully transferred to the chemical domain, proposing generative modeling solutions to classical problems from molecular design to synthesis planning.
These new methods have shown potential for optimizing chemical laboratory operations, initiating a new era of data-driven automation in scientific discovery.
However, despite these recent successes, specialized models for each chemical task are typically needed, requiring problem-specific fine-tuning and neglecting tasks' dependencies.
However, the lack of a unified representation between the information expressed in natural language and chemical representations is the main limiting factor in the interaction between humans and the models. Inspired by recent advances in generative transfer learning, we explore a multi-task language model that can tackle a large variety of tasks in the chemical and natural language domains.
We rely on mono-domain, frozen encoder models and jointly fine-tune a decoder on multiple domains.
In doing so, we relieve the cross-domain training from computationally expensive, data-hungry pretraining, leveraging the power of language models trained on unstructured data.
Furthermore, we apply multi-task learning to increase model expressivity and information sharing between modalities.
In this way, our model handles chemical and natural language concurrently and can solve numerous chemical and natural language-based tasks using a single set of weights.
We quantitatively evaluate our method against state-of-the-art baselines, exploring different strategies to adapt and fine-tune cross-domain language models.
Our work paves the way for robust and efficient language models accelerating discovery in physical sciences.

8:50 AM MD02.09.04
Growing Strings in a Chemical Reaction Space for Searching Retrosynthesis Pathways Federico Zipoli, Carlo Baldassari, Matteo Manica, Jannis Born and Teodoro Laino; IBM Research Zurich, Switzerland

Machine learning algorithms demonstrated remarkable accuracy in predicting the outcomes of chemical reactions, often outperforming human experts. Simultaneously, a high level of precision was achieved in the single-step retrosynthesis prediction problem. However, designing a synthesis pathway leading to a given product is a challenging task that runs up against the limits of many currently available ML-driven algorithms. Like the game of chess, retrosynthesis route prediction entails putting together a series of steps to create a given product from existing substances, with the goal of optimizing the synthesis efficiency by taking advantage of specific strategical game rules like protection, deprotection, FGI, etc. Because current machine learning models are trained on single reaction steps, they lack knowledge of these strategy rules. Here, we recast the retrosynthesis problem as a string optimization problem, capitalizing on the homology between the chemical reaction space and a multidimensional geometrical space. If we think of chemical reactions as multidimensional vectors (fingerprints), then a synthesis in this space is a string that involves three or more connected fingerprints. An extensive corpus of chemical synthesis, comprising approximately 1.2M examples, was extracted and added as strings to the chemical reaction space. We use the Euclidean metric to minimize the distance between the trajectory of the growing retrosynthesis string and the existing strings. By doing so, we aim to assemble steps that, in the chemical reaction space, will grow along paths more similar to existing retrosynthesis, thereby inheriting the strategic guidelines compiled by domain experts. We integrated this approach into the RXN platform (https://rxn.res.ibm.com/) and present the method's application to complex synthesis as well as its ability to produce better synthetic strategies than current methodologies.

9:05 AM MD02.09.05

Structure–Property Relationships for Electron Trapping in Amorphous Oxides Cameron Chevalier[1,1], Alex Greaney[1] and Mahesh R. Neupane[2]; [1]University of California, Riverside, United States; [2]U.S. Army Research Laboratory, United States

Amorphous oxides are promising functional materials for use in a number of next generation electronics applications, both because of their ability to accept and immobilize electrons in multilayer devices, and because of the tunability of the amorphous atomic packing. In this talk, we present our multi-scale approach to modeling the macroscopic electronic properties of materials that are inherently structurally inhomogeneous. For this, we link classical molecular dynamics simulations with small-scale high fidelity density functional theory calculations of electronic structure to generate an effective "representative volume" sampling of the amorphous material. Using the same approach, we study the distribution of trapping probabilities from impurity and stoichiometric defects in a-Al_2O_3, and use machine learning methods to identify structural outliers, or packing defects, in these systems.

9:20 AM *MD02.09.06
Operator Learning for Predicting Fracture Paths in Brittle Random Media Ariana Quek and Johann Guilleminot; Duke University, United States

We present an operator learning approximation framework for brittle fracture. The proposed approach aims to alleviate the computational cost associated with full-scale, phase-field simulations in studying brittle fracture in heterogenous materials. Our strategy relies on the combination of dimensionality reduction and learning between function spaces. We first explore optimal strategies to encode and decode smooth and non-smooth physical fields, including the use of linear and nonlinear reduction techniques. A probabilistic learning technique is subsequently leveraged to map between the latent spaces. The accuracy of the method is finally demonstrated considering fracture path simulations in a random medium exhibiting stochastic spatially varying toughness.

SYMPOSIUM

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SESSION NM01.01: Janus Nanomaterials—Fabrication
Session Chairs: Sambeeta Das and Zhifeng Ren
Wednesday Morning, April 12, 2023
InterContinental, Fourth Floor, Telegraph Hill

8:00 AM NM01.01.01
Deposition of Boron Nitride by Micro Hollow Cathode Discharge Claudia Lazzaroni, Manoel Jacquemin, Hiba Kabbara, Alice Remigy, Ovidiu Brinza, Guillaume Lombardi and Vianney Mille; LSPM CNRS USPN, France

In this presentation, we propose an alternative synthesis method to deposit thin film material hexagonal boron nitride (h-BN) assisted by microplasma source. h-BN thin films are the focus of interest for electronic and optoelectronic applications due to its wide band gap semiconductor (and 2D layered structures). In other hand, microplasmas have attracted growing attention in recent years because of possible applications in various fields such as surface treatment, light sources and nanomaterial synthesis. They can be generated at high pressure which is a favourable condition to better dissociate N_2 molecules, a prerequisite to the synthesis of nitride materials at lower temperatures compared to conventional processes.

Our deposition reactor is composed of two chambers and the micro-plasma is located at the junction between them. The plasma source is generated by a micro hollow cathode discharge (MHCD) which consists of an anode-dielectric-cathode sandwich through which one hole of 400 µm in diameter is drilled. The injected gas is an argon/nitrogen mixture. The higher pressure chamber (several tens of mbar), favors the production of high density plasma, and consequently high nitrogen dissociation, while the lower pressure chamber (several mbar) limits the nitrogen recombination. The polarizable and heating substrate holder is located in the lower pressure chamber where the boron precursor (BBr_3) and hydrogen are injected. The polarization of the substrate holder with a DC positive voltage of several hundreds of volts allows the discharge to be expanded from the hole to the substrate. Suitable conditions can be defined to achieve the BN growth. We report the growth of BN on silicon and sapphire substrates at temperatures below 1000°C and present the characterizations of the different BN deposited. The synthetized BN type depends of the nature of the substrate, the deposition duration, the gas compound and the distance between the MHCD source and the substrate. This latter has a major role on the stoichiometry and the stability of the deposited films.

8:15 AM NM01.01.02
Engineering Light-Activated Microswimmers for Controllable Motion and Interparticle Interactions John A. Castaneda[1], John G. Gibbs[1] and Jennifer Martinez[1,2]; [1]Northern Arizona University, United States; [2]Los Alamos National Laboratory, United States

Inspiration for new materials often comes from observations of natural phenomena, such as the swarming of flocks of birds and schools of fish. That dynamic and concerted motion of the natural world can also be observed at the micron and nanoscale, where collections of engineered and self-propelled nano- or micron-particles "swim" in viscous fluids. These active matter microswimmers consume energy and through that catalysis exert mechanical motion. Beyond creating materials that can actively control and manipulate their environment, active materials hold promise for new applications in both the synthetic and living worlds, if only their catalytic activity and subsequent motion can be precisely engineered.

An example of artificial, nonbiological microswimmers is a catalytic Janus particle that has surface-asymmetry with specific physico-chemical properties at different locations upon the particle. Controlling this asymmetry may allow one to engineer these kinds of dynamics exhibited but here we are interested in self- propulsion. Two primary methods have been established for self-propulsion: (1) ejection of bubbles, akin to jet- propulsion, and (2) sustained creation of temperature or concentration gradients. As the scale decreases, only the latter appears possible, but this method requires high catalytic activity of the particles as well as asymmetry in either the shape or materials properties of the particles themselves. These Janus microswimmers are synthesized with a catalytic material (e.g., bulk metal gold or platinum) selectively deposited on one side of micron-particle. The morphology of the particle enables the sustained thermodynamic gradient that induces motion.

Unfortunately, bulk metal surfaces are not nearly catalytically active nor selective enough to enable future applications in active matter, particularly as the active matter particle decreases in size. Metal nanoclusters, however, because of their ultrasmall size, unique packing and high surface to volume ratios, tend to have far higher photocatalytic and substrate selectivity than do nanoparticles or bulk surfaces of similar compositions.

To date, there are two primary limitations in the field of active matter that we can, eventually, overcome using clusters as the catalytic booster: (1) low overall catalytic efficiency, which should be overcome with the high catalytic activity of clusters; and (2) little ability to tune the directionality of the active matter motion. The latter should be overcome by directional deposition of different clusters within the same titanium dioxide (TiO2) micron-particle; wherein the motion of the particle would change as a function of which cluster is activated. Clusters and their activation will differ by bandgap/wavelength of excitation or catalytic selectivity/reagent addition. The successful extrapolation from our results suggests that differing sized nanoclusters, with different band-gaps, may tune the light needed for TiO2 activation, thus creating an important knob for coupling active matter to the environment.

In this talk, I will focus on the approach, design and fabrication of my microswimmers to achieve the catalytic activity required for propulsion. I propose that it is possible to engineer photoactive microswimmers for desired motion directly from a metal oxide photocatalyst, magnetic materials and combing these microscale swimmers with other nanoscale structures through: (1) Physical Vapor Deposition (PVD) and Glancing Angle Deposition (GLAD) with electron beam and thermal evaporating systems; (2) Constructing microswimmers from photoactive material such as TiO2 that gives a more effective level of control in comparison to traditional catalysts since the activity, intensity of propulsion can be turned on-and-off using UV light; (3) Creating microswimmers with a coating of precise nanoclusters. Combined, these ideas allow for the creation of active microswimmers that exhibit controllable collective motion and behavior.

8:30 AM *NM01.01.03
Distinct Chemical and Physical Properties of Janus Nanosheets Peiran Wei and Emily Pentzer; Texas A&M University, United States

Janus particles have recently garnered significant attention for their distinct properties compared to particles that are homogeneously functionalized. Moreover, high aspect ratio Janus particles that are rod-like or planar (i.e., nanosheets) are especially intriguing considering their interfacial properties as well as their ability to assemble into higher-order and hybrid structures. To date, major challenges facing the exploration and utilization of 2D Janus particles are scalability of synthesis, characterization of tailored chemical functionalization, and ability to introduce a diverse set of functionalities. Herein, a facile method to access Janus 2D graphene oxide (GO) nanosheets by combining a Pickering-type emulsion and grafting-from polymerization via ATRP is reported. Janus GO nanosheets bearing PMMA on one face as well as the symmetrically functionalized analogue are prepared, and the chemical, thermal, structural, surface, and interfacial properties of these materials are characterized. Time-of-flight secondary ion mass spectrometry coupled with Langmuir−Blodgett films is shown to be an ideal route to conclusively establish asymmetric functionalization of 2D materials. This work not only provides a facile route for the preparation of Janus nanosheets but also demonstrates the direct visualization of polymer grown from the surface of GO.

9:00 AM *NM01.01.04
Surface Engineering of Patterned Polymer-Tethered Nanoparticles Eugenia Kumacheva; Univ of Toronto, Canada

Patterning of colloidal particles with chemically or topographically distinct surface domains (patches) has attracted intense research interest. Surface-patterned particles act as colloidal analogues of atoms and molecules, serve as model systems in studies of phase transitions in liquid systems, behave as 'colloidal surfactants' and function as templates for the synthesis of hybrid particles . The generation of micrometer- and submicrometer-sized patchy colloids is now reached the state of the art, however surface patterning of nanoparticles with dimensions of the order of tens of nanometres remains a challenge.

We develoepd a strategy for surface patterning nanoparticles by utilizing thermodynamically driven segregation of polymer ligands from a uniform polymer brush into surface-pinned micelles following a change in solvent quality. The methodology offers the ability to control the dimensions of patches, their spatial distribution and the number of patches per nanoparticle, in agreement with a theoretical model. The versatility of the strategy is demonstrated by patterning nanoparticles with different dimensions, shapes and compositions, tethered with various types of polymers and copolymers and subjected to different external stimuli. These patchy nanocolloids have potential applications in fundamental research, the self-assembly of nanomaterials, diagnostics, sensing and colloidal stabilization.

9:30 AM BREAK

10:00 AM *NM01.01.05
Scale-Up Production of Janus Graphene by Interfacial Nano-Reactor for Enhanced Oil Recovery Applications Sehoon Chang, Gawain Thomas and Wei Wang; Aramco Americas, United States

As an emerging enhanced oil recovery (EOR) technology, nanofluid flooding has been developed for the oil displacement or injectivity improvement in oil reservoirs. However, current nanofluids with conventional nanoparticles show relatively low efficiency for EOR, especially with low concertation under laboratory condition. The research aims to investigate a new type of nanomaterials, Janus nanofluids, as highly effective alternative nano-agents for EOR applications under reservoir conditions and introduce a new cost-effective scale-up synthesis method for industrial applications. A lyotropic liquid crystal phase as a novel “interfacial nano-reactor” system has been demonstrated to synthesize Janus nanomaterials at numerous liquid-liquid interfaces. Compared to the conventional bi-phase reaction system, the new “interfacial nano-reactors” could greatly enhance the efficiency of the interfacial reaction by more than a million times, and thus allow production of Janus nanomaterials in mass quantity at low cost for industrial applications. Large quantities of Janus graphene nanosheets have been successfully synthesized via this method and characterized by scanning electron microscopy (SEM), Langmuir-Blodgett (LB), contact angle, fluorescence imaging and interfacial tension (IFT) measurements. With a low concentration of Janus graphene nanosheets in nanofluid formula, microfluidic imaging and core-flooding experiments have been performed to evaluate the efficiency of the nanofluids for oil displacement in carbonate reservoirs.

The Janus graphene nanosheets with proper hydrophilic/hydrophobic functionalization can be directed and assembled onto the interface of water and oil, which has been characterized by microfluidic imaging. The Janus graphene nanosheets can significantly lower the interfacial tension (IFT) values between brine and crude oil at simulated reservoir conditions. The core flooding measurements have demonstrated that the Janus nanofluids at ultra-low concentrations (less than 0.01 wt %) remarkably promote oil displacement in simulated carbonate reservoirs. A novel scale-up method for mass production of Janus graphene nanosheets at low-cost (about one million times more efficient than the conventional bi-phase method) has been demonstrated. The novel Janus graphene nanofluids have been utilized for improving efficiency of oil recovery at ultra-low concentration (less than 0.01 wt%).

10:30 AM *NM01.01.06
Synthesis and Self-Assembly of Janus Au-Fe_3O_4 Nanoparticles Shan Jiang; Iowa State University of Science and Technology, United States

We have developed methods to fabricate Janus nanoparticles. In one example, Janus Au-Fe_3O_4 dumbbell nanocrystals (< 20 nm) were synthesized with the hydrophobic ligands coated on the Au lobe and negatively charged hydrophilic ligands coated on the Fe_3O_4 lobe. We can control the self-assembly of nanoparticles in aqueous solutions by systematically balancing the hydrophobic and hydrophilic moieties. The strong interparticle plasmonic coupling displayed a red-shift in surface plasmon resonance, with larger structures formed by Au-Au-Fe_3O_4 assembly extending into the near-infrared region.

11:00 AM NM01.01.07
Scalable Continuous Flow Synthesis of Janus-Like Gold-Polystyrene Particles with Tailored Morphology and Optical Properties Julia S. Seifert and Robin N. Klupp Taylor; Institute of Particle Technology (LFG), Germany

A wide range of Janus and, more broadly, patchy particles, have been reported over the last decade. Impressive control over single particle and collective properties has motivated interest from numerous application fields. Nevertheless, commercial exploitation is currently held up by a considerable lack of techniques to produce such particles on a large scale. In this contribution, we give details of a simple process for the synthesis of Janus-like and patchy particles which is both highly tunable in terms of the product morphology and properties, and also scalable. Our approach, which produces gold patches on polystyrene core particles, is based on a continuous flow process realized as a cascade of two millimeter scale T-mixers. Such an arrangement is an excellent compromise between high mixing intensity and scalability. In the first mixer the core particles, which are positively charged, are heterocoagulated with a small number (typically fewer than four) ultrafine negatively charged gold nanoparticles. The latter function as seeds for an electroless gold plating reaction initiated at the second T-mixer resulting in typically < 20 nm thick conformal gold patches. Simple variations of the reaction and process conditions enable us to tailor the coverage, thickness and density of the patches, thus accessing a wide range of Janus-like and patchy morphologies. Moreover, the local surface plasmon resonance of gold nanostructures offers the possibility of product particles with tunable visible and near-infrared properties as well as a convenient means to investigate and optimize the synthetic process. Regarding the latter, in the present contribution we will introduce a process-property function which relates a dimensionless parameter representing the amount of gold precursor per seed to the optical properties and metal patch morphology. Moreover, we will show how this relationship is affected by the concentration of other key parameters like the reducing agent, chloride ion concentration and core particle size.
The high tunability of optical product properties mentioned above makes our Janus-like particles relevant for various application fields, e.g. in pigments, sensors or theranostics. In this context, we demonstrate how particle concentration and sample volume can be scaled-up with our continuous flow set-up. We will also demonstrate that the necessary post-synthetic treatment (washing, stabilization etc.) can be achieved without significant reduction in product properties.

11:15 AM NM01.01.08
Hierarchically Grown Nanostructure for Suppressing Leaching in Fiber Optic Chemical Sensing Adil Alshoaibi; King Faisal University, Saudi Arabia

Owing to fiber-optic pH sensing, phenolphthalein immobilized SiO2 nanoparticles (P-SNPs) and phenolphthalein immobilized SiO2–TiO2 nanoparticles (P-STNPs) are synthesized by low-temperature sol-gel route. The P-SNPs revealed hierarchical structure, surface roughness (Ra) 7 nm, surface area ~442 m2/g, n (refractive index) 1.37 at 550 nm which is significant for pH sensing. The P-STNPs exhibited granular structure, low Ra 3 nm, surface area ~219 m2/g, n around 1.52 at 550 nm. Both matrices are thermally stable around 250 C. The P-SNPs and PSTNPs sensitivity is calculated ~22 counts/pH and 19 counts/pH with the determination coefficient (R2) ~ 0.99.
The pka value of P-SNPs is measured ~9.5 and time response 0.11s within pH 12 without leaching which is higher than P-STNPs (9.1) and 3.9 s with leaching. Experimental findings suggested P-SNPs have the potential for practical usage in intense basic media.

11:30 AM NM01.01.09
Synthesis of Patchy Nanoparticles by Atomic Stencils for Scaled-up Self-Assembly Chansong Kim, Ahyoung Kim, Lehan Yao, Eric Yang, Yu-Shen Liu, Xiaoying Lin and Qian Chen; University of Illinois, Urbana-Champaign, United States

In this talk, we will discuss our recent work in developing and implementing a universal atomic-stencil method to prepare polymer-patched gold nanoparticles (NPs) with different shapes and patch patterns at a superior monodispersity and synthesis yield. The facet-dependent adsorption energy of ligands allows for selective attachment of block copolymer onto different sites of NPs, including the hard-to-achieve facet patches. We demonstrated our synthesis method is universally effective for diverse shapes of NPs from simple faceted polyhedral to complicated-crystalline spherical NPs. As a result, we were able to achieve a wide library of facet-specifically decorated patchy NPs. Furthermore, scaled-up assemblies (tens of micrometers) of the patchy NPs were also made through a careful control of solvent evaporation, which show novel mechanical and optical properties. We expect that our study will provide the groundwork for high-quality patchy NPs and their assemblies which are crucial for practical applications in diverse areas.

11:45 AM NM01.01.10
Correlated Electrostatic Interactions in High-Capacitance Zwitterion Containing Thin Films Loren G. Kaake; Simon Fraser University, Canada

Given their oppositely charged ends, zwitterionic small molecules are perhaps the smallest example of a Janus nanomaterial. We have synthesized an imidazolium and trifluorosulfonoimide based zwitterionic molecule that can be doped into conventional polymers like poly(methyl methacrylate) (PMMA). At low zwitterion doping levels, the films act as expected under an applied electric field, including zwitterions provides a small but measurable increase to the capacitance. However, above a critical concentration, the zwitterions begin to interact electrostatically with each other. This interaction results in a sharp increase in the thin film capacitance, approaching that of an electrostatic double layer. Polarized optical microscopy and grazing angle wide angle x-ray scattering shows a dramatic increase in the overall film crystallinity, presumably as a result of electrostatically driven ordering of the zwitterionic molecules. The high capacitance of the thin films can be used to create both n-type and p-type field effect transistors that operate below 5 V, demonstrating the utility of zwitterion containing thin films as high capacitance ambipolar electrolyte dielectric materials.

SESSION NM01.02: Janus Nanomaterials—Structure/Property

Session Chairs: Zhifeng Ren and Christopher Wirth
Wednesday Afternoon, April 12, 2023
InterContinental, Fourth Floor, Telegraph Hill

1:30 PM NM01.02.01
Correlated TERS and KPFM Imaging of the SeMoS Janus Monolayer Crystals Ziyang Gan[1], Antony George[1], Andrey Krayev[2] and Andrey Turchanin[1]; [1]Institute of Physical Chemistry, Jena University, Germany; [2]Horiba Scientific, United States

We report the first time nanoscale, tip enhanced Raman scattering (TERS) imaging of the SeMoS Janus monolayers crystals both as-grown on gold foil and transferred from the growth substrate to the gold-coated silicon wafers. Due to the preferential enhancement of the out-of-plane modes in the gap-mode of TERS, the TERS spectra of SeMoS differ from the conventional Raman spectra reported earlier [1, 2]. The $A_1^1$and A_1^2 out-of-plane modes are shown to be the first and the second strongest Raman peaks in TERS, while in conventional Raman spectroscopy the A_1^2 mode is extremely weak. Interestingly, the red shift of the spectral position of A_1^2 mode correlates with a decrease of the contact potential difference in Kelvin probe force microscopy (KPFM) images.. While the TERS maps mostly show the Raman spectra characteristic to the high quality SeMoS Janus monolayers, we observed in some cases narrow, below 20-30 nm, areas that featured a peak at 406 cm^{-1} which could be interpreted as the A' band of MoS_2. The ability to detect the nanoscale imperfections in Janus monolayer crystals is a mandatory condition for optimizing their synthetic routes. TERS imaging cross-correlated with KPFM measurements demonstrate the applicability for the nanoscale assessment of the structural homogeneity of both the as-grown and transferred SeMoS Janus monolayer crystals.
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2. Marko M. Petrić, Malte Kremser , Matteo Barbone et.al. PHYSICAL REVIEW B 103, 035414 (2021)

1:45 PM *NM01.02.02
Janus Particle-Laden Fluid Interfaces—Microstructure, Rheology and Stability Sepideh Razavi, Dimitrios Papavassiliou and Elton Corriea; University of Oklahoma, United States

The behavior of colloidal particles in vicinity of fluid interfaces has intrigued scientists since the early 1900s. The large binding energy, relative to the thermal energy, causes particles to irreversibly adsorb at the interface, a useful attribute in the engineering of interfacial systems in various applications including pharmaceutics, food stabilization, oil recovery, and personal care products. The use of Janus particles in interfacial applications is of particular interest since they combine the colloidal-scale properties of particle stabilizers (i.e., large desorption energy from fluid interfaces) with the molecular-scale properties of surfactants (i.e., tunable amphiphilicity). In many such applications, interfacial materials become subjected to deformations that produce compression/expansion and shear stresses. Therefore, it is important to understand the impact that the Janus character brings to interfaces. In this talk, I will review our findings on how Janus particles influence the stability and rheology of fluid interfaces. I will discuss the impact of particle amphiphilicity on the capillary interactions, the resulting interfacial microstructure, and their connection to the flow behavior. Building on this information, I will present our research in understanding the dynamics of complex interfacial systems comprised of colloidal particles and surfactant molecules under an applied stress, especially in elucidating the rich physical mechanisms that affect their synergism at interfaces.

2:15 PM *NM01.02.03
Active Surface Agents—Swimmers at Fluid Interfaces Jiayi Deng[1], Mehdi Molaei[2], Nicholas Chisholm[3] and Kathleen Stebe[1]; [1]University of Pennsylvania, United States; [2]The University of Chicago, United States; [3]Worcester Polytechnic Institute, United States

Active colloids, self-propelled microscale objects, have generated tremendous excitement because of their ability to swim, interact, and self-organize. Active colloids interact with boundaries, fundamentally changing their swimming behavior. However, the effect of fluid interfaces on active colloid motion is unknown. Fluid interfaces are highly non-ideal, complex domains that impose constraints that alter swimming behavior. We study bacteria as model active colloids to understand these constraints and their implication. Bacteria attach to interfaces with pinned contact lines, which fix the angle of the cell bodies at the interface and constrain the arrangement of the flagellum. As a result, similar bacteria have different trapped configurations and widely different swimming behaviors. Interfacial stresses further constrain the interfacial flow via diverging Marangoni stresses-surface tension gradients- that dictate divergence-free motion or incompressibility in the interface.
We focus on swimming behaviors and hydrodynamics of *Pseudomonas aeruginosa* PA01 at aqueous- hexadecane interfaces. The bacteria can swim adjacent to the interface, or they can adsorb directly and swim in an adhered state with complex trajectories that differ from those in bulk in both form and spatio-temporal implications. To understand their impact on interfacial transport, we visualize the interfacial flows generated by PA01 in pusher modes and find flow fields with unexpected symmetries that differ significantly from their bulk fluid counterparts. Analysis reveals that these flow fields can be decomposed into two dipolar hydrodynamic modes associated with incompressible interfaces. The relative importance of these modes is determined by the cell bodies' trapped configurations.
Hydrodynamic theory allows us to understand this flow field fundamentally and to explore its implications on mixing in the interface. Our aim is to advance the concept of an *Active Surface Agent*, an active colloid trapped at fluid interfaces whose motion and trapping state can be designed to promote mixing and structure formation. This concept represents an important and largely untapped degree of freedom for interfacial engineering. By understanding how biological swimmers move at fluid interfaces, we can develop design rules for artificial biomimetic systems to promote transport at fluid interfaces with broad implications in chemical engineering processes.

2:45 PM BREAK

3:15 PM NM01.02.04
Magnetic Janus Microrobots for Cellular Manipulation Fatma Ceren Kirmizitas, Sudipta Mallick, Max Sokolich and Sambeeta Das; University of Delaware, United States

Inspired by the biological motors at the micron and nanoscale, various microscale robots have been developed that can be actuated in cellular environments and are on the same length scale as biological motors. However, motion at such low length scales is hard to control due to thermal fluctuations. In our group we have developed microscale robots that can be actuated using magnetic fields in dense cellular environments. In this work we will present the fabrication and manipulation of magnetic Janus microrobots which can be navigated in tight channels mimicking blood vessels. We will also demonstrate automated control of microrobot motion and its application for cellular manipulation. This precise wireless control of Janus microrobots is also able to transfer cells against fluid flows.

3:30 PM NM01.02.05
Study on the Low-Damage Atomic Layer Etch of Various Two-Dimensional Materials Dongryul Lee[1] and Jihyun Kim[2]; [1]Korea University, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)

In the recent processes of nano-electronics and ultra-integrated semiconductors, good electrical/chemical properties of ultra-thin materials are essential. Silicon is an appropriate material with manufacturing and doping potential that is suitable for commercial processes, but it has limitations in electrical properties due to the short-channel effect in application to ultra-integrated and scale-downed devices that advance every year. Two-dimensional (2D) materials, incorporating graphene, hexagonal boron nitride, and transition metal dichalcogenide materials are suitable for the nanometer-scale processes owing to their atomic-scale thickness and excellent electrical/optical properties. In addition, the surface dangling bonds and defect sites of the exfoliated/grown thin film are nominal in the atomically-flat surfaces of 2D materials. 2D materials can be applied as a component of a next-generation semiconductor that is sensitive to malfunction.
Numerous studies of 2D material-based nano-electronics and optoelectronic devices with outstanding electrical/optical performances have been reported. However, applying the 2D materials to commercial dry- and wet-etch processes is limitary because of the chemical/mechanical stability due to their atomically clean surface. In the past, radicals with physical energy have been used to break a stable surface state, but there are two restrictions. 1) Precisely controlling the etch thickness is difficult. 2) The properties of the material deteriorated by the surface damage caused by energetic ions. Therefore, to apply 2D materials as a commercial semiconductor, introducing an atomic-layer etching (ALE) technology that cuts off one or two layers while suppressing damage and precisely controlling the etching rate is necessary.
In this study, a plasma-based ALE method with low damage was demonstrated and proved applicable to various two-dimensional materials (Graphene, h-BN, MoS_2, $MoTe_2$, WSe_2, WS_2). Atomic force microscope analysis was proceeded to confirm the precisely controlled etching rate of 1 to 2 layers and the roughness of the surface. The crystalline quality of the etched region was analyzed by Raman spectroscopy measurement. Through the fabrication of few-layer-thick 2D material-based field-effect transistors with ALE technology identifies the possibility of application to electronic devices. This ALE technology has high versatility as it can be progressed by the conventional dry-etch equipment of commercial semiconductor processes. The traditional gas used in the etching causes little damage to the polymer mask, this ALE can be arranged to self-aligned and selective etch processes. Our work can contribute to the introduction of a commercial electronic device manufacturing process with 2D materials. More details of our work will be discussed in the presentation.

3:45 PM NM01.02.06
β-Ga_2O_3 Metal-Semiconductor Field-Effect Transistor with High Breakdown Voltage Applied h-BN Slant Field-Plate Jeongmin Kim, Dongryul Lee and Jihyun Kim; Seoul National University, Korea (the Republic of)

The fast growth of green energy, electric vehicle, and aerospace industries has necessitated the development of power electronics technology, encouraging the research into wide bandgap semiconductor materials. Wide bandgap semiconductors are suitable for high-power and radio frequency (RF) applications due to their fast switching and excellent breakdown characteristics allowing high-voltage or high-current operations. Beta gallium oxide (β-Ga_2O_3) is an ultrawide bandgap (4.9 eV) semiconductor material one of the five phases of the gallium oxide family. Baliga's figure of merit (BFOM) is a parameter representing the relative performance of semiconductor materials as a power device, and the BFOM of 3444 for β-Ga_2O_3 demonstrates its superior characteristics compared to silicon carbide (340) and gallium nitride (870). The metal-oxide-semiconductor field-effect transistor (MOSFET) is the basic building block of integrated circuits, where the interface between the channel and the dielectric material is critical to its performance. Compared to that of silicon-based MOSFETs, the performance of β-Ga_2O_3-based MOSFETs is far more degraded by the high trap density of the interface between the gate oxide to the channel. Metal-semiconductor field-effect transistor (MESFET) structure was introduced to resolve this problem. In a MESFET, the channel is switched on and off by the electric field induced by the bias applied at the top-gate, where the Schottky barrier at the contact between the gate metal and the semiconductor minimizes the gate leakage current. In RF devices, the MESFET structure is suitable due to its lack of the oxide dielectric layer, leading to low capacitance level owing to the Schottky contact, and far less interface traps. In a MESFET, however, concentration of the electric field occurs at the edge of the interface between the gate metal and the semiconductor. This electric field concentration acts as a point of electrical breakdown, instigating premature breakdowns. The electric field concentration can be alleviated, and thereby increasing the breakdown voltage, by the implementation of the field-plate structure. In this research, a gate field-plate structure using hexagonal boron nitride (h-BN), a two-dimensional material with high thermal conductivity and excellent insulating performance, is adopted for a MESFET with a β-Ga_2O_3 channel. Although the electric field concentration is relieved by the h-BN field-plate structure, the junction where β-Ga_2O_3, h-BN, and gate metal meet still experiences the concentrated electric field which induces reduction in the breakdown voltage. A slant field-plate structure was designed to reduce the angle of h-BN sidewall in contact with the gate metal and Silvaco simulation software was utilized to predict the lateral distance of the h-BN edge to the source electrode to optimize the attenuation of electric field concentration. Electron-beam lithography and downstream plasma etching techniques were used to etch the part of h-BN to reduce the angle of the h-BN sidewall by the undercut induced by the isotropic etching. Ni/Au gate was deposited on β-Ga_2O_3 and h-BN by electron-beam lithography and electron-beam evaporation. The angle of the h-BN sidewall was measured to be approximately 30° by atomic force microscopy and the breakdown characteristic of the device assessed by the 3-terminal breakdown measurement showed improvement compared to that of the conventional gate field-plate structure. The application of the slant field-plate structure can be expected to realize the full potential of β-Ga_2O_3 as a power device.

4:00 PM NM01.02.07
Non-Oxidized Bare Metal Nanoparticles in Air—Negatively Charged Surface with Excess Electrons Transferred from Two-Dimensional Electride Athira Thacharon and Sung Wng Kim; Sungkyunkwan University, Korea (the Republic of)

Athira Thacharon[1], Sung Wng Kim[1]
Department of Energy Science, Sungkyunkwan University, Republic of Korea[1]

Instability of metal surface toward oxidation has been of classical issue, but still important in fundamental science and practical applications. Passivation of metal surface with additional moieties or post-treatments have been considered as the most prominent solutions for impeding oxidation, especially in the field of nanoscience and technology. Indeed, non-oxidized bare metal nanoparticles (NP) in air have been hardly realized. Here, we report oxidation-resistant bare metal NPs in air by mimicking the cathodic protection in nanoscale using electride as an electron source [1]. Cu NPs grown on electrides are thoroughly investigated by atomic scale observations and chemical analyses combined with theoretical calculations revealing that ultra-high oxidation-resistant behavior is originated from the large work function difference between Cu and electride, inducing negatively charged surface state on Cu NPs. Furthermore, we developed a rational approach for non-oxidized bare metal NPs by wet chemical solution process employing electride as an electron-donating agent to reduce diverse metal precursors in alcoholic solvents [2]. Atomic-scale structural and chemical analyses confirm all synthesized bare Cu, Ag, and Sn nanoparticles are ultra-stable in ambient air, exhibiting no trace of metal oxides. These obtained results suggest a revolutionary breakthrough for rational protection of Cu and other metal NPs against oxidation in ambient air for various practical applications such as heterogeneous catalysts [3].

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4:15 PM NM01.02.08
Surface Patterning of Au Tetrahedra with Block Copolymer Patches Xiaoying Lin[1], Chansong Kim[1], Thi Vo[2], Haihua Liu[3], Tommy Waltmann[2], Jiahui Li[1], Sharon Glotzer[2] and Qian Chen[1]; [1]University of Illinois at Urbana-Champaign, United States; [2]University of Michigan–Ann Arbor, United States; [3]Argonne National Laboratory, United States

Patterning of nanoparticles with distinct surface patches has attracted intense research interest through the past decade. Here, we demonstrate the synthesis of patchy tetrahedra focused on the thermodynamic and scaling behaviors of amphiphilic block copolymers. By engineering the surface chemistry via facet-selective ligands and controlling polymer-solvent interactions, the copolymers form different patterns on the surface of Au tetrahedra, including vertex-patches, edge-patches, and clover-like patches. We also demonstrate the controlled clustering of the patchy tetrahedra and study their plasmonic coupling properties. Our study expands the fundamental studies on the polymer behaviors on nanoparticles with novel geometry and sophisticated surface chemistry and shows as a promising strategy for the design of functional nanomaterial and composites.

4:30 PM NM01.02.09
Two-Phase Janus Nanoparticles Obtained from Thin Fe/Au Bilayers Chen Errera and Eugen Rabkin; Technion–Israel Institute of Technology, Israel

Metallic Janus nanoparticles (NPs) are usually synthesized employing wet chemistry methods. Such NPs are thermodynamically unstable at elevated temperatures due to interdiffusion and reactions between constituent metals. In this study, we fabricated thermodynamically stable Janus NPs containing face centered cubic Au-based and body centered cubic Fe-based phases employing a solid state dewetting (SSD) of thin Fe/Au bilayers deposited on sapphire substrate. We found that the size distribution and morphology of the Janus NPs can be varied by changing the overall compositions, the deposition order of individual sub-layers, and the SSD parameters. The combination of Au, which is an inert, conducting, optically active at the nanoscale and biocompatible metal, along with the ferromagnetic Fe, results in unique set of properties that can be utilized in the opto-magnetic and sensing applications. In particular, by selective etching of Fe we obtained single-phase Au NPs with unusual shapes, enhancing their optical response

SESSION NM01.03: Poster Session: Janus Nanomaterials
Session Chairs: Sambeeta Das and Wei Wang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM NM01.03.01
Metal-Metal Phosphide Synthesis—Selective Phosphidation of Ag-Cu Nanocrystals Xiao Ma and Abdessadek Lachgar; Wake Forest University, United States

The incorporation of phosphorous into metal nanoparticles is an important strategy to affect material's structure and bonding, its electronic structure, and its catalytic property. Colloidal synthesis, hot injection in particular, is well known for its versatility and can be an alternative approach for Janus nanomaterials synthesis.
In this work, we present the colloidal synthesis of metal-metal phosphides, by preparing metal-metal nanoparticles followed by selective phosphidation. We applied this strategy to convert Ag-Cu to Ag-Cu_3P. Ag-Cu nanoparticles were prepared using $W(CO)_6$ as the reducing reagent as previously described by Quan *et al*.[1] Phosphidation of Cu nanoparticles was performed using tris(trimethylsilyl)phosphine and trioctylphosphine as previously reported by Schaak *et al*.[2] Partial phosphidation of the Cu-Ag nanoparticles led to the formation of Ag-Cu_3P nanocrystals. The materials before and after phosphidation were used as electrocatalysts for hydrogen evolution in 0.1 M NaOH. The onset potential of Ag-Cu_3P is 200 mV smaller than that for Ag-Cu, indicating that incorporation of phosphorus into metal-metal nanocrystals not only enhances their stability but also their catalytic activity. The phosphidation conversion described here can be achieved when substituting Cu by Ni, Co, Fe, and substituting Ag by Au if the Janus metal-metal can be obtained.

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5:00 PM NM01.03.02
Integration of Mesopores into Paper Materials Using Sol-Gel Chemistry Dominik Richter, Joanna Mikolei and Annette Andrieu-Brunsen; Technische Universität Darmstadt, Germany

Cellulose based materials are beneficial economically and ecologically due to their renewability, recyclability and biodegradability. The hierarchical porosity of cellulosic fibers in paper is a prerequisite and key factor to optimize application potential e.g. in the field of lab-on-chip-technology, sensors, point of care diagnostics, etc. The reason for this impact of fiber structure is its influence on capillary fluid imbibition, wettability, or mechanical stability of paper. Upon paper production, porosity can be drastically reduced, especially on the mesoscale. Attempts to reintroduce porosity into paper often come with the use of environmentally problematic chemicals or great technical effort. Here, we present a method to modify cellulose fiber and thus paper porosity by coating with (mesoporous) silica using sol-gel chemistry and evaporation induced self-assembly (EISA) combined with dip-coating. Applying different sol-gel solution compositions using two different types of cellulose fibers, namely cotton linter and eucalyptus fibers, not only mesoporosity was designed into paper but systematic insights into the mechanism of pore formation and fluid flow control were obtained. The modified paper sheets were characterized with respect to their porosity, silica distribution and fluid imbibition using small-angle x-ray scattering (SAXS), argon and krypton gas sorption, and confocal laser scanning microscopy (CLSM) to localize the silica coating relatively to the fiber structure within the paper sheet. The combined characterization techniques reveal that successful mesopore formation within paper has been achieved, that specific surface area can be adjusted by sol-gel chemistry and dip-coating which allows to adjust fluid transport velocity in paper. Interestingly, mesopore formation thereby relies on a synchronization of solvent evaporation rate, critical micellar concentration and paper-intrinsic capillary fluid imbibition velocity. The simple process allowing tuning of fluid imbibition and designing nanoscale pore space for application engineering in paper together with the fundamental mechanistic understanding is expected to impact the design of future hybrid materials for new sensing or separation devices.

5:00 PM NM01.03.03
Smart Catalytic Nanomaterials towards Green Chemistry Ji Yang and Ji Su; Lawrence Berkeley Lab, United States

Direct molecular transformation into desired structures without extra chemical transformations represents an ultimate goal in designing chemical processes, which highly depends on the development of advanced catalytic nanomaterials. Our vision is based on tailoring coordination microenvironment of a reactive atom at the atomic level to develop “reaction-matched” catalytic nanomaterials for green chemical transformations. Here, we demonstrated single-site Au with controllable coordination configurations for distinct ethanol conversion pathways. A functional nanomaterial to exclusively produce acetaldehyde from ethanol dehydrogenation was established, in which Au site was immobilized by oxygen vacancy on TiO_2; another two catalytic materials with cation vacancy-embedded Au active site on ZrO_2 or CeO_2 would give complex product distributions (C4+). By employing advanced spectroscopic studies, we attributed the distinct ethanol conversion pathways to unique electronic configurations of Au sites and vicinal coordination atoms. The concept of coordination configuration engineering demonstrated here will give unique insights and provide feasible pathways into rational design of smart catalytic nanomaterials, approaching the vision of green chemical transformations.

5:00 PM NM01.03.04
Viral-based Janus Particles for Nanomotor Assembly Xi Ding and Elaine D. Haberer; University of California, Riverside, United States

Viral nanoparticles are monodisperse, self-assembled biomaterials. Their structure and chemistry, including exact shape and site-specific functional groups, is genetically encoded and known with atomic scale precision, establishing a benchmark unrivaled by synthetic nanoparticles. Importantly, the biodiversity of viruses is vast, including an array of geometries and surface chemistries. Of specific interest, here, are viruses with asymmetric capsid proteins, like the M13 bacteriophage, that can serve as programmable bio-derived Janus particles. The M13 is a high aspect ratio, 880 nm long and 6.5 nm diameter filamentous virus. It contains approximately 2700 copies of p8 major coat protein along its length and 5 copies of p3 minor coat protein at the proximal end of the filament. Each of these proteins can be modified to create a low-symmetry template with peptide affinity for two different materials. In addition, using simple chemical exposure, this filamentous template can undergo a shape transformation to form 150 nm rods or 50 nm spheres, while maintaining site-specific affinity. The capacity for extreme modification of morphology combined with the asymmetric placement of the p3 and p8 on the viral surface make the M13 bacteriophage a potentially powerful scaffold for Janus particle assembly. In this work, the asymmetric Janus-like structure and functionality of the M13 bacteriophage capsid was used to create nanoswimmers. A cysteine-rich peptide fusion was inserted into the minor coat protein (p3) at the virus tip and Pt nanoparticles were attached via metal-thiol bonding. Using a brief chloroform treatment, the shape of the hybrid organic-inorganic Janus materials was transformed from filament to spheroid. The size and morphology of the resulting nanomaterials were characterized. The viral-based Janus particles were fluorescently tagged and exposed to low concentrations of H_2O_2 to fuel self-propulsion. Using confocal fluorescence microscopy, the nanomotor trajectory was explored, diffusion coefficients were measured, and particle motion was correlated to size and shape.

5:00 PM NM01.03.05
Multidimensional Characterization Approaches for Janus and Patchy Particles Julia S. Seifert, Andreas Völkl, Paola Cardenas Lopez, Johannes Walter and Robin N. Klupp Taylor; Institute of Particle Technology (LFG), Germany

Janus and, more broadly, patchy particles open up many opportunities as anisotropic components of tailored functional materials. Nevertheless, their promise brings with it significant challenges, in particular the characterization of their often rather complex morphologies. Improvements in this area are especially needed to support the development of large-scale processes to synthesize Janus and patchy particles, which, just like isotropic particles, tend to have broader morphological dispersity than when produced in the minute quantities often used for basic scientific studies.
We have developed various scalable continuous flow processes to synthesize Janus-like particles by coating dielectric core particles with patches of as silver or gold. Due to the localized surface plasmon resonance of the metal nanostructures, their morphology has a direct influence on their optical properties, leading to resonances in the visible and near-infrared spectral regions. To improve the later and target the product particles towards applications, it is necessary to optimize the process. The target here is to narrow the distributions of coating thickness, coverage and density. However, this can only be possible, if these parameters can be routinely and accurately measured. In this contribution, we will demonstrate how we use three different characterization techniques to extract complementary information from our complex particle system.
Firstly, we will show how automated analysis of scanning electron micrographs can be performed to investigate the metal patch yield (fraction of core particles possessing a patch), thickness and coverage. Here a significant challenge is the random orientation of the particles, meaning that statistical corrections need to be applied to account for possible “hidden” patches. Next, as an ensemble characterization technique we perform multiwavelength analytical ultracentrifugation. This technique has proven itself to be very powerful for the multidimensional characterization of anisotropic particles. Here we will show how the metal to core particle mass ratio can be determined and, taking the thickness distribution determined by microscopy, an estimate of the patch coverage distribution obtained. Finally, we will show how a new technique, single particle extinction and scattering, can be used to identify the patch yield (fraction of core particles possessing a patch) and reveal trends in patch coverage and density.

5:00 PM NM01.03.06
Automated Local Polymer Writing into a Mesoporous Silica Thin Film Using a Commercially Available Fluorescence Microscope and Oxygen Tolerant PET-RAFT Robert Lehn, Claire Förster and Annette Andrieu-Brunsen; TU Darmstadt, Germany

Functionalization of mesoporous material with polymers to modify its attributes e.g. ion transport or wettability is a much-studied field. A localized functionalization can then be used for e.g. lab-on-a-chip devices with hydrophobic barriers and hydrophilic reaction chambers or janus membrane-like structures for fluid-based material separation. One way to produce locally confined polymer functionalization is to use light-induced polymerization in combination with local illumination. The use of photomasks allows for locally restricted illumination and is well suited for mass production but lacks flexibility when developing new patterns. A direct “writing” of polymer with a precisely controlled local illumination is needed for rapid prototyping in research and development. While the use of UV-induced polymerization is well-known, the development of visible light-induced methods made the usage of commercially available fluorescence microscopes with laser illumination for polymer writing possible. A key step to make this approach more feasible was the development of an oxygen tolerant polymerization, making special equipment for the control of reaction conditions, like a glove-box, unnecessary. Here, we present an oxygen tolerant photoinduced electron/energy transfer reversible addition–fragmentation chain transfer polymerization (PET-RAFT) in combination with a commercially available fluorescence microscope (Nikon Ti2-E) for automated precise and flexible micrometer-scale polymer writing into mesoporous silica thin films. Optimization of illumination time and power was performed resulting in the ability to "write" any given monochromatic pixel image with a chosen polymer into the mesoporous silica film within a reasonable time frame. Three monomers with varying attributes were tested with the system (DMAEMA, MEP, METAC). A consecutive polymerization of all three monomers in close proximity as well as a re-initiation of polymerization with a different monomer at the same spot for the functionalization with block-copolymers was successfully performed.

5:00 PM NM01.03.08
X-Ray Induced Photodynamic Therapy With CsI(Na)@MgO Nanoparticles Zhizi Feng; University of Georgia, United States

Photodynamic therapy (PDT) is an emerging therapeutic approach to kill tumor cells by using photosensitizer (PS, both singular and plural) molecules that can be activated by light to produce reactive oxygen species (ROS), most important singlet oxygen ($^1O_2$). Only the combination and co-localization of light and PS can cause cell death, which is highly selective. Also PDT may be applied repeatedly without resistance, and can be used with chemotherapeies and immunotherapies for synergistic therapies. But the limited tissue penetration restrains PDT from the mainstream cancer treatment options. X-ray induced photodynamic therapy (X-PDT) combines the advantages of radiotherapy and PDT, potentially solves the challenge of conventional photodynamic therapy for deep-penetrating cancer therapy, and is applied by us and other groups for cancer treatment. Herein, we report a streamlined X-PDT strategy based on CsI(Na)@MgO nanoparticles and 5-aminolevulinic acid (5-ALA). The combination of CsI(Na)@MgO-and-5-ALA can kill cancer cells with the existence of X-ray, because CsI(Na)@MgO nanoparticles produce strong ~410 nm X-ray luminescence, which matches the Soret band of PpIX. While 5-ALA is a photosensitizer approved by FDA, converted to protoporphyrin IX (PpIX) in mitochondria of cancer cells. So after X-ray irradiation, protoporphyrin IX (PpIX) converted from 5-ALA can produce ROS in mitochondria with the ~410 nm X-ray luminescence caused by CsI(Na)@MgO nanoparticles, causing damages to mitochondria, and synergizes with DNA-targeted irradiation. While scintillator nanoparticles and photosensitizer are administered separately, the approach forgoes issues such as self-quenching or uncontrolled release of photosensitizers. When tested with 4T1 cells *in vitro*, the combination of CsI(Na)@MgO and 5-ALA elevated radiation-induced reactive oxygen species (ROS), which enhance damages to mitochondria, DNA, and lipids, and eventually reduced cell proliferation and clonogenicity. When tested in 4T1 models *in vivo*, the combination of X-PDT with the CsI(Na)@MgO and 5-ALA significantly improved tumor suppression and animal survival comparing with radiation therapy (RT) alone. After treatment, the scintillator nanoparticles, made of low-toxic alkali and halide elements, were efficiently excreted, causing no detectable harm to the hosts. Overall, separately administering CsI(Na)@MgO nanoparticles and 5-ALA represents a safe and streamlined X-PDT approach with a potential in clinical cancer treatment.

5:00 PM NM01.03.09
Polycation Stabilized Electrohydrodynamic Co-Jetted Janus Nanoparticle for Drug Delivery. Albert Chang and Joerg Lahann; University of Michigan–Ann Arbor, United States

Currently, poorly water-soluble drugs account for a major portion of the market-available drugs or potential drug candidates in pharmaceutical research setting. They usually require additional surfactants for solubility while also suffer from poor and high variably in bioavailability, thus limit their effectiveness in providing oral or parenteral administration. One drug delivering strategy involves exploiting hydrogels for its biocompatibility and sustainable delivery. However, existing hydrogel formed by either polymer or protein are usually hydrophilic, thereby having low compatibility and dosing efficiency with hydrophobic drugs. Nanoparticle albumin bound (NAB) technology is an efficient encapsulating method that allowed the inclusion of hydrophobic molecules into protein structure. In this work, we report the coupling of NAB technology with the adaptive electrohydrodynamic co-jetting to produce polycation-stabilized Janus nanoparticles (JNPs) for co-delivery of hydrophobic drugs. Quantitative and qualitative analysis by scanning electron microscopy (SEM) and structure illumination microscopy (SIM) show and corroborated distinct compartments in JNPs with good monodispersity at sub 200 nm in diameter. The JNPs have positively charged surface and maintained size stability for extended period characterized through dynamic light scattering (DLS). Kinetic studies of drug release show that the JNPs are pH-responsive and display different releasing profile in various settings. Our finding suggests that the polycation-stabilized NAB-JNPs is a platform that can be tailored for co-delivery of hydrophobic drugs. Furthermore, we envision that the positively charged nanoparticles can add additional mucoadhesive properties owing to its positively charged surface for targeting and adhesion that can be elucidated in further *in vitro* and *in vivo* studies for insight on therapeutic effects.

5:00 PM NM01.03.11
Fast Responsive Optically Functionalized Mesoporous Gold Nanostructures for pH Sensing Adil Alshoaibi; King Faisal University, Saudi Arabia

Two different routes turkivish and sol-gel methods are used to synthesize sodium citrate and polyethylene glycol functionalized gold nanostructures. Field emission scanning electronmicroscope (FESEM) analysis confirms spherical-shaped gold nanoparticles (AuNPs) and self-assembled Au nanodendritic (AuNDs) structures. Highresolution transmission electron microscopy (HRTEM) confirmed the spherical and dendritic morphology with particle sizes 9 nm of AuNPs and 3 nm of AuNDs, respectively. An atomic force microscope (AFM) shows average surface roughness (Ra) ~2.5 nm of AuNPs which is reduced to 1.5 nm in AuNDs. The AuNPs and AuNDs show heterogeneous chemical bonding and thermal stability at high temperatures. Brunauer-Emmett-Teller-based surface area is calculated at around 18 m2/g for AuNPs and 54 m2/g for AuNDs. The creosol red immobilized AuNPs (CR-AuNPs) and AuNDs (CR-AuNDs) sol demonstrate pka around 8.9 and 9.2 at 575 nm, respectively. The CR-AuNDs sol exhibit a time reaction 0.5 s which is relatively high than CR-AuNPs ~0.6 s. Both Au-structures show non-leachable behavior.

SESSION NM01.04: Janus Nanomaterials—Application

Session Chairs: Wei Wang and Christopher Wirth
Thursday Morning, April 13, 2023
InterContinental, Fourth Floor, Telegraph Hill

8:15 AM NM01.04.01
Interactions and Chemical Reactivities Between a Janus Tubular Aluminosilicate and the Cement Matrix—Case of Nuclear Waste Stabilization

Estelle Puel, Antoine Thill, Fabienne Testard, Celine Cau Dit Coumes and Arnaud Poulesquen; Commissariat à l’énergie atomique et aux énergies alternatives, France

This work deals with the conditioning of non-incinerable radioactive oil, issued from the nuclear industry, and which is still deprived of an appropriate treatment. The investigated strategy consists in using Janus particles with dual affinities for cement and oil to encapsulate oil in cement.
The chosen Janus particles are hybrid nano-clays (hybrid aluminosilicate imogolites) with tubular shape[1]. Their Janus character come from the specific properties of their internal and external surfaces. The internal surface of the nanotubes being covered by Si-CH_3 groups, this one is hydrophobic and can trap and stabilize hydrophobic compounds. The external surface formed by alumina surface is on the contrary hydrophilic and positively charged up to pH~10. It thus has good affinity for the mixing water used for cement hydration.

In this presentation, after a brief demonstration of the favorable interaction between oil and imogolite[2], we will focus on the impact of hybrid imogolites in the cement formulation with respect to oil incorporation and Portland cement hydration[3].

Previous research work shows that Pickering emulsions can be formed between oils and hybrid imogolites[2]. The stabilization mechanism is a two steps process. The first one consists in a fast stabilization of the water/oil interfaces by the nanotubes, controlled by the hybrid imogolites adsorption (pendant droplet technique). The second step shows that the adsorption allows to form a solid/gel layer that evolves slowly with time generating a stable gel structure between the drops. Direct Pickering emulsions incorporate oil up to 60% by volume by only adding a mass fraction of hybrid imogolite materials lower than 1 wt%. These emulsions stabilized by an original Janus particle have a typical behavior of both gel and Pickering emulsion, allowing to efficiently encapsulating oils.

Hexadecane was used as a non-radioactive surrogate of the contaminated oil. Hydration of cement pastes with variable contents of imogolites and / or oil was monitored using isothermal microcalorimetry. Unlike hexadecane, hybrid imogolites were shown to retard the hydration process. The delay depended both on the imogolite and water contents. To understand the mechanism involved in this delay, a simplified system, consisting in hybrid imogolites and tricalcium silicate $3CaO.SiO_2$, the main constituent of Portland cement, was thoroughly investigated. Hydration of tricalcium silicate was stopped by the solvent displacement method after increasing periods of time and the solid fraction of the paste samples was characterized by solid state NMR (^{29}Si and ^{27}Al), XRD and TGA. Imogolites were progressively destabilized under the highly alkaline conditions set by the cement paste, releasing aluminate ions to the solution, which were consumed to precipitate an aluminum-substituted calcium silicate hydrate (referred as C-A-S-H phase). This early precipitation of C-A-S-H could be responsible for the delay in cement hydration, since it is known that C-A-S-H particles do not act as nucleation and growth sites for further calcium silicate hydrate (C-S-H)[4,5]
The role of this C-A-S-H phase formation for the affinity with oil of the hydrated hybrid cement paste is still to be explored.

Acknowledgments: The authors gratefully acknowledge the French Alternative Energies and Atomic Energy Commission (CEA) and the FOCUS research program for funding.

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8:30 AM NM01.04.02
Exploring the Janus Structure to Improve Kinetics in Sulfur Conversion of Li-S Batteries Jun Hyuk Moon and Donghee Gueon; Sogang University, Korea (the Republic of)

Lithium-sulfur batteries, which have a larger theoretical capacity compared to lithium-ion batteries, have been attracting attention as a next-generation energy storage system. A typical cathode of a lithium-sulfur battery uses sulfur loaded on a porous or high specific surface area carbon support. During charging and discharging, the electrolyte soluble lithium polysulfide (LiPS) is converted to an electrically insulating solid lithium sulfide (Li_2S), where random deposition of lithium sulfide on the cathode substrate sluggish complete conversion of sulfur. Many previous efforts to introduce metal compounds to strongly adsorb LiPS and/or to promote conversion do not entail morphological control over Li_2S deposition. In this study, we introduce a Janus structure of a metal compound/carbon to simultaneously control the growth of Li_2S as well as promote the adsorption/conversion of LiPS. The Janus particles are prepared by directional thermal deposition of MoO_3 onto CNT-agglomerated spherical particles. Under potentiostatic discharge, we observe that Li_2S is deposited predominantly on MoO_3-coated regions on CNT particles, accompanied by high discharge capacity. As the deposition of Li_2S is microscopically controlled, the diffusion path of ions/charges in the electrode is preserved. Moreover, it is confirmed that the adsorption and catalytic properties of MoO_3 are greatly promoted by its lithiation during the charge/discharge process. Janus particle cathode cells achieve excellent performance, especially under kinetically limited conditions, such as ultra-high C-rates or high cathode sulfur densities.

8:45 AM *NM01.04.03
Dynamic Optical Structures for Sensing Based on Complex Janus Emulsions Timothy M. Swager; MIT, United States

This lecture will focus on the design of systems wherein reconfiguration of complex liquid Janus emulsions (droplets) and related materials can be triggered chemically, biochemically, or with magnetic fields. The utility of these methods is to generate new transduction mechanisms by which chemical and biological sensors can be developed. Complex liquid Janus droplets behave as optical lens systems and small changes in surface tensions can change focal lengths or cause systems to switch between optically transmissive or scattering states. Central to this scheme is that the fluids in the droplets have different densities and hence are aligned by the earth’s gravity. The induced optical changes can be triggered with chemical, photochemical, or biochemical stimuli and thereby create new generations of sensors. Demonstrations of these methods for the detection of enzyme concentrations, pathogens, and antibodies will be presented. Janus droplets containing birefringent liquid crystals (LCs), including chiral nematic phases, have been prepared and designer surfactants cause either planar of vertical anchoring at the water-liquid crystal interface. The liquid crystals can be used for precise positioning of magnetic particles and biomolecular elements. Magnetic particles can be used to create novel optical functions, including steering of light and selective reflection, which will be detailed.

9:45 AM *NM01.04.05
Janus Nanomaterials: Design, Synthesis and Applications for Oil Industry Wei Wang; Aramco Americas: Aramco Research Center-Boston, United States

Anisotropic nanomaterials composed of two halves of different structure, chemistry, or polarity, known as Janus nanomaterials, have distinct properties compared to symmetrically functionalized analogues and therefore have recently been paid significant attention in many applications such as electronic thin films, drug delivery, sensors, optics, oil/water separation membranes, photoactivated micromotors, photocatalysts, and interfacial modification. However, it remains a big challenge to synthesize the Janus nanostructures in large quantity with precise turnability of surface property. In this review, we summarize and discuss rational design and fabrication of Janus nanostructures, especially the methods for scale-up synthesis. Current progress on application of the Janus nanomaterials for oilfield chemistry in oil industry is discussed and prospected.

9:45 AM BREAK

10:45 AM NM01.04.07
Transducing Metal Catalyst Reactivity to Selective Chemical Sensing with Pentiptycene Metallopolymer/Single-Walled Carbon Nanotubes Suprastructural Complexes Shao-Xiong Lennon Luo, Haosheng Feng and Timothy M. Swager; Massachusetts Institute of Technology, United States

Single-Walled Carbon Nanotubes (SWCNTs) possess desirable electronic properties to function as the transducer material in a chemiresistive sensor. However, pristine SWCNTs make poor chemical sensors as they lack the functionalities for the selective molecular interaction with target analytes. Our group has demonstrated that catalysis can be a powerful design principle for chemical sensing. By taking advantage of the high reactivity and chemoselectivity of the metal catalysts, we can build chemical sensors with high sensitivity and selectivity that mirror the catalytic processes. To this end, it is essential to develop a general methodology for the seamless integration of metal catalysts in SWCNT-based chemiresistors that can facilitate the effective transduction of the desired chemical interactions to electrical sensing readouts.
In this project, we show that by using a family of pentiptycene-containing conjugated polymers, which are found to effectively bind SWCNTs to form stable dispersions, we can chelate metal catalysts to form suprastructural complexes that are capable of translating the reactivity of the embedded metal catalysts to the selective detection of gas analytes. Chemiresistive chemical sensors constructed based on these metallopolymer/SWCNT complexes find applications in diverse areas such as environmental monitoring and health diagnostics. In particular, we demonstrate that by incorporating a methane oxidation catalyst in these metallopolymer/SWCNT complexes, we can detect the potent greenhouse gas in high humidity at room temperature, overcoming the weakness in most chemiresistive methane sensors. Moreover, we have built a sensitive and selective sensor for the detection of ammonia in breath, which is an important biomarker for the screening and monitoring of chronic kidney disease. For better utility, wearable sensors can also be realized by immobilizing the metallopolymer/SWCNT complexes on flexible substrates. Furthermore, by varying the metal catalysts and tuning the polymer ligand structures, these hybrid sensory nanomaterials can be readily derivatized to construct sensor arrays for the accurate classification and differentiation of analytes in a complex mixture.

10:45 AM DISCUSSION TIME

11:00 AM NM01.04.08
Effective Optical Nanoparticles and Nanocomposites Based on a Carbon Nanotubes-Organic–Inorganic Nanohybrid for Industrial Pollutant Removal Adil Alshoaibi; King Faisal University, Saudi Arabia

Improving the optical properties of zinc oxide to meet the practical requirements of photocatalytic reactions and solar cells is an ongoing challenge. To address this challenge, different nanostructures of ZnO were prepared from an organic–inorganic-CNTs nanohybrid. The nanohybrid was formed through intercalation of the long chain fatty acid $C_{17}H_{35}COOH$ and carbon nanotubes into Zn–Al nanolayered structures. X-ray diffraction revealed an increase in the interlayer spacing of the Zn–Al layered double hydroxides from 0.75 nm to 2.1 nm after admixing with the CNTs and organic fatty acid. Thermal analyses and FTIR confirmed the formation of the CNTs–C18–Zn–Al nanohybrid. Three different thermal treatments were used to transform the nanohybrid into nanostructures of doped zinc oxide nanoparticles and zinc aluminum oxide nanocomposites. As a result of changes in the nano size and structure, the band gap energy of the products decreased from 3.3 eV to 1.8 eV, to give efficient photocatalysts. The nanomaterials were used to purify water through the photocatalytic degradation of colored pollutants under UV light. A kinetic study showed that water purification was achieved within a short time, demonstrating the effectiveness of the nanomaterials. The nanohybrid and its derivatives are attractive materials for designing-efficient photocatalysts for pollutant degradation.

SESSION NM01.05: Virtual Session
Session Chairs: Sambeeta Das, Zhifeng Ren, Wei Wang and Christopher Wirth
Wednesday Morning, April 26, 2023
NM01-virtual

8:00 AM NM01.05.01
Development of Nano-prodrug&Hydrogel for Locoregional Therapy Liu Zhixiang; Tohoku university, Japan

Malignant skin ulcerations are caused by skin cancer or metastatic spread to the skin, resulting in the loss of epithelial tissues. In the present study, we aimed to develop nano-prodrug@hydrogel materials for locoregional therapy of malignant skin ulcerations. Compared to drugs in the molecular state, nano-prodrugs (NPDs), which are composed of only prodrug molecules, have high pharmaceutical activity due to high permeability to the tissue. Polydopamine nanoparticles (PDA-NPs) are introduced into poly(N-isopropylacrylamide) (pNIPAM) hydrogel to fabricate a PDA-NPs/PNIPAM hydrogel system. PDA-NPs, as a near infrared (NIR) sensitive material, can be heated under 808 nm NIR light and shrink the temperature sensitive pNIPAM hydrogel. Thus, this system is designed that can use NIR light to rapidly excite and release NPDs on demand. Here, we reported the fabrication of PDA-NPs/pNIPAM hydrogel loaded with SN-38-cholesterol nano-prodrugs (SN-38-chol NPDs).
SN-38-chol NPDs were prepared by reprecipitation method.The size of the NPDs was about 120 nm . PDA-NPs/pNIPAM hydrogel drug delivery system loaded with SN-38-chol NPDs was successfully fabricated . The drug loading of the SN-38-chol NPDs@hydrogel was about 0.05 mg/g (drug weight/hydrogel weight), indicating a good drug loading capacity of the system. To evaluate *in vitro* cytostatic activity, SN-38-chol NPDs dispersion and SN-38-chol NPDs@hydrogel were applied to HCT-116 (human colon cancer) cell at the same final concentration and incubated for 48 h. As a result, SN-38-chol NPDs dispersion and the SN-38-chol NPDs@hydrogel showed similar cytostatic activity

8:15 AM NM01.05.02

Structural and Chemical Mechanisms Governing the Stability and Electronic Properties of Inorganic Janus Nanotubes Ivano Eligio Castelli; Technical University of Denmark, Denmark

One-dimensional inorganic nanotubes hold promise for technological applications due to their distinct physical/chemical properties. Still, so far advancements have been hampered by difficulties in producing single-wall nanotubes with a well-defined radius. In this work, based on Density Functional Theory (DFT), we investigate the formation mechanism of different prototypes of inorganic nanotubes formed by the intrinsic self-rolling driving force found in asymmetric 2D Janus sheets. We show that for isovalent Janus sheets, the lattice mismatch between inner and outer atomic layers is the driving force behind the nanotube formation. At the same time, in the non-isovalent case, it is governed by the difference in chemical bond strength of the inner and outer layers leading to steric effects. From our pool of candidate structures, we have identified a handful of nanotubes with a preferred radius below 15 Å, which we hypothesize can display distinctive properties compared to their parent 2D monolayers. We investigate electronic properties and show that many of these nanotubes exhibit sizable band gaps and size-dependent electronic properties. Moreover, we observe that the flexoelectricity in these nanotubes is significantly larger than those of other nanotubes and their 2D counterparts. This work opens up an avenue of structure-property relationships of Janus nanotubes and demonstrates exciting new properties, which can accelerate the green transition to a more sustainable future.

8:30 AM *NM01.05.03
Assembly and Propulsion of Magnetic Janus Particles Bhuvnesh Bharti; Louisiana State University, United States

Janus particles are widely considered as a fundamental building block for fabricating intricate machines able to perform complex functions at sub-micron scale. Due to their dual surface functionality, these particles have dissimilar surface interactions with surrounding particles and medium. The inherent asymmetry of Janus particles can drive their assembly into complex phases and/or generate net force on the particles inducing a motion. In this talk I will present the use external magnetic field as to tool to direct the assembly and propulsion of Janus particles suspended in ferrofluids. First, I will show how the intrinsic anisotropy in magnetic interactions combined with the asymmetry of the Janus particles can induce unusual magnetic interaction energy landscape around the particle. By combining patchy and non-patchy particles, we modulate these interactions to construct clusters with morphologies resembling colloidal molecules. I will discuss the assembly of such clusters, their programmability by manipulation of patch size, their in-situ tunability using the magnetic field, and I will show a technique to permanently bind them once assembled. Secondly, I will demonstrate how to use time-periodic magnetic fields to drive the coherent dynamic surface rolling of Janus particles in the ferrofluids. I will show how external field allows controlling characteristics of the active motion such as rolling, rotation, speed, and direction of motion of the Janus particles. Our experimental results display the potential in microstructuring at the single cluster level as well as controlling active motion and collective behaviors of the Janus colloids, using a single external magnetic field. The simplicity and versatility of the approach stems from exploiting the anisotropy of magnetic interactions combined with the asymmetry of the Janus particles enabling a precise control over both the equilibrium assembly and non-equilibrium motion of the particles.

9:00 AM *NM01.04.06
Optical Manipulation of Janus Particles Using Optical Nanofibers Sile Nic Chormaic; OIST Graduate University, Japan

Janus particles, which are small composite particles, are of interst for biomedical applications, where they act as actuators, carriers, or imaging agents. One major technical challenge is efficient manipulation of Janus particles. Long-range methods depending on chemical reactions or thermal gradients have limited precision and depend on the environmental fluid. Here, we demonstrate the optical manipulation of Janus particles consisting of silica microspheres half-coated with gold in the evanescent field of an optical nanofiber. The Janus particles have faster propulsion along the nanofiber compared to pure dielectric particles of the same size.

SYMPOSIUM

April 11 - April 14, 2023

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Kwabena Bediako, University of California, Berkeley
Fang Liu, Stanford University
Andres Montoya-Castillo, University of Colorado, Boulder
Justin Sambur, Colorado State University

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SESSION NM02.01: Discovery and Synthesis of Functional 2D Materials I
Session Chairs: Andres Montoya-Castillo and Justin Sambur
Tuesday Morning, April 11, 2023
InterContinental, Fifth Floor, Sutter

10:30 AM *NM02.01.01
2D Polymers and Their van der Waals Heterostructures for Electronic and Ionic Devices Yu Zhong; Cornell University, United States

Artificial van der Waals (vdW) solids assembled from 2D crystals represent a new type of materials that can be engineered at the atomic scale. 2D polymers, made by cross-linking molecules into a 2D network, are not only an emerging library of 2D building blocks for making vdW solids but also offer unlimited structural tunability on the molecular level. In this talk, I will introduce an approach to synthesizing monolayer 2D polymers on a large scale. This approach allows for scalable and facile integration of 2D polymers into electronic and ionic devices. The 2D polymer films can serve as the thinnest semipermeable membranes, which deliver a record high osmotic power generation density. Furthermore, I will show the programmed assembly of hybrid 2D heterostructures using 2D polymers and inorganic 2D materials. This approach allows for integrating versatile molecular building blocks into layered nanomaterials to develop ultrathin electronic, ionic, and electrochemical devices.

11:00 AM *NM02.01.02
Manufacturing 2D Materials at Low Temperatures and High Spatial Selectivity Zakaria Al Balushi; University of California, Berkeley, United States

The multitude of 2D materials in regard to composition, crystal structure and layer thickness leads to a variety of material properties covering all of the components necessary to address voltage, interconnect, energy, and dimensional scaling issues in a variety of applications. For 2D materials to be technologically competitive, it is imperative to develop manufacturable materials deposition protocols with spatial selectivity and low temperatures at any location on demand without wafer transfer processing. In this talk, a low temperature spin coating process will be discussed to form transition metal dichalcogenides at low temperatures using a modified spin coating technique from low decomposition temperature molecules. Furthermore, to achieve spatial selectivity of grown 2D materials, this talk will also describe a novel process to spatially measure and modulate the surface energy of van der Waals surfaces at growth temperatures to achieve selective area growth of 2D materials into a variety of form factors.

SESSION NM02.02: Nanoscale Imaging and In Situ Spectroscopy I
Session Chairs: Kwabena Bediako and Fang Liu
Tuesday Afternoon, April 11, 2023
InterContinental, Fifth Floor, Sutter

1:30 PM *NM02.02.01
Spatiotemporally Following Ions and Carriers and Heat (oh my!) at the Nanoscale in Few-layer Materials Hannah L. Weaver[1], James Utterback[1], Livia Belman-Wells[1], Stephanie Hart[1], Leo Hamerlynck[1], Rongfeng Yuan[1], Cora Went[2], Dipti Jasrasaria[1], Joeson Wong[2], Alex King[3], Elena Vasquez[1], Eran Rabani[1], Harry A. Atwater[2], Adam Weber[3] and Naomi S. Ginsberg[1]; [1]University of California, Berkeley, United States; [2]California Institute of Technology, United States; [3]Lawrence Berkeley National Laboratory, United States

Electronic, thermal, and ionic transport are all important to the myriad roles that 2D materials play in science and technology and particularly in electrochemistry. I will describe our recent work to characterize each type of transport using the single umbrella of time-resolved optical elastic scattering microscopy. This approach allows these different forms of energy flow to be imaged separately and together, with temperature change sensitivity down to 0.1 K. I will separately show results imaging the co-evolution of excitons and heat in few layer MoS_2 and results imaging the redistribution of ions in an electrolyte during an electrochemical reaction. I will finally describe efforts to unite these two separate foci so that ion intercalation and electrochemistry can be characterized simultaneously with electronic and thermal transport.

2:00 PM *NM02.02.03
Hot Carrier Dynamics & Many-Body Effects in TMD-Based Electrochemical Cells Revealed Using Nonlinear Spectroscopy & Theory Yusef R. Farah, Rachelle Austin, Thomas Sayer, Andres Montoya-Castillo, Justin Sambur and Amber T. Krummel; Colorado State University, United States

Commercial hot carrier devices have not yet been realized, in part due to the poor understanding of how operational device conditions impact hot carrier dynamics. Single monolayer transition metal dichalcogenides (2D TMDs) are promising active materials for hot carrier devices due to their broad and large visible light absorption, atomically thin geometry, and slow hot carrier cooling. To push hot carrier devices towards being a disruptive technology, one must understand the tuning parameters available in the devices and how to predict behaviors of the 2D TMDs. In this talk, I will describe efforts in combining theory with experiment to characterize and describe hot carrier dynamics in a monolayer (ML) MoS_2-based electrochemical cell. Results from in operando spectroscopy, including steady-state photocurrent spectroscopy and transient absorption spectroscopy, will be presented. We have built a model electrochemical cell in which ML MoS2 makes intimate contacts with an electron selective solid contact and a hole selective electrolyte contact. All measurements are made as a function of applied potential. Photocurrent and absorbance measurements performed simultaneously as a function of applied potential reveal which optical states generate charge carriers first. In operando transient absorption measurements provide signatures of hot carrier extraction and the time scales associated with hot carrier extraction and charge carrier dynamics. We observe the extraction of hot carriers within 50 fs and high photocurrent yields in our device that exceed photocurrent yields observed in bulk MoS_2. Throughout this work we monitor the formation of excitons and trions as a function of applied potential. Finally, the experiments are interpreted within a theoretical framework that allows for: 1. the origin of the experimental observations to be described and 2. A streamlined modelling approach taken to describe many-body effects that are observed in the experiments.

2:30 PM BREAK

3:00 PM *NM02.02.04
Ultrafast Charge Carrier and Polaron Dynamics in 2D-Transition Metal Chalcogenides Hirendra N. Ghosh; Bhabha Atomic Research Centre, India

Research on two-dimensional (2D) transition metal dichalcogenides (TMDC) have gained incredible interest and importance in recent times, attributable to their fascinating optical, electronic and mechanical properties. They offer both fundamental and technological implications in various advanced electronic, optoelectronic and gas sensing devices, energy storage systems, photovoltaics and photo-catalysis. To optimize the efficiency of any devices it is very important to understand the ultrafast charge carrier dynamics of these 2D TMDC materials. In the present talk we will discuss photo-excited charge carrier dynamics of few TMDC materials with the aid of Femto-second broad-band pump-probe spectroscopy and Femtosecond Terahertz spectroscopy. We have discussed free-carriers, exciton and other quasi particles like bi-exciton and trion dynamics in TMDC on excitation with ultrafast laser pulse.

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3:30 PM *NM02.02.05
Spatial and Temporal Imaging of Exciton Transport in Two-Dimensional Heterostructures Libai Huang; Purdue University, United States

Charge-transfer (CT) excitons at hetero-interfaces play a critical role in light to electricity conversion using nanostructured materials. However, how CT excitons migrate at these interfaces is poorly understood. Atomically thin and two-dimensional (2D) nanostructures provide a new platform to create architectures with sharp interfaces for directing interfacial charge transport. Here we investigate the formation and transport of interlayer CT excitons in van der Waals (vdW) heterostructures based on semiconducting transition metal dichalcogenides (TMDCs) employing transient absorption microscopy (TAM) with a temporal resolution of 200 fs and spatial precision of 50 nm.

We have investigated interlayer exciton dynamics and transport modulated by the moiré potentials in WS$_2$-WSe$_2$ heterobilayers in time, space, and momentum domains using transient absorption microscopy combined with first-principles calculations. Experimental results verified the theoretical prediction of energetically favorable K-Q interlayer excitons and unraveled exciton-population dynamics that was controlled by the twist-angle-dependent energy difference between the K-Q and K-K excitons. Spatially- and temporally-resolved exciton-population imaging directly visualizes exciton localization by twist-angle-dependent moiré potentials of ~100 meV. Exciton transport deviates significantly from normal diffusion due to the interplay between the moiré potentials and strong many-body interactions, leading to exciton-density- and twist-angle-dependent diffusion length. These results have important implications for designing vdW heterostructures for exciton and spin transport as well as for quantum communication applications.

We have also imaged the transport of interlayer CT excitons in 2D organic-inorganic vdW heterostructures constructed from WS$_2$ layers and tetracene thin films. Photoluminescence (PL) measurements confirm the formation of interlayer excitons with a binding energy of ~ 0.3 eV. Electron and hole transfer processes at the interface between monolayer WS$_2$ and tetracene thin film are very rapid, with time constant of ~ 2 ps and ~ 3 ps, respectively. TAM measurements of exciton transport at these 2D interfaces reveal mobile CT excitons, with diffusion constant of ~ 1 cm^{2}s^{-1}. The high mobility of the delocalized CT excitons could be the key factor to overcome large CT exciton binding energy in achieving efficient charge separation.

SESSION NM02.03: Nanoscale Imaging and In Situ Spectroscopy II
Session Chairs: Kwabena Bediako, Fang Liu, Andres Montoya-Castillo and Justin Sambur
Wednesday Morning, April 12, 2023
InterContinental, Fifth Floor, Sutter

8:00 AM *NM02.03.02
Exciton Propagation in 2D Semiconductors Alexey Chernikov; TU Dresden, Germany

Transport of photoexcited charge carriers in semiconducting solids plays a central role from both fundamental and technological perspectives. In two-dimensional systems with strong Coulomb interaction the propagation of optically injected carriers is dominated by excitons instead of free electrons or holes. These correlations determine the flow of energy stored in the electronic system and can facilitate transport of information encoded in spin or pseudospin degrees of freedom.

In this talk I will present recent studies focused on propagation of mobile exciton quasiparticles in semiconducting van der Waals monolayers and hybrid perovskite materials. In these systems, the electron-hole correlations present a particularly interesting case combining the properties of Wannier-Mott excitations in inorganic semiconductors with high exciton binding energies that are more characteristic for Frenkel-like states in molecular crystals. I will discuss non-linear and anomalous diffusion, indications of quantum transport for excitons, as well as high-density propagation phenomena in van der Waals heterostructures at the Mott transition.

8:30 AM *NM02.03.03
Probing Excited State and Charge Transfer Dynamics at 2D Interfaces Keshav M. Dani; Okinawa Institute of Science and Technology, Japan

In this talk, I will discuss our recent results using time- and angle-resolved photoemission spectroscopy (TR-ARPES) to study the excited state and charge transfer dynamics at the interfaces of few layer transition metal dichalcogenides (TMDC).

9:00 AM BREAK

9:30 AM NM02.03.04
Mechanistic Insights into 2H to 1T Phase Transitions in Transition Metal Dichalcogenides by *In Situ* Optical Microscopy Juhwan Lim, Jung-In Lee, Christoph Schnederman, Manish Chhowalla, Akshay Rao and Arturo Medina; University of Cambridge, United Kingdom

Phase engineering of transition metal dichalcogenides (TMDs) allows for the tuning of electric and optical properties and enhancement of the device performance. The most well studied example of this kind of phase transformation is use of charges and intercalating lithium ions to change semiconducting octahedral (2H) TMDs to metallic trigonal prismatic (1T) phase using n-butyllithium (n-BuLi).
In this study, we optically tracked the chemically-induced 2H to 1T phase transition of MoS_2, $MoSe_2$, WS_2, and WSe_2 in n-BuLi in real time, using in-situ optical reflectance interferometric contrast microscopy (RICM). The different optical properties of 2H- and 1T- TMD allow us to quantify reaction dynamics of mechanically exfoliated mono-, bi-, and multilayer flakes in diffraction limited resolution (~200 nm). We show that mechanism of the phase transformation is dependent on the transient metal atom present, as MoS_2, $MoSe_2$ exhibit a single spatially propagating phase front for the conversion, while WS_2 or WSe_2 has no wavefront or two wavefronts propagating closely, respectively.
These observations are correlated with cyclic voltammetry(CV) and electrochemical measurements to build a mechanistic picture of the phase transformation reaction in different TMDs. In electrochemical measurement, MoX_2(X= S/Se) has electrical potential for a phase transition closer to the redox potential of n-BuLi(1V), while WX_2 have lower potential (MoS_2 : -0.07 V, $MoSe_2$: +0.08V, WS_2 : +0.22V, WSe_2 : +0.2V, versus Li/Li^+). This correlates to the optical observation of a more spontaneous phase transition for MoX_2. Additionally, the potential difference between phase transition and conversion is discrete for MoX_2, while close or overlapped for WX_2(MoS_2 : ~0.5V, $MoSe_2$: ~0.3V, WX_2: < 0.1V). This could be incorporated with the light-driven phase transition which only MoX_2 displayed discrete 1T phase while WX_2 undergo conversion reaction. We also carefully examined each flake with different phase in ex-situ, such as the change of A-exciton PL, arising of Raman J peaks, and shifts of Raman peaks, and suggest systematic interpretation for this behavior. This study could suggest mechanistic insight of phase transition by incorporating the correlation between electrochemical- and chemical- reaction, for application in phase engineering, chemical exfoliation and energy application of TMDs.

9:45 AM NM02.03.05
Electroless Excitation of Semiconductors through Semiconductor-liquid Interfaces Shengyang Li, Kexun Chen, Ville Vähänissi, Hele Savin and Jani Oksanen; Aalto University, Finland

Electrochemistry of inorganic semiconductors has been studied extensively in the context of photoelectrocatalysis (e.g., water splitting, CO_2 reduction), corrosion and microfabrication technologies. On the other hand, little attention has been placed on studying the possibility of electroless excitation of semiconductors through semiconductor-liquid interfaces. We recently showed that electroless excitation takes place during metal-assisted chemical etching (MACE) of Si by using two different approaches. In the first approach,[1] a charge carrier collecting p-n junction structure coated with silver nanoparticles (AgNPs) was used to convert the chemical energy released during MACE to electricity using an electroless approach, i.e. without using any counter electrode, reaching a power density of 0.43 mW/cm^2. In the second approach,[2] we designed both n- and p-type Si photoconductors covered with AgNPs to probe their response to MACE. The experiments show that both n- and p-type photoconductors exhibit a strong response to MACE, seen as a significant increase of the currents through the photoconductors when exposed to the etching solution. All these experimental results imply that electroless excitation of Si takes place during MACE.
In this presentation, we discuss the origin of these findings and the possibility to generalize the mechanisms of electroless excitation of semiconductors to other fuel-oxidizer systems. In particular, we discuss a framework for describing the thermodynamic and kinetic properties of the charge flow across the semiconductor-liquid interfaces during electroless excitation, aiming to establish the limits for the thermodynamic feasibility of the process.
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10:00 AM *NM02.03.06
Phase Transitions of Excitons in Two Dimensions Xiaoyang Zhu; Columbia University, United States

An exciton is a quasi-particle consisting of an electron and a hole bound by the Coulomb potential. It is a solid and excited state analog of the hydrogen atom. Excitons are fundamental to semiconductors and determine a range of processes involving the conversion of light to charge or charge to light. As bosonic particles, excitons can form quantum phases, e.g., Bose-Einstein condensates (BECs). Unlike their 3D counter parts, the Coulomb and exchange interactions are poorly screened in 2D> This results in large exciton binding energies and strong dependences of semiconductor bandgaps on charge carrier concentrations. In 2D transition-metal dichalcogenide (TMDC) heterojunctions, charge separation across the interface results in interlayer excitons with lifetimes five orders of magnitude longer than those of their intralayer counterparts. Both the dipolar nature and long lifetime make interlayer excitons ideal models for the exploration of many body interactions and phase transitions. Moreover, moiré pattern formation and site-specific interlayer hybridization result in periodic potentials for interlayer exciton arrays that may serve as quantum simulators. We show the sensitivity of moiré trapped excitons to local strain, from 0D unstrained QD arrays to 1D strained wires. With increasing exciton density, inter-exciton interaction leads to two distinct phase transitions: from trapped excitons in the moiré-potential to the modestly mobile exciton gas as exciton density increases to $n \sim 10^{11}$ cm^{-2} and from the exciton gas to the highly mobile charge separated electron/hole plasma for $n > 10^{12}$ cm^{-2}. We explore the ordering of interlayer excitons into quantum phases using trilayer structure as predicted in recent theory.

10:30 AM NM02.03.07
Quantifying Energy Level Alignment at Monolayer MoS_2/Electrolyte Interface Rafael Almaraz, Justin B. Sambur and Justin Toole; Colorado State University, United States

Transition metal dichalcogenides (TMDs) have unique optical and electronic properties for photo-electrocatalysis applications. The fundamental problem is that the interfacial energetics of TMD/electrolyte interfaces in photoelectrochemical cells are poorly understood. The weakly screened Coulomb potential leads to a large exciton energy and a strong renormalization of the bang gap energy as a function of carrier concentration. Hence, my talk will focus on quantifying how the conduction and valence band energies move as a function of applied potential in an electrochemical cell. To do so, we utilize potential-dependent spatially resolved absorption spectroscopy to quantify the energy levels of monolayer MoS2 in electrochemical cells. The spatially resolved measurements are necessary to distinguish monolayer from few layer-thick material on the sample and, therefore, simplifies data interpretation. I will discuss how we 1) use optical data to extract the carrier concentration of the semiconductor as a function of applied bias and 2) construct band energy diagrams as a function of applied potential.

10:45 AM NM02.03.08
Probing of the Electrical Response of the Air/Graphene/Liquid Interface without the Presence of any Underlying Substrate Rodrigo G. Lacerda; Univ Federal de Minas Gerais, Brazil

Graphene is a crystalline 2D material and considered the thinnest possible membrane. Because of its high chemical stability, combined with its physical properties, graphene is promising in a variety of applications. Particularly, liquid/graphene interfaces have been exploited for bio-applications on cellular flow sensing, liquid sensing, DNA sequencing, and transparent windows in liquid cells. In such devices, understanding the interaction between water and graphene is crucial for building up novel and smart bio-interfaces. Additionally, the study of reactivity and structure of water at the graphene interface has also generated intriguing questions and controversial results. For instance, several experimental works demonstrate that the charge transfer process that happens between graphene and water molecules is highly dependent on the underlying substrate. Thus, it would be highly desirable to elucidate the above discussion by probing the electrical response of a suspended graphene membrane in contact with water without the presence of any substrate. We also believe that a precise understanding of the electrochemical behavior of water/graphene interface would be fundamental for developing novel and superior electrical, mechanical and optical devices. In this work, we develop a microfluidic platform that integrates suspended graphene membrane windows (with electrical contacts) with buried fluid channels to probe the electrical response of a graphene membrane in contact with water [1,2,3]. The platform design provides a direct probing of the electrical response of the air/graphene/liquid interface without the presence of any underlying substrate.

I will present a detailed study of the water-induced electromechanical response in suspended graphene atop a microfluidic channel. The graphene membrane resistivity rapidly decreases ~ 25% upon water injection into the channel, defining a sensitive "channel wetting" device – a *wetristor*. The physical mechanism of the *wetristor* operation is investigated using two graphene membrane geometries, either uncovered or covered by an inert and rigid lid (h-BN multilayer or PMMA film). The *wetristor* effect, namely the water-induced resistivity collapse, occurs in uncovered devices only. AFM and Raman spectroscopy indicate substantial morphology changes of graphene membranes in such devices, while covered membranes suffer no changes, upon channel water filling. Our results suggest an electromechanical nature for the *wetristor* effect, where the resistivity reduction is caused by un-wrinkling of the graphene membrane through channel filling, with an eventual direct doping caused by water being of much smaller magnitude, if any. The *wetristor* device should find useful sensing applications in general micro- and nano-fluidics and provides novel insights on the interface interactions of 2D materials with liquids.

Acknowledgments: The authors acknowledge the support of FAPEMIG (Rede 2D), CNPQ/MCTI, and INCT de Nanocarbono.

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11:00 AM *NM02.03.09
Nanoscale Photoemission Spectroscopy as a Local Voltage Probe of Operating 2D Material Devices Søren Ulstrup; Aarhus University, Denmark

Understanding electronic and structural mechanisms that define intrinsic and extrinsic performance limits of two-dimensional (2D) materials integrated in functional device architectures is essential for the realization of truly 2D technologies. Obtaining such insights demands a probe that is capable of visualizing electronic structure on mesoscopic length scales and during operating conditions of devices.

Here, I will demonstrate the ability to visualize the energy- and momentum-dependent quasiparticle dispersion in 2D devices composed of graphene supported on a hexagonal boron nitride (hBN) dielectric and a graphite back-gate. The charge carrier-dependent spectral function of graphene is resolved using angle-resolved photoemission spectroscopy with nanoscale spatial resolution (nanoARPES) while the back-gate voltage is tuned. I will discuss how such measurements directly reveal the doping-dependent renormalized Fermi velocity of Dirac quasiparticles and elucidate electron-phonon and electron-plasmon interactions in graphene [1,2]. Position-resolved measurements of the graphene Dirac cone in the presence of an electrical transport current provide a map of the local electrostatic potential, which is combined with the local doping to estimate the spatially-dependent carrier mobility of graphene on hBN [3,4]. The work demonstrates the powerful concept of unifying spectroscopic and transport measurements on 2D materials, which allows for a simultaneous noninvasive local measurement of composition, structure, many-body effects and carrier mobility in the presence of high current densities and tunable charge carrier concentrations.

[1] R. Muzzio *et al.*: *Momentum-resolved view of highly tunable many-body effects in a graphene/hBN field-effect device*. Phys. Rev. B **101**, 201409(R) (2020)
[2] A. J. H. Jones *et al.*: *Observation of Electrically Tunable van Hove Singularities in Twisted Bilayer Graphene from NanoARPES*. Adv. Mater. **32**, 2001656 (2020)
[3] D. Curcio *et al.*: *Accessing the spectral function in a current-carrying device*. Phys. Rev. Lett **125**, 236403 (2020).
[4] P. Majchrzak *et al.*: *In Operando Angle-Resolved Photoemission Spectroscopy with Nanoscale Spatial Resolution: Spatial Mapping of the Electronic Structure of Twisted Bilayer Graphene*. Small Sci. **1**, 2000075 (2021)

SESSION NM02.05: Current Understanding and Theoretical Description of the 2D Electrode/Electrolyte Interface I
Session Chairs: Kwabena Bediako and Justin Sambur
Wednesday Afternoon, April 12, 2023
InterContinental, Fifth Floor, Sutter

3:00 PM *NM02.05.01
Optically Excited States and Their Dynamics in Atomically Thin Semiconductor Heterostructures Tony F. Heinz; Stanford University and SLAC National Accelerator Laboratory, United States

Combining semiconductor monolayers of van-der-Waals materials by stacking leads to a wide variety of new excited electronic states, which have the potential for various optoelectronic and electrochemical applications. In this paper, we will review recent progress in understanding the fundamental nature and dynamics of the interlayer excited states, the so-called interlayer excitons, that are supported in transition metal dichalcogenide heterostructures. In particular, we will discuss how time-resolved ARPES measurements, carried out in collaboration with the group of Keshav Dani, provide a methodology for directly imaging both the electron and hole component of these interlayer states in momentum space. This methodology allows us to track the ultrafast dynamics of the charge transfer processes leading to the formation of interlayer excitons, as well as the exciton decay dynamics.

We will also describe the new interlayer states that arise in semiconductor heterotrilayers, particularly in angle-aligned $WSe_2/WS_2/WSe_2$ stacks. In these materials, we find that symmetrical interlayer excitons can be created. These states exhibit much weaker exciton-exciton interactions than those seen in bilayers, since excitons in the former have no static dipole moment, while the latter have a substantial dipole moment. The so-called quadrupolar excitons in the trilayer structure can be continuously tuned by an external electric field to the dipolar limit, thus creating a material with a programmable exciton-exciton interaction. For the symmetric structure, we see at high exciton density signatures of a transition to a staggered dipolar phase. This phase transition is driven by attractive interaction between oppositely aligned interlayer exciton dipole moments. We will discuss the evidence for this new excitonic phase, the significant and distinctive influence of moiré effects in these trilayer structures, and the potential applications of such novel excited states.

3:30 PM *NM02.05.02

Theoretical Treatment of Electrocatalytic Reactions on 2D Transition Metal Dichalcogenides under Electrochemical Conditions Taylor Aubry[1], Elisa Miller-Link[1,2], Derek Vigil-Fowler[1] and Jao Van de Lagemaat[1,2]; [1]National Renewable Energy Laboratory, United States; [2]Renewable And Sustainable Energy Institute, United States

Two-dimensional semiconductors such as MoS2 and WSe2, etc. are known (photo)electrocatalysts for the electrochemical reduction of water to form H2, CO2 to form C1 and higher products, N2 to form NH3, and other relevant reactions for a future low-carbon economy. These reactions are complex and involve multiple steps. When performed on the 2-dimensional systems, they are often catalyzed by defects or step edges or to need a semiconductor to metal phase transition to be efficiently catalyzed on intact basal planes. The reactions also involve multiple electron and proton transfer events that are often thought to happen in an intricately coupled manner. At the same time, it is known from experiment that electrochemical conditions, such as electrical bias, strongly modify the electronic properties of the (photo)electrocatalyst by effects such as bandgap renormalization, non-uniform shifts of catalyst and molecular electronic states with applied potential, phase transitions, and other effects that can radically alter the energetics and kinetics of the steps involved. Also, these materials can have very strong light-matter interactions that modify their electrochemical behavior. This complexity makes it hard to make predictions about the electrocatalytic behavior of these materials.

In this contribution, we investigate the above-mentioned reactions using density functional theory calculations performed in the Grand Canonical Ensemble, as implemented in the JDFTx software package that can accurately address realistic electrochemical conditions (electrified interfaces, dielectric response, ionic strength, etc.) while still fully treating spin- polarization and other electronic effects. We study the reaction pathways, intermediate energies and the electronic properties of the intermediate complexes to gain a better understanding of the electrochemical reduction reactions in their actual microenvironments. We find that the electrochemical conditions modify electrocatalytic pathways in a non-trivial manner and that the local structure of the 2-D semiconductor changes considerably during the reaction sequence. We investigate the bonding environment between catalytic site and substrate and find that effects such as pi-back bonding to the transition metal sites and local relaxation of the microenvironment are essential in understanding the reaction pathway and the dependence of the reaction thermodynamics on electrochemical bias. Most significantly we find that traditional methods of calculating intermediate state energies in vacuum environment, while informative to study intermediate conformation, are not able to treat the reaction particulars well and, in many cases, the wrong reaction step can be identified as rate limiting.

Lastly, in this contribution, we connect our theoretical calculations to experiments performed in our group and in the literature and talk about the implications of the new theoretical insight on our understanding of fuel-forming reactions on 2-dimensional semiconductors and other related electrocatalytic systems. We demonstrate that it is essential to more fully treat the electrochemical microenvironment in order to model and understand these complex multi-step reactions and that local bias effects are much more important than previously understood and cannot be ignored or approximated by simple Coulomb approximations. This new insight has the potential to alter our understanding of electrocatalytic reactions in (photo)electrochemical systems considerably.

4:00 PM NM02.05.03

Disentangling Spectral Signatures of 2D Material Interfaces Under Bias—Cracking the Mysterious Case of the Shifting A Exciton in Monolayer Transition Metal Dichalcogenides Thomas Sayer[1], Yusef R. Farah[2], Rachelle Austin[2], Justin Sambur[2], Amber T. Krummel[2] and Andres Montoya-Castillo[1]; [1]University of Colorado, Boulder, United States; [2]Colorado State University, United States

A fundamental challenge in elucidating, controlling, and exploiting nonequilibrium relaxation in condensed phase systems is the ability to employ physically transparent models to assign and interpret the spectral signatures of processes spanning charge and energy transfer, quasiparticle formation, and even chemical reactivity. Two-dimensional materials, such as transition metal dichalcogenides (TMDs), offer one such challenge, especially under applied fields. In this talk, I will discuss our critical assessment of the ability of a physically intuitive Hamiltonian, consisting of an infinitely heavy exciton immersed in a fermi sea of conduction band electrons, to capture and offer an interpretation of the spectral features in the linear and transient absorption optical signals of this material under an applied bias. We leverage our analysis to identify, physically, how trion formation moves, broadens, and resizes the "A exciton" absorption of our working device. We further unify the interpretation over various sources of such TMD spectral shifts: applied bias, fluence, and (TA) delay time. Our work thus delineates open questions that are only now becoming possible to address with theory and experiment about the interplay of spectral signatures of various quasiparticles, and identifies the underlying physical process responsible for previously misidentified spectral features in 2D materials that changed with applied voltage, fluence, and time.

4:15 PM NM02.05.04

Dynamics, Hybridization and Thermalization of Phonons in Optically Excited Twisted TMD Bilayers Johnathan Georgaras and Felipe H. da Jornada; Stanford University, United States

One primary limitation to implementing van-der-Waals (vdW) stacked materials in future nanodevices is the management of heat between layers. Recent experiments and calculations show that heterostructures of transition metal dichalcogenide (TMD) bilayers are surprisingly inefficient heat conductors. They display a thermal boundary conductivity across layers as small as 1.4 W $m^{-1}K^{-1}$ – comparable to the thermal resistance of 300nm of glass. This is particularly relevant to the dynamics of excitons in TMD bilayers, which are typically initialized optically first as an intralayer exciton, but quickly relax within ~50 fs into a spatially separated interlayer exciton, releasing phonons with a non-thermal distribution. Here, we evaluate the role of individual phonons and interfacial twist angle in the interlayer heat transfer. We focus on initial phonons created by the relaxation of intralayer excitons in twisted TMD bilayers and explore the mode- and time-resolved phonon dynamics, including phonon-phonon interactions, from first-principles-parametrized atomistic calculations. These methods give insight into the effects of atomic relaxation and the formation of strain solitons in these large-scale moiré TMDs, elucidating how one might engineer more efficient interlayer heat transfer.

4:30 PM *NM02.05.05

Coherences and Populations in Mixed Classical–Quantistic Bosonic Systems—A Many–Body Perspective Andrea Marini; Istituto di Struttura della Materia and Division of Ultrafast Processes in Materials (FLASHit) of the National Research Council, Italy

Excitons are routinely used to interpret a wealth of physical concepts [3], both at equilibrium and out–of–equilibrium. The commonly accepted picture is simple: a photo–excitation creates a bound electron–hole pair that evolves as a population in time inducing an observable induced field and governing the carriers distribution. Phonons [1, 7] are equally ubiquitous in condensed matter physics. The electron–phonon interaction is at the basis of the description of such disparate phenomena. There are few key differences between excitons and phonons. Excitons are not exact bosons while phonons are. On the other hand one of the most successful approach to calculate phonons is based on Density–Functional Perturbation Theory, a semi–classical approach where atoms are treated within the classical Born–Oppenheimer approximation. On the contrary excitons are obtained from a fully quantistic theory.

In this talk I will discuss how the external field (in the case of excitons) and trajectories (in the case of phonons) are just different manifestations of coherence. I will, then, discuss their link with the Many–Body Green's function concept. I will also investigate the processes that lead to a coherence transfer to the quantistic dynamics leading to the formation of real populations and, eventually, macroscopic phenomena. I will first describe three different aspects of the excitonic physics: the photo– induced band insulator to excitonic insulator (EI) transition [5], the ultrafast rise time of the transient

absorption in an MoS2 monolayer [6] and the discovery of the exciton internal structure by means of exciton–phonon coupling [4]. In the case of phonons I will discuss the clear and sharp distinction between the coherent, classical, trajectory concept and the quantistic fluctuations [2]. I will then conclude my talk by describing the rich physics of a paradigmatic
mixed classical–quantistic system, the Semi–classical Swing where classical fields oscillate immersed in a quantistic liquid. The different aspects discussed will contribute to give an unconventional description of the excitonic an phononic states opening the path to further theoretical and experimental investigations.

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SESSION NM02.06: Poster Session: 2D Materials for Electrochemical Applications
Session Chairs: Kwabena Bediako, Andres Montoya-Castillo and Justin Sambur
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM NM02.06.01
Engineering Topological and Atomic Defects for Electrochemical Reactions in 2D Materials Bryan J. Kim, Kaidi Zhang and Kwabena Bediako; University of California, Berkeley, United States

Understanding the factors that govern interfacial electron transfer and manipulating these interfacial reactions is vital for the design of new materials for energy conversion. 2D materials offer immense tunability and potential as electrochemical interfaces. Stacking multiple 2D layers is demonstrative of such tunability, as shown in trilayer graphene (TLG) systems. Natural TLG exhibits two distinct stacking modes (ABA and ABC), which we show here to possess different reaction kinetics for an outer-sphere redox reaction. We also show that the introduction of topological defects, such as interlayer twists between individual graphene layers, produces artificial stacking modes (AAA and AAB) that act as electron transfer reaction hotspots. Such topological defects unlock an additional degree of freedom to tune the electrochemistry. The electrochemistry of other 2D materials can similarly be improved by introducing atomic defects, specifically sulfur vacancies in MoS2. By irradiating monolayer MoS2 with a Raman laser, we show that sulfur vacancies emerge that act as reaction hotspots for electrocatalytic reactions such as the hydrogen evolution reaction.

5:00 PM NM02.06.02
Fabrication and Application of Fluoropolymer-Modified Electrocatalysts to Produce NH_3 with High Faradaic Efficiency from Nitrate Reduction Profulla Mondol[1], Dipak Panthi[2], Adan J. Ayala[1], Samuel Odoh[1] and Christopher Barile[1]; [1]University of Nevada, Reno, United States; [2]Boise State University, United States

Ammonia (NH_3) is an extremely important chemical feedstock and is used extensively in the fertilizer, pharmaceutical, and dye industries.[1-2] As a result, NH_3 is the fifth most produced chemical in the world by volume.[3] Additionally, NH_3 has recently been considered as an alternative renewable fuel in fuel cells.[4] The most well-established route to generate NH_3 on an industrial scale is the Haber-Bosch process.[5]
In light of the enormous energy footprint of the Haber-Bosch process (1-2% of global energy consumption), alternative green routes of generating ammonia (NH_3) are needed.[2] The electrochemical reduction of NO_3^- from waste streams is a promising method to produce NH_3 using renewably sourced electricity. However, catalyst selectivity is a grand challenge that hinders NO_3^- to NH_3 conversion technologies.
In this work, we fabricate Nafion-modified (6 mm thickness) Cu catalysts for NO_3^- reduction. Although Nafion composites are commonly used to facilitate proton transfer, this research investigates electrodes covered by Nafion overlayers, which possess unique reactivity. We find that Cu versions of these catalysts reduce NO_3^- to NH_3 with a Faradaic efficiency of up to (91 ± 2) % making them among the most selective catalysts reported. We also investigated the effect of polymer hydrophobicity by using PVDF polymer on NH_3 production efficiencies. Voltammetry studies, surface-enhanced Raman spectroscopy, and density functional theory calculations indicate that the Nafion overlayer activates the N-O bond of a key Cu-NO intermediate, thus facilitating NH_3 production.
Lastly, we tested the practicality of the Nafion-modified Cu electrode by using it to remove NO_3^- from a real-world groundwater sample. We obtained groundwater from Silver Springs, Nevada, which is in an agricultural valley 30 miles east of Reno, Nevada. This catalyst can remove 97 % of the initial NO_3^- within one hour of electroreduction.

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5:00 PM NM02.06.03
Restacking-Resistant 3D MXene/Metal Selenide Microspheres Fabricated by a Ultrasonic Spray Pyrolysis for Energy Storage Application Seung Keun Park and Oh Hong Geun; Chung-Ang University, Korea (the Republic of)

Two-dimensional (2D) MXenes are considered as promising electrode materials for energy storage, owing to their high electronic conductivity and low diffusion barrier. Nevetheless, similar to most 2D materials, MXene nanosheets easily restack during the electrode preparation, which degrades the electrochemical performance of MXene-based materials. A novel synthetic strategy is proposed for converting MXene into restacking-resistant 3D balls coated with metal selenide. This strategy involves the preparation of metal oxide@ carbon/MXene microspheres via a ultrasonic spray pyrolysis and subsequent selenization process. Such 3D structuring effectively inhibits interlayer restacking, increases the surface area, and promote ion transport, while maintaining the attractive properties of MXene. Furthermore, combining metal selenides and carbon with 3D MXene microspheres provides more ion storage sites and enhances the structural stability of the electrode. The resultant 3D microspheres exhibit excellent electrochemical performance in potassium-ion batteries. This structural design strategy will inspire the development of 2D materials with excellent performance in the energy field.

5:00 PM NM02.06.04
Non-destructive Fabrication of Highly Dispersed Low-dimensional Nanocarbon Paste for Li-ion Battery Electrodes Jungmo Kim; Korea Electrotechnology Research Institute, Korea (the Republic of)

Application of 1-D and 2-D nanocarbon materials (i.e. carbon nanotubes (CNTs), graphene) in the Li-ion battery electrodes has long been the topic of interest, owing to the potential of enhancing the performance and stability of the batteries. The expectations has grown further with the successful commercialization of multi-walled CNTs (MWCNTs) as the conductive agents in Li-ion battery (LIB) cathodes, and the industries are currently making approaches to use single-walled CNTs (SWCNTs) and graphene as the next step.
In order to fully utilize SWCNTs and graphene as the components in the LIB electrodes, the materials must be prepared in a highly-dispersed state while maintaining their morphological and crystallographic characteristics. Unfortunately, the conventional procedures used for the MWCNTs are ineffective in the cases of SWCNT and graphene, and alternative strategies are required.
Herein, I introduce an efficient and effective method to disperse SWCNTs and graphene and demonstrate the application strategy of the low-dimensional nanocarbon materials as the conducting agent as well as current collector.
In the first part, non-oxidative debundling and exfoliation of SWCNT and graphene using charge transfer phenomena during chemical intercalation process is explained. The nanocarbon materials are charged when they are exposed to electron solutions formed by dissolving alkali metal in hexamethylphormamide (HMPA), and can be directly dispersed by introducing shear forces, resulting in highly dispersed paste with nanocarbon material content up to 1 wt%. The re-dispersion into other solvents commonly used in the industries are also showed.
In the second part, the application of the highly dispersed nanocarbon materials as the LIB electrode component is shown:
i) Facile fabrication of free-standing nanocarbon current collector; the free-standing film nanocarbon current collector allows significant weight reduction of the batteries, and can be extensively applied to the highly-stable flexible batteries;
ii) The production strategy for a nanocarbon-coated micro silicon particle and their application as the LIB anode active material; the coating allows enhanced cyclic stability as well as the increased energy density as the result of tightly formed percolation networks, suppressing the random formation of SEI layer.

5:00 PM NM02.06.05
An Efficient Method of Screening Chemical Receptors for the Electrochemical Detection of Biocides Haney Lee[1] and Hyeonseok Yoon[2,1]; [1]Department of Polymer Engineering, Graduate School, Chonnam National University, Korea (the Republic of); [2]School of Polymer Science and Engineering, Chonnam National University, Korea (the Republic of)

Biocides are any substances capable of eliminating, neutralizing, preventing, or controlling the harmful effects of any organism, whether it be through chemical or biological means. Biocides have been used for decades in many different industries, including those that produce food, drink, cosmetics, medicines, and household goods. A major issue is that some biocides may have unintended negative effects on human health. The potential for severe lung injury caused by isothiazolinones (ITZs) exposure has made pulmonary toxicity a pressing concern in recent years. Here, we describe the DFT-based evaluation of the recognition efficacy of several small-molecule-based chemical receptors that we designed for a specific ITZ. We also conjugated chemical receptors to graphene and tested their ability to detect biocides on an electrochemical platform. A statistical method for determining correlations in multivariate data was also used to check if the responses of the synthesized receptors immobilized on graphene could isolate the target ITZ from the interferences.

5:00 PM NM02.06.06
Electrochemical Storage Performance of N-doped $CoSe_2$/MXene Composites— Application for Sodium and Potassium Ion Batteries Oh Hong Geun, Seung Keun Park and Youngjae Yoo; Chung-Ang University, Korea (the Republic of)

Sodium and potassium have attracted much attention as next-generation energy storage systems to replace lithium based on abundant resources. However, sodium and potassium have a sizeable ionic radius than lithium. Therefore, electrode design for their practical application is essential and currently faces significant challenges.
This research synthesized a unique two-dimensional structured composite derived from MXene nanosheets and a metal-organic framework. First, a Co-based zeolitic framework (ZIF-67) was deposited on the surface of MXene nanosheets. After selenization, the ZIF-67 transformed into N-doped $CoSe_2$. This unique structure can improve the electrons and ion transportation owing to shorten pathways and provide sufficient space to accommodate the volumetric expansion of the active materials during the cycling. Also, the N-doped carbon matrix and MXene nanosheets can improve the robustness of the electrode materials. Therefore, the composites exhibited an increased electrochemical performance in sodium-ion and potassium-ion batteries.

5:00 PM NM02.06.07
Tunnel Oxide Passivated Contact on Silicon Photoelectrodes for Tandem Photoelectrochemical Water-splitting Devices Choongman Moon[1], Filipe Martinho[2], Gihun Jung[1], Jaehyuk Koh[1], Hajijafarassar Alireza[2], Canulescu Stela[2] and Byungha Shin[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Technical University of Denmark, Denmark

Crystalline silicon has been considered one of the most promising materials for the bottom cell of a tandem photoelectrochemical (PEC) water-splitting device because of its appropriate band gap (1.12 eV) as well as the industrial maturity. The tandem PEC water-splitting device, especially when made of earth-abundant materials, would be a sustainable way of producing hydrogen fuels; thus, considerable efforts have been made to acquire the best performance out of the large band gap top cell and Si bottom cell. Despite these efforts, there have been only a few studies that enable unassisted solar water splitting by using a tandem PEC device with a silicon bottom cell because 1) the photovoltage from the tandem device is not sufficient to drive the water splitting reaction by itself, and 2) poor thermal stability of a Si bottom cell severely limits the choice of the top cell material and processing conditions. Therefore, improving the photovoltage and thermal stability of the Si bottom cell would provide a great opportunity to realize tandem PEC devices for solar fuel applications.

In this work, we report silicon photoelectrodes based on a tunnel oxide passivated contact (TOPCon), which exhibits superior properties as a potential bottom cell for a monolithic tandem device. Our TOPCon Si photoelectrodes yielded photovoltages in the range of 640 - 650 mV in both photocathode and photoanode configurations under a broad range of pH (0 – 14) conditions of working electrolytes, which are the highest values reported for photoelectrodes based on crystalline silicon. Furthermore, the TOPCon device retained its superior property after thermal annealing at 600 °C for 1 hour in air. The capability of operating in the both configurations (photocathode and photoanode) over a broad range of pH and high thermal stability provides great flexibility in the design of a tandem PEC device: TOPCon Si is capable of stable operation in any pH and is compatible with a top cell semiconductor of any type (n-type or p-type) that may require a high processing temperature. As a preliminary study of a monolithic tandem device based on TOPCon Si, we tested wired tandem devices using a $BiVO_4$ photoanode or halide perovskite photocathode as a large band gap counterpart of TOPCon Si photoelectrodes to show the feasibility of unassisted solar water splitting. The $BiVO_4$-TOPCon Si and perovskite-TOPCon Si tandem devices yielded solar-to-hydrogen conversion efficiencies of 0.24 and 3.6 %, respectively. Notably, STH efficiency from perovskite-TOPCon Si (3.6 %) is one of the highest values from tandem PEC devices based on earth-abundant elements.

5:00 PM NM02.06.08
Density Functional Theory Study of the Adsorption of N_xO_y Functional Groups on Diamond (100) Surfaces Jenille Cruz[1], Ruzmetov Dmitry[2], A G. Birdwell[2], Elias Garratt[2], James Weil[2], Pankaj Shah[2], Tony Ivanov[2], Michael Groves[1] and Mahesh Neupane[2]; [1]California State University, Fullerton, United States; [2]DEVCOM Army Research Laboratory, United States

Diamond's unique structural, thermal, and electronic properties make it an interesting material for high-field, high-frequency device applications, such as radio-frequency field-effect transistors, power amplifiers, and communication satellites. Recent experimental evidence suggests that adsorbing N_xO_y functional groups on hydrogen-terminated diamond surfaces could play an important role in improving device parameters, such as current density and threshold voltage. In this study, we performed Density Functional Theory (DFT) calculations of N_xO_y functional groups adsorbed on bare and hydrogen-terminated diamond (100) surfaces. The adsorption energies were calculated to predict the most favorable structure. Band structures and density of states will be reported to explain the electronic properties of the most favorable system for device design. Nudge Elastic Band calculations will also be reported for the adsorption pathways to form these most stable absorbate configurations. Overall, this research will present several models of N_xO_y functional groups adsorbed on bare and hydrogen-terminated diamond (100) surfaces and will provide critical insight into surface electronic properties of diamond surfaces for surface doped diamond devices.

5:00 PM NM02.06.09
Mechanisms of Gas Intercalation, Transport, and Selectivity in Nanoconfined Ionic Liquids Revealed by Molecular Dynamics Simulations Fikret Aydin, Stephen E. Weitzner, Amanda Muyskens, Alexander Abelson, Steven F. Buchsbaum, Tuan Anh Pham and Eric R. Meshot; Lawrence Livermore National Laboratory, United States

Understanding gas transport through confined ionic liquids (ILs) becomes important for a wide range of emerging energy related technologies. The structure and dynamics of IL filling under confinement have been characterized previously [1]; however, the mechanisms governing gas transport and selectivity remain largely unknown, specifically a detailed understanding of the effects of the IL type, morphology and charge state of the nanopores on the gas separation is still missing. Here, we investigate the mechanism of CO, CO_2, N_2, O_2 or NH_3 transport and selectivity in widely/commonly used imidazolium-based ionic liquids, specifically a 1-butyl-3-methylimidazolium cation (bmim) with either hexafluorophosphate (PF6) or acetate (Ac) anion confined in carbon nanotubes (CNTs) with a diameter of 2.1 nm by using molecular dynamics simulations and enhanced free energy sampling methods. The two ILs have been identified using an informatics-based approach that enables an efficient screening of IL candidates to be used in electrochemical systems [2]. Our simulations provide free energy surfaces associated with selective interaction of various gases with ILs and reveal the underlying mechanism of specific gas selectivity. Our simulations show that the gas selectivity in these systems can be explained by the competition between a complex interplay between confinement, charge state of CNTs and type of IL. Our findings can provide insight into the conditions that optimize selectivity of gas molecules transporting through IL-CNT systems, which in turn may assist practical design and fabrication of real electrochemical systems.
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5:00 PM NM02.06.10
Mechanistic Studies of the Nitrogen Reduction Reaction on 2D-Transition Metal Dichalcogenides in Realistic Media; Understanding the Effects of Electrified Interfaces Taylor Aubry, Logan M. Wilder, Derek Vigil-Fowler, Elisa Miller-Link and Jao Van de Lagemaat; NREL, United States

Improving electrocatalysts is a promising strategy towards clean and sustainable production of many globally important fuels and chemicals. Yet, to date, poor catalyst performance has limited their implementation in a variety of energy conversion technologies such as hydrogen evolution, CO2 reduction, and nitrogen reduction, among others. Two-dimensional (2D) transition metal dichalcogenides (TMDCs) are a class of materials that are advantageous for (photo)electrocatalysis due to their high surface area, favorable electronic transport properties, efficient light absorption, and highly tunable electronic structure. One important albeit challenging reaction to catalyze is the nitrogen reduction reaction (NRR) ($N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$), which is highly desired to enable sustainable ammonia production for fertilizers and energy storage. Although 2D materials have shown promise for NRR, their activity and selectivity are hampered by competitive H_2 generation, poor N_2 solubility in aqueous media, and slow reaction kinetics. In order to engineer them for optimal performance, improved mechanistic understanding of the NRR on 2D-TMDCs is necessary.
In this work, perform density functional theory (DFT) calculations on the 6-step NRR pathway while considering the effects of solvent and applied potential. We use a joint-DFT software package (JDFTx) that employs continuum solvation models to handle solvent interfaces and grand-canonical DFT for fixed potential calculations, thereby more accurately describing the true behavior of electrochemical systems. We focus on one of the most widely studied and particularly promising TMDCs for NRR; MoS_2. We determine the catalysts active sites and selectivity over the hydrogen evolution reaction. We find that applied potential modifies the reaction mechanism for the NRR, an effect we believe is due to the ability of N_2 to undergo p-backbonding with the d-metals in the TMDC catalyst. This work highlights the importance of treatment of electrified interfaces in studying electrocatalytic systems. With improved understanding of how tuning TMDCs can impact NRR, the goal is to guide future catalyst design and generate competitive catalysts for NRR and other important reactions.

5:00 PM NM02.06.12
A Comparison of Vertically Aligned Graphene with Various Graphene Forms for Biosensing Applications Abdulrahman Al-hagri[1,2], Selvakumar Palanisamy[1] and Matteo Chiesa[1,2]; [1]Khalifa University, United Arab Emirates; [2]The Arctic University of Norway, Norway

Vertically aligned graphene nanosheet arrays (VAGNAs) have a large surface area, superior electron transport properties, excellent mechanical strength, high chemical stability, and enhanced electrochemical activity, making them highly suitable for supercapacitors, batteries, fuel cell catalysts, etc. We fabricated VAGNAs terminated with a high-quality bilayer graphene sheet without needing an additional catalyst using plasma-enhanced chemical vapor deposition [1]. A new electrochemical biosensor for detecting dopamine (DA) biomolecules (in human serum and drug samples) is reported in this study based on VAGNAs. Graphene structures of various types were compared with VAGNAs for their electrochemical behavior towards DA sensing. The fabricated VAGNAs-based sensor provided a highly selective and sensitive option with a detection limit of 2 nM and response range of up to 326.3 µM

compared to other graphene material (prepared by various methods) based biosensors. This finding strongly indicates that VAGNAs can be used as a real-time biosensor to detect DA at low levels.
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5:00 PM NM02.06.13
General Synthesis of Inorganic/Reduced Graphene Oxide Nanocomposites and Their Applications in Lithium Batteries Wanyu Zhang, Zhe Su, Shan Yi and Donghui Long; East China University of Science and Technology, China

Two-dimensional (2D) graphene and its derivatives are promising candidates for electrochemical applications due to their versatility. Hitherto, various metal oxides have been decorated onto graphene sheets to form composite artificial materials with unprecedent characteristics and performances, taking fully advantages of 2D graphene and ultrafine metal oxides in a synergistic manner [1,2]. However, the adhesion of rigid inorganic nanoparticles generally induces more wrinkled and agglomerated structure, possibly due to the formation of inhomogeneous compressive stress during the synthesis, leading to limited application potential.
Herein, for the first time, we present a general heterogenous nucleation and diffusion-controlled growth route to synthesize dozens of sandwich structured metal oxide/reduced graphene oxide (rGO)/metal oxide nanocomposites [3], and further confirm their applications in both lithium metal and lithium sulfur batteries. The details are as follows: (1) Such sandwich structured materials could be applied as solid-state electrolyte to optimize lithium-ion conduction by interconnected amorphous organic–inorganic interphases with polyethylene oxide in lithium metal batteries[4]; (2) Furthermore, tailored metal oxide/sulfide heterostructures on rGO surface with rational balancing of strong adsorption and high catalytic activity could also be prepared through adding thiourea in the precursor solution, enabling an unrestricted adsorption-diffusion-conversion of polysulfides in lithium sulfur batteries[5].
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SESSION NM02.07: 2D Materials for Next-Generation Electrochemical Applications
Session Chairs: Andres Montoya-Castillo and Justin Sambur
Thursday Morning, April 13, 2023
InterContinental, Fifth Floor, Sutter

8:00 AM *NM02.07.01
Multidimensional Metal Sulfide Electrocatalysts for CO_2 and CO Conversion to Alcohols Jesus M. Velazquez; University of California, Davis, United States

Electrocatalytic production of oxygenate and hydrocarbon fuels from sequestered CO_2 and green H_2 is a promising carbon-neutral technology that can be readily coupled with solar, wind, or hydroelectric power. The development of solid-state synthetic pathways of electrochemically active materials that address the growing dichotomy of simultaneously increasing energy demands and carbon emissions is an imperative that has progressively affected energy-related research efforts. To this end, our work establishes structure—function relationships for solid-state materials within the multinary chalgogenides comprised of MX_2 (M = Mo, W; X = S, Se) and Chevrel-Phase (CP) $M_yMo_6X_8$ (M = alkali, alkaline, transition or post-transition metal; y = 0-4; X = S, Se, Te) chalcogenides. The molybdenum sulfide structures from both families exhibit exceptional promise as CO_2R catalysts. Furthermore, we have identified the CP catalyst framework as being selective towards the electrochemical reduction of CO_2 and CO to methanol (only major liquid-phase product) under applied potentials as mild as -0.4 V vs RHE. Reactivity toward the electrochemical reduction of CO_2 and CO to methanol is correlated with the increased population of chalcogen states, as confirmed via X-Ray Absorption Spectroscopy. Overall, this work seeks to unravel optimally reactive small-molecule reduction catalyst compositions.

8:30 AM *NM02.07.02
Electrochemical Nitrogen and Proton Reduction using 2D Transition Metal Dichalcogenides Elisa Miller-Link; National Renewable Energy Laboratory, United States

We use 2D transition metal dichalcogenide (TMDC) catalysts to facilitate the nitrogen (N_2) reduction to ammonia and proton reduction to hydrogen via dark electrocatalysis. These two reduction pathways are very important to understand and control for NH_3 and H_2 electrochemical production, where both products can be used as energy carriers, for energy storage, and as direct fuels. TMDCs are good catalyst candidates for these electrochemical reduction reactions because they can be reduced to 2D, where their quantum confined properties are easily manipulated for various applications. Transition metal-based catalysts offer a unique opportunity to exploit the d electrons and orbitals as well as chalcogenide plane for N_2 activation and/or H^+ adsorption, where we specifically compare theoretically and experimentally MoS_2, TiS_2, and VS_2. In addition, the 2D TMDC catalysts are highly tunable 2D catalysts, where the band energetics, surface functionalization, defects, and phase can be tuned to control the reduction mechanisms. Also through various attempts and iterations to generate NH_3, we have many lessons learned about experimental and theoretical approaches for N_2 reduction that will be communicated.

9:00 AM NM02.07.03
Local Atomic Environment of Single-Atom Pt in Metallic TMDC Nanosheets Boosts Catalytic Performances of Li-O_2 Batteries Joo-Won Lee and Sohee Jeong; Korea Institute of Science and Technology, Korea (the Republic of)

2D Transition metal dichalcogenides (TMDCs) show changeable electronic properties corresponding to the polytype and chemical modification at the atomic level of 2D TMDCs. Metallic TMDCs comprising the trigonal structure (1T or 1T' phase) have been investigated as efficient catalysts due to their

proper electrochemical properties compared to semiconducting TMDCs with the 2H phase. These metallic TMDCs catalysts have been prepared by atomic-scale chemical modifications such as single-atom doping. However, a detailed role of single-atom doping in TMDCs is still ambiguous because it is unclear that the enhanced catalytic activities stem from whether the metallic properties or electrochemical properties of single-atom.
Here, we report the facile one-pot synthesis of metallic WSe_2 few-layer nanosheets. Subsequent solution treatments at room temperature enabled isolated incorporation of single atoms such as Rh, Pd, Ir, and Pt into metallic WSe_2 nanosheets. Extensive experimental analysis reveals that considerably high Pt content (~5 wt%) was doped in metallic WSe_2 nanosheets (Pt_{SA}-WSe_2). Local atomic structure of Pt_{SA}-WSe_2 was proved through X-ray analysis including XPS and XPDF, which supports that single-atom Pt is individually distributed inside of WSe_2. For efficient Li-O_2 batteries, cathode materials are required to overcome the sluggish kinetics of oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). Pt_{SA}-WSe_2 shows enhanced ORR/OER activities by dissociative oxygen adsorption on the W sites of the basal planes as well as single-atom Pt sites in metallic WSe_2, which is demonstrated through experimental analysis and DFT calculations as well. Eventually, Pt_{SA}-WSe_2 shows the enhanced Li-O_2 battery performances with the capacity of 27,000 $mAhg^{-1}$ and stable discharge/charge cycles of 350.

9:15 AM DISCUSSION TIME

9:30 AM BREAK

10:00 AM *NM02.07.05
Tuning of Physical and Chemical Properties of Graphene by Electrolyte Gating Matěj Velický, Martin Jindra, Ghulam Abbas, Martin Kalbáč and Otakar Frank; The Czech Academy of Sciences, Czechia

Electrolyte gating is an efficient way of controlling physical and chemical properties of two-dimensional (2D) materials.[1,2] However, despite its advantages over the more traditional dielectric gating, commonly used in condensed matter physics and electrical engineering, electrolyte gating has not been adopted at a significant scale by researchers outside the electrochemistry field.

We will demonstrate the power of electrolyte gating on a newly developed in situ spectroelectrochemical technique, which allows application of potential through a microdroplet electrochemical cell with a simultaneous Raman spectroscopy measurement.[3] Using this technique, we can monitor localized electrochemical and spectral responses of the basal planes of monolayer graphene with varying levels of disorder. Charge doping-dependent Raman G band shifts as well as cyclic voltammetry of a redox mediator both reveal contributions from two distinct processes, originating from the pristine and defective areas on the basal plane surface. This indicates the existence of two independent charge transfer processes with slower and faster rates on the same surface, each restricted to the defect-free and defect-rich areas, respectively.

In order to frame our results with a wider context, we evaluate the available literature on electrolyte doping of graphene using in-situ Raman spectroelectrochemistry measurements and draw conclusions on its limitations, applicability, and efficiency.

References:

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10:30 AM NM02.07.06
Large Scale Integration of 2D material for Memristors Clotilde Ligaud[1], Lucie Le Van-Jodin[1], Bruno Reig[1], Clémence Hellion[1], Pierre Trousset[1], Jean Coignus[1], Céline Vergnaud[2], Hanako Okuno[3], Djordje Dosenovic[3], Stéphane Cadot[1], Rémi Gassilloud[1] and Matthieu Jamet[2]; [1]CEA-Leti, Univ. Grenoble-Alpes, France; [2]Université Grenoble Alpes, CEA, CNRS, CEA, Grenoble INP, IRIG-Spintec, France; [3]University Grenoble Alpes, CEA, IRIG-MEM, France

2D materials are promising candidates for next generation devices. Their various properties combined with their intrinsic thinness and flexibility could enable the realization of high-performance devices. For instance, MoS_2 has demonstrated switching behavior [1] which allow the manufacturing of memristors [2] or high cut-off frequency RF switches[3]. Nevertheless, the high growth temperature of 2D material by physical or chemical methods prevents their fabrication directly on partially processed integrated circuits. An intermediate transfer step from the growth substrate to the final substrate is necessary to achieve their large-scale integration. Today, most publications are based on individual devices with a great lack of reproducibility and statistics. In this work, we report the successful large-scale integration of MoS_2 in memristors reaching the current state of the art.
In this work, bottom electrodes are patterned on a 200 mm wafer. About 250 dies of 1 cm^2 were thus obtained. On each die are designed several structures such as van der Pauw, Hall bar, RF switches, memories… By transferring and patterning MoS_2 and top electrodes on the dies, vertical memories are performed with the following structure: bottom electrode/2D material/top electrode.
Planar bottom electrodes are made of a stack of Ti/AlCu/Ti/TiN, performed with standard deposition and patterning processes. The 2D material consists of three monolayers (ML) of MoS_2 grown by Atomic Layer deposition on 200 mm SiO_2/Si wafer. MoS_2 is transferred above by wet transfer method using polystyrene as support layer. Then 2D material is patterned using deep UV lithography and plasma etching. Finally, top electrodes are deposited by ebeam evaporation and patterned by photolithography and lift-off. Three metallic electrodes are tested: Ag, Ni and Cr/Au.
An in-depth TEM study is performed on the stack SiO_2/MoS_2/Ag. It shows the very good quality of the device. It confirms the preservation of each of the three MoS_2 layers and the clean interfaces with electrodes. A study of Raman spectroscopy at each step of the process confirms the MoS_2 preservation. Optical and electronic microscopy images confirmed the quality of the devices.
Finally, several devices are tested by electrical measurements. Direct current characterization demonstrates resistance-switching behavior. Several cycles are observed on several devices with Ni and Au as top electrodes. Set (switching from OFF to ON state) and Reset (from ON to OFF state) cycles are reproducible between devices. The Set voltage is roughly 2V whereas the reset voltage is around -1V. Except for the first cycle during which the OFF-state current is lower than during the other cycles, the I_{ON}/I_{OFF} ratio is around 10^4. Several cycles (7) are obtained on the devices.
In summary, we developed a large-scale 2D material integration process compatible within standard microelectronics clean room facility. With this process, we were able to manufacture MoS_2-memristors reaching the current state of the art.
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10:45 AM NM02.07.07
2D MXenes Monolayers are More Thermally Stable than Multilayers Hui Fang[1], Claudia Pereyra[1], Anupma Thakur[2], Babak Anasori[2], Andrew M. Rappe[1] and Zahra Fakhraai[1]; [1]University of Pennsylvania, United States; [2]Indiana University−Purdue University Indianapolis, United States

2D MXenes have demonstrated potential applications in optoelectronic devices. The thermal stability of these ultrathin films must be carefully considered due to ambient humidity, unavoidable heating caused by light absorption, current flow, *etc.* Here, we use in-situ spectroscopic ellipsometry to study $Ti_3C_2T_x$ MXenes oxidation and evaluate the resultant structures using AFM. We demonstrate that degradation can be dramatically suppressed upon heating in ambient conditions, after various pre-heat treatments in a vacuum. Contrary to conventional wisdom, our work shows that $Ti_3C_2T_x$ MXene monolayers are more thermally stable than their multilayer counterparts. We discuss how to improve thin film stability through thermal drying in a vacuum and establish the appropriate conditions for each type of film. Density functional theory calculations elucidate possible reasons for the improved stability of monolayers. Our findings provide important design rules for $Ti_3C_2T_x$-based devices, which is very important for the further market application of MXenes.

11:00 AM NM02.07.08
Moiré-Based Topological Defects for Tunable Electrochemistry Kaidi Zhang, Kwabena Bediako and Bryan J. Kim; Univerrsity of California, Berkeley, United States

Interfacial electron-transfer reactions underpin the interconversion of electrical and chemical energy. At electrode–electrolyte interfaces, atomic defects like vacancies and step edges are frequently implicated as active sites that mediate reactivity by introducing high densities of localized electronic states. However, these sites are challenging to deterministically synthesize and control at an atomic level. Moiré superlattices of atomically thin layers generate flat electronic bands and associated localized states that are precisely tunable by the interlayer twist angle. Here we show systematic, >80-fold control over the interfacial electron-transfer rate constant by controlling the stacking configuration and moiré angles in few-layer graphene. At small angles of twisted graphene, the kinetic modulation is governed by well-defined `topological' defects of the moiré superlattice, consisting of atomic configurations that cannot be realized independently of the moiré. These topological defects mediate outer-sphere electrochemical reactions with rates comparable to bulk metals, notwithstanding their consisting of only three atomic layers. Moiré superlattices therefore serve as an unparalleled platform for systematically interrogating and exploiting the dependence of electron-transfer rates on electronic structure.

11:15 AM *NM02.07.09
Accelerating Electrocatalysis on 2D Working Electrodes with a Backside Gate C. D. Frisbie; University of Minnesota, United States

Heterogeneous catalysis is well-known to be sensitive to electron accumulation or depletion on surfaces, but electron density is usually controlled by chemical doping (e.g., promoters) in the case of thermocatalysis, or electrochemical potential in the case of electrocatalysis. The recent advent of ultrathin two dimensional (2D) catalysts prepared either by exfoliation or thin film growth methods opens up a third approach — the transverse field effect, so central to silicon CMOS technology—to modulate the carrier density in a catalyst or electrocatalyst. In this approach the 2D catalyst material is deposited on top of a metal/dielectric stack (the “gate”) to make a capacitor; application of a voltage between the catalyst and the metal causes positive or negative charge to accumulate in the catalyst, depending on the sign of the voltage. This charge in turn tunes the reactivity of active sites, accelerating rates of reaction on the catalyst top surface. This talk will describe some early results for outer-sphere and inner-sphere electrochemical reactions at 2D working electrodes with a backside gate electrode. In particular, we show that a backgate voltage can significantly lower the required overpotential for H_2 evolution at 10 mA/cm^2 at MoS_2 electrodes. In general, 2D working electrodes with a backside gate provide a novel platform for fundamental investigations in electrochemistry.

SESSION NM02.08: Discovery and Synthesis of Functional 2D Materials II

Session Chairs: Kwabena Bediako, Andres Montoya-Castillo and Justin Sambur
Thursday Afternoon, April 13, 2023
InterContinental, Fifth Floor, Sutter

1:30 PM *NM02.08.01
Exploring Dynamical Many-body Effects on Optoelectronic Properties of Low-Dimensional Materials Diana Qiu; Yale University, United States

In low-dimensional and nanostructured materials, the optical response is dominated by correlated electron-hole pairs---or excitons---bound together by the Coulomb interaction. Understanding the energetics and dynamics of these excitons is essential for diverse applications across optoelectronics, quantum information and sensing, as well as energy harvesting and conversion. By now, it is well-established that these large excitonic effects in low dimensional materials are a combined consequence of quantum confinement and inhomogeneous screening. However, many challenges remain in understanding their dynamical processes, especially when it comes to correlating complex experimental signatures with underlying physical phenomena through the use of quantitatively predictive theories. In this talk, I will discuss how excitons in low-dimensional and nanostructured materials, such as monolayer transition metal dichalcogenides and layered perovskites, differ from typical bulk materials. In particular, we will look at how long-range quantum interactions can give rise ultrafast energy transport in low dimensions and explore the transfer of spin, charge and chirality across heterointerfaces. Finally, we will explore the kinetics of phase transitions that accompany Li intercalation in layered van der Waals materials, which has promising energy storage applications and can drive the formation of new charge density wave (CDW) phases.

2:00 PM *NM02.08.02
Polarons in Two-Dimensional Materials—Boron Nitride and Beyond Feliciano Giustino; The University of Texas at Austin, United States

The polaron is an emergent quasiparticle that consists of an electron dressed by a cloud virtual phonons. Polarons arise from the interaction between electrons and phonons in solids, and are responsible for a plethora of unusual properties. Very recently, new spectroscopic capabilities have enabled the direct observation of polarons in several important 3D materials, shedding light on quantum many-body effects that were previously inaccessible. In contrast with these advances in the physics of polarons in 3D bulk materials, very little is known about polarons in 2D atomic crystals. It is currently unknown whether polarons can form in 2D materials, whether they are localized and to what extent, how they respond to probes such as electric and magnetic fields, and whether they exhibit collective phenomena such as Bose-Einstein condensation and superconductivity.

In this talk I will present recent work aimed at answering some of these questions by developing an *ab initio* theory of polarons in 2D materials. I will show that the physics of polarons in 2D is fundamentally different from their 3D counterparts as the effective Coulomb interaction between electrons and phonons becomes short-ranged. This effect alters the energetics and localization of polarons and gives rise to a critical condition for the existence of polarons in 2D which has no counterpart in bulk 3D materials.
To illustrate these concepts, I will first discuss *ab initio* calculations of polarons on bulk and monolayer hexagonal boron nitride (h-BN). Then I will present an *ab initio*-inspired model of polarons in realistic 2D materials which links widely available materials properties, such as dielectric constants and carrier effective masses, to the atomic-scale properties of polarons. This theoretical framework naturally identifies the most important materials descriptors of polaronic properties in 2D, and is suitable for high-throughput screening of two-dimensional polarons.

2:30 PM BREAK

3:30 PM *NM02.08.03
Excitation Transfer in Atomically Thin Materials Andreas Knorr; Technische Universität Berlin, Germany

Atomically thin semiconductors and hybrid structures constitute a remarkable playground for exciton physics in two dimensions. This involves optically accessible (bright) as well as spin- and momentum-forbidden (dark) excitonic states including intravalley and intervalley excitations. The nonlinear, coherent and incoherent exciton dynamics induced by light pulses results from the interplay of intrinsic exciton-exciton and exciton-phonon interactions. Here, we present applications of the theory to:
-biexcitons and exciton-exciton scattering induced coherence decay,
-detection of exciton wave function dynamics in time resolved ARPES, and
-different charge-, Dexter- or Förster-type transfer processes in atomically thin semiconductors functionalized with organic molecules, graphene or metal nanoparticles.
A comparison to experiments is provided throughout the talk.
This work is done in coilaboration with Malte Selig, Florian Katsch, Dominik Christiansen, Manuel Katzer, Lara Greten, Robert Salzwedel and Henry Mittenzwey (TU Berlin).

4:00 PM *NM02.08.04
Structural Design of Optical Selection Rules in Two-Dimensional Semiconductors Sivan Refaely-Abramson; Weizmann Institute of Science, Israel

Excited-state processes in functional materials are essential for emerging applications, from energy conversion to quantum information science. The associated transport and relaxation mechanisms are coupled to optical selection rules, directly related to the underlying material structure. In this talk, I will discuss our theoretical approach to compute excited-state phenomena in structurally-complex two-dimensional semiconductors from first-principles. I will present our recent study relating non-analytical discontinuities in the excitation energies with the early stages of excited-state propagation, and discuss an extension to compute exciton scattering and transport. I will further show our recent research on exciton complexity in transition metal dichalcogenide, relating electro-optical and magneto-optical signature to the presence of atomic defects and heterostructure composition.

4:30 PM *NM02.08.05
Interplay Between Structural and Electronic Properties of TMDC Heterostructures Felipe H. da Jornada[1,2]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States

The synthesis of quasi-two-dimensional materials, such as monolayer transition metal dichalcogenides (TMDCs), opened the door to the study of new classes of systems with nanoscale dimensionality confinement and weak electronic screening, leading to strongly enhanced electron interactions. However, the interplay between the structural details in such twisted bilayer structures (including atomistic relaxation effects), extrinsic fields, and doping on the excited-state properties of such materials is poorly understood, and often relies on empirically fitted continuum models. In this talk, we present results obtained from recent formalisms and methods we developed to bridge these effects and phenomena.

I will discuss how moiré effects can lead to large localization of excitons and the emergence of excitons with qualitatively different spatial distributions. I will also discuss a formalism our group recently developed to understand excitons in moiré materials, which can bridge the atomistic and moiré length scales from first principles. I also first show how the thermal conduction between a pair of vertically stacked 2D materials can be engineered with the interfacial twist angle. I will also show a novel heat transport regime, aided by electron-phonon interactions, which effectively increases the interfacial thermal conductivity by almost two orders of magnitude.

SESSION NM02.09: Current Understanding and Theoretical Description of the 2D Electrode/Electrolyte Interface II

Session Chairs: Kwabena Bediako, Fang Liu, Andres Montoya-Castillo and Justin Sambur
Friday Morning, April 14, 2023
InterContinental, Fifth Floor, Sutter

8:30 AM NM02.09.02
Observing Floquet-Bloch States in van der Waals Semiconductors Vivek Pareek[1], David Bacon[1], Xing Zhu[1], Yang-Hao Chan[2], Fabio Bussolotti[3], Nicholas Chan[1], Joel Perez Urquizo[1], Kenji Watanabe[4], Takashi Taniguchi[4], Michael K. Man[1], Julien Madéo[1], Diana Qiu[5], Kuan Eng Johnson Goh[3,6], Felipe H. da Jornada[7] and Keshav M. Dani[1]; [1]Okinawa Institute of Science and Technology Graduate University, Japan; [2]Academia Sinica, Taiwan; [3]Agency for Science, Technology, and Research (A*STAR), Singapore; [4]National Institute for Materials Science, Japan; [5]Yale University, United States; [6]National University of Singapore, Singapore; [7]Stanford University, United States

Floquet engineering has generated much interest in recent years as a powerful approach to manipulating the electronic structure and topology in the material and manifest quantum states otherwise inaccessible in equilibrium. Typically, an intense optical field is used to create the Floquet states in materials1–3. Despite its potential, the experimental realizations of Floquet engineering using optical fields have been challenging due to detrimental effects such as multi-photon absorption, heating, and scattering. Recently, oscillating bosonic fields within the material, such as excitons or phonons, have been proposed as an alternate route to Floquet engineering4. In the case of the exciton, its presence in the material alters the original ground state Hamiltonian by dynamically changing the many-electron screened-exchange interaction. This results in a time-dependent coupling that oscillates periodically at the exciton frequency and is responsible for driving the Floquet states in the material. So far, such proposals of Floquet engineering driven

by quasi-particle fields, such as excitons, have not been achieved experimentally.
In this work, using time-resolved angle-resolved photoemission spectroscopy (tr-ARPES), we show that the valence band in monolayer tungsten disulfide (WS2) gets replicated in energy due to the oscillating field generated by excitons. We find that the strength of the exciton-driven Floquet effect is two orders of magnitude stronger than the optically driven counterpart. Consequently, we observe that the exciton-driven Floquet replica of the conduction band hybridizes with the bare valence band resulting in a distinct Mexican-hat-like dispersion with a local dip at the center of the valence band. This work also reproduces the predicted changes in the band structure for the BEC to BCS transition in non-equilibrium excitonic insulators. Our findings open new avenues to Floquet engineering using quasi-particle fields such as excitons, phonons, or plasmons.
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Vivek Pareek, David Bacon and Xing Zhu contributed equally to this work.
Corresponding authors: Felipe H. da Jornada and Keshav Dani.

8:45 AM NM02.09.03
Electrostatic Gating to Tailor Interfacial Charge Transfer at 2D MoS_2 Electrodes Sonal Maroo and Kwabena Bediako; University of California Berkeley, United States

Tailoring electron transfer dynamics across solid-liquid interfaces are fundamental to electrical and chemical energy interconversion. Marcus–Gerischer[1] formalism suggests that the electronic states of the electrode around the Fermi level have a significant influence on the rate of electron transfer. Studies have also shown that the faster electron transfer kinetics observed on introducing defects is due to localized enhancements in the electronic states around the fermi level that are available to participate in the reaction. Electrostatic gating in field effect transistor mode is one of the widely used strategies to manipulate the charge carrier density and energy band alignment in semiconductors. It has been demonstrated that the heterogeneous charge transfer kinetics at the MoS_2 monolayer[2] is strongly modulated by applying an external electric field on the working electrodes. Herein, I reevaluate the electric field effect on the interfacial electron transfer at a few layers MoS_2 using Scanning Electrochemical Cell Microscopy (SECCM). MoS_2 electrodes were fabricated in a field effect transistor (FET) configuration with a solid-state graphite bottom gate. The bottom gate voltage (V_{BG}) applied to graphite was used to alter carrier density and control the band alignment. I combined in-situ SECCM experiments with the electrostatic manipulation of the band alignment with V_{BG} to study the effect of charge carrier concentration on the interfacial electron transfer. I also obtained spatially resolved voltammetric responses to understand the role of in-plane charge transport in governing the electrochemical responses of 2D electrodes, especially at conditions of low carrier densities. The experimental approach and results presented here serve as a benchmark for future studies of the electrochemical behavior of two-dimensional materials.

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Two-Dimensional MoS 2 Electrodes. Nano Lett. 17, 7586-7592 (2017).

9:00 AM NM02.09.04
2D van der Waals Inorganic Crystal for Anhydrous Proton Conductor Shingo Ohta[1,2], Hiroshi Nozaki[2], Liang Wang[1], Hongfei Jia[1], Nikhilendra Singh[1], Timothy Arthur[1], Daniel Hashemi[1] and hideo Iizuka[1,2]; [1]Toyota Research Institute of North America (TRINA), United States; [2]Toyota Central R&D Labs., Inc., Japan

We succeeded in synthesizing a novel two-dimensional (2D) van der Waals (vdW) inorganic oxychloride ion conductor which has an applicable potential for high-temperature fuel cell fuel cells (FCs).
The significant reduction of CO2 emissions is extremely important to severely address climate change mitigation. Various electrochemical devices, such as Ni-MH batteries, lithium (Li)-ion batteries (LIBs), Na-S batteries, Li-ion capacitors, FCs, solid oxide fuel cells (SOFC), and water splits, are being used to replace internal combustion engines as new power sources for energy storage and generation.
The most important key materials common to these devices with regard to electrolytes and membranes are ion conductors of hydrogen ions (proton), Li ions, sodium ions, oxygen ions, and hydroxide ions. To develop ion conductors that can be used in these devices, a wide variety of ion conductors, whether liquid, solid, organic, or inorganic, have been developed. Among these, inorganic solid ion conductors are attractive candidates as electrolytes for next-generation batteries and FCs, and they are expected to operate at high voltages and temperatures because inorganic solid materials have significant advantages: (i) high-temperature stability, (ii) wide electrochemical potential windows, and (iii) chemical stability in water and air.
Inorganic solid ion conductors are attractive candidates as electrolytes for next-generation lithium-ion batteries (LIBs) and FCs which are expected to operate at high voltage and temperature due to their high stability and oxidation resistance. However, in previously developed inorganic ion conductors derived from natural minerals, mobile ions are strongly bonded to anions, resulting in low conductivity. Thus, in this study, we present a 2D vdW inorganic proton (H+) conductor for inserting protons into halogen vdW layers. In the best case, conductivity is ~10 mS cm−1 at 120 °C, which is two orders of magnitude larger than that of inorganic conductors previously developed from natural minerals. The design of ion conductors using 2D-vdW inorganic materials can provide a route for high-performance LIBs and FCs.

9:15 AM NM02.09.05
Single-Atom-Catalysts of Non-Noble Metals on Carbon for Alkaline Hydrogen Evolution Reaction Juchao Yan; Eastern New Mexico Univ, United States

Alkaline water splitting for hydrogen production broadens the selection of the electrocatalysts to non-noble metal or metal oxides, but has more sluggish kinetics than acidic water splitting. To address this, the researchers have developed a number of atomically dispersed electrocatalysts based on earth abundant metals, which was coined as single-atom-catalysts (SACs). SACs exhibit high activity for hydrogen evolution reaction (HER), due to the high atom utilization, high activity, and high selectivity. In this talk, I will review various preparations of SACs on carbon, and discuss the electrocatalytic performance for alkaline HER. Emphasis will be on how to increase the metal atom loading for industrial applications.

9:30 AM BREAK

SESSION NM02.10: Nanoscale Imaging and In Situ Spectroscopy III
Session Chairs: Kwabena Bediako, Fang Liu, Andres Montoya-Castillo and Justin Sambur
Friday Morning, April 14, 2023
InterContinental, Fifth Floor, Sutter

10:00 AM *NM02.10.01
Defective Molybdenum Sulfide for Catalysis Hong Li; Nanyang Technological University, Singapore

Electrochemical energy conversion and storage driven by renewable energy sources such as solar and wind are drawing ever-increasing interest due to their critical roles in sustainable development. Advances in these applications rely on highly active and cost-effective electrocatalysts to accelerate the sluggish kinetics of the electrochemical reactions involved. A substantial amount of such electrocatalysts have been exploited recently thanks to the advances in material science and continuous breakthroughs in engineering tools. In particular, molybdenum sulfide (MoS_x) furnishes a classic platform for study of catalysis fundamentals as well as exploration of new applications in hydrogen evolution reaction (HER), nitrogen reduction reaction (NRR), CO_2 reduction reaction (CO_2RR), polysulfide conversion reaction (metal-sulfur batteries), *etc*. Recent studies of MoS_x have focused on activating its inert part [*e.g.*, basal plan of two-dimensional (2D) molybdenum disulfide (MoS_2)] by tailoring its electronic structure through defect engineering. In this talk, I will recap recent theoretical and experimental advances in the use of defective MoS_x for various electrocatalytic applications with a highlight of our own progress. I will start with a brief description of the structure and basic electrocatalytic applications of 2D MoS_2 with 2H, 1T, and 3R crystalline phases. Then, I will discuss the employment of defective MoS_2, which is a model system thanks to its atomically isolated structure, as the electrocatalyst for the popular HER. Next, I will detail the recent development in defect-enhanced non-2D MoS_x-based (*i.e.*, amorphous and cluster structures) HER catalysts. For HER applications, I highlight the combination of theoretical and experimental tools for rational design of defects and understanding of the detailed reaction mechanisms. Lastly, I will briefly discuss the applications of defective MoS_x as catalysts for emerging application such as NRR, CO_2RR, metal-sulfur batteries, and metal-oxygen/air batteries, with a particular emphasis on the synergy built on defects for performance breakthroughs.

10:30 AM *NM02.10.02
Painting Potential Landscapes on an Atomically Thin Canvas Archana Raja; Lawrence Berkeley National Laboratory, United States

Atomically thin van der Waals crystals like graphene and transition metal dichalcogenides allow for the creation of arbitrary, atomically precise heterostructures simply by stacking disparate monolayers without the constraints of covalent bonding or epitaxy. While these are commonly described as nanoscale LEGO blocks, many intriguing phenomena have been discovered in the recent past that go beyond this simple analogy. In this talk, I will discuss two stories from our joint experimental and theoretical work focusing on the rotationally-aligned 2D semiconductor heterostructure of monolayer WS2 and WSe2. In part one, we use electron microscopy and electron energy loss spectroscopy to directly visualize and correlate the nanoscale real space localization of excitonic states and structural reconstruction within the moiré unit cell, opening up the possibility for on-demand engineering of excitonic superlattices with nanometer precision. In part two, we use time- and spatially-resolved spectroscopies to investigate the diffusion of various interlayer exciton species as a function of temperature. We uncover the role of low energy moiré phonons or phasons in enabling exciton diffusion in the moiré potential even at low temperatures. These works are a result of fruitful collaborations with colleagues at various institutions including Berkeley Lab, UC Berkeley, Purdue University, Imperial College, Stanford Unviersity and NIMS Tsukuba.

11:00 AM NM02.10.03
Redox-Active 2D Molecular-Transition Metal Dichalcogenides Bilayer Crystals Mengyu Gao, Ce Liang, Tomojit Chowdhury and Jiwoong Park; The University of Chicago, United States

Understanding the interfacial behaviors is key to electrochemistry. Two dimensional (2D) materials, such as graphene and transition metal dichalcogenides (TMDs), are atomically flat surfaces where electrical and mass transport under electrochemical conditions could be well defined, *in situ* monitored, and precisely engineered. What's more, 2D materials can be used as a synthetic template affording atomic precision for the growth of new 2D systems that are otherwise impossible.

In this work, we present the electrochemical studies on a unique hybrid 2D system, where large-scale, crystalline redox-active 2D molecules were grown on monolayer TMDs as a *2D molecular-TMD bilayer crystal*. This system features ultrathin geometry, atomic precision, and chemical cleanness, and can be used as an ideal model system for electrochemical investigation at 2D interface. As a hybrid 2D system, the intimate interaction between the 2D molecular crystal and the underlying 2D TMD represents a unique interfacial problem, which remains less understood.

Here, toward this goal, we developed an *in situ* electrochemical setup, combining optical microscopy/spectroscopy and electrical transport measurement, to study the electrochemical behaviors of atomically thin 2D hybrid crystals with spatial, temporal and spectral resolution. Specifically, we introduced redox control of 2D molecular crystals made of ordered monolayer perylene diimide (PDI) and PDI-derivatives on monolayer MoS_2 with electrolyte gating. The uniformity, crystallinity and monolayer thickness of the 2D molecular crystals were confirmed by polarization microscopy, scanning-tunneling microscopy and cross-section transmission electron microscopy. Because of the wafer-scale crystallinity and distinct polarized optical responses, the electrochemical properties (such as redox states) of the 2D molecular crystals were accessible via far-field microscopic observations and electrical transport measurements. As the doping level was well controlled electrochemically, we optically and electrically monitored the band filling behaviors of 2D molecular crystals. Coupled with conventional electrochemical testing methods, such as electrochemical impedance spectroscopy, our integrative setup and high-quality growth of 2D molecular crystals are highly versatile, which unlocks new potentials in the electrochemical applications at 2D interface, such as electrochemical transistors, organic batteries, etc.

11:15 AM NM02.10.04
Electroactive 2D TMDC Based Polymer Hybrid and Hydrogel Matteo Crisci[1], Sara Domenici[2], Jonas Pflug[1], Felix Boll[1] and Teresa Gatti[3,1]; [1]Justus Liebig University, Germany; [2]Università di Padova, Italy; [3]Politecnico di Torino, Italy

Since the first discovery of graphene by Novoselov in 20041, graphene and in general 2D materials showed an increasing interest in the scientific community. Specifically Transition Metal Dichalcogenides (TMDC) showed a surge in interest, due to their different properties and flexibility due to the large amount of variability in the group. Not only this, but they can be easily engineered in different ways to tune their properties, examples are doping, functionalization and hybridation with other material2. In this last context, Conductive Polymers (CP)3 show complementary electrochemical properties to the 2D TMDC materials and can be exploited to further improve their performances. Here, we report on the synthesis of hybrids based polyaniline (PANI) and 2D transition metal dichalcogenides (TMDCs), employing different methodologies and formulations. In particular, we resort to liquid phase exfoliation (LPE)4 to produce 2D TMDCs in both the 2H and 1T phase and to in-situ polymerization to produce PANI chains directly on the surface of these nanomaterials to further amplify the electrochemical properties of the 2D material. Then the as obtained material can be further characterized electrochemically and can be also used in conjunction with flexible polymer scaffold in order to obtain piezo- active hydrogels. The as-obtained hydrogels are characterized through a combination of techniques and their swelling behaviour and mechanical properties are investigated.

11:30 AM NM02.10.05
Distinctively Structured WS_2 Nanotubes Embedded in SiOC Fibers for High-Rate Sodium Ion Storage Sonjoy Dey and Gurpreet Singh; Kansas State University, United States

Layered transition metal dichalcogenides (TMDs) such as tungsten disulfide (WS_2) are promising materials for a wide range of applications, including charge storage in batteries and supercapacitors. Nevertheless, TMD-based electrodes suffer from bottlenecks such as capacity fading at high current densities, voltage hysteresis during the conversion reaction, and polysulfide dissolution. To tame such adverse phenomena, we fabricate composite with WS_2 nanotubes. Herein we report on the superior electrochemical performance of ceramic composite fibers comprising WS_2 nanotubes (WS_2NTs) embedded in a chemically robust molecular polymer-derived ceramic matrix of silicon-oxycarbide (SiOC). Such hheterogeneousfiber structure was obtained via electrospinning of WS_2NT/preceramic polymer solution followed by pyrolysis at elevated temperatures. The capacity fading in WS2NT was curbed by the synergistic effect of the composite WS_2NT/SiOC electrode-high initial capacity of 454 mAh g^{-1}, and capacity retention of the composite electrode is 2-4 times higher compared to neat WS_2NT electrode.

SYMPOSIUM

April 11 - April 27, 2023

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SESSION NM03.01: Plasmonics
Session Chairs: Matthew Sheldon and Wei David Wei
Tuesday Morning, April 11, 2023
InterContinental, Fifth Floor, Ballroom A

10:30 AM *NM03.01.01
Electroconversion Beyond the Equilibrium Limit Using Plasmons Prashant K. Jain; University of Illinois Urbana-Champaign, United States

Electroconversion is seeing a resurgence due to its utility for the manufacturing of chemicals and fuels powered by renewable energy. While catalyst design and engineering has been the key strategy for optimizing electroconversions, we have found that light excitation can instead be used to modulate the electrochemical activity in cases where the electrocatalyst is comprised of noble metal nanoparticles. The localized surface plasmon resonances of these nanoparticles allow strong absorption of light and the generation of non-equilibrium conditions at the electrode–electrolyte interface. As an outcome, the electrosynthetic activity is boosted beyond the equilibrium limit. I will describe important examples of such phenomena, including electrocatalytic ammonia oxidation, ammonia synthesis, methanol oxidation, and hydrogen evolution. I will also describe the mechanisms by which plasmonic excitations boost or modulate catalytic and electrocatalytic transformations.

11:00 AM NM03.01.02

Plasmons and Excitons in Pd-Doped Ag Nanoparticles from an *Ab Initio* GW-BSE Approach Emma Simmerman, Aaron Altman, Supavit Pokawanvit and Felipe H. da Jornada; Stanford University, United States

Combining transition-metal catalyst materials with plasmonic metals can enhance photocatalytic reaction rates, selectivity, and open non-equilibrium reaction paths. These effects are initiated by surface plasmon resonances (SPRs) in the plasmonic metal, and direct electron-hole (e-h) interactions can also significantly alter the landscape of excited states and affect SPR evolution. However, *ab initio* calculations in realistic nanoparticle systems have mostly either neglected e-h interactions or been limited to very small (<35 atom) clusters that display zero-dimensional-like excitation spectrum due to strong confinement effects and fail to describe plasmons due to use of the Tamm-Dancoff approximation (TDA). Here, we study Pd-doped Ag nanoparticles of up to 147 atoms with varying dopant levels, including e-h interactions and e-h recombination terms that are not present in the TDA, through the first-principles GW plus Bethe-Salpeter equation (BSE) approach. Applying new low-rank approximations and spectral folding techniques to accelerate these calculations, we can directly obtain excited states of nanoparticles capturing both plasmonic and excitonic effects. For small systems, we observe strong e-h interactions that redshift the spectrum by up to ~2 eV, demonstrating the importance of excitonic effects for spatially confined metallic systems. We also analyze the excitonic and plasmonic character of the excitations as a function of size and doping, and the impact of many-body interactions for reactions involving excited-state potential-energy surfaces.

11:15 AM NM03.01.03
Plasmon-Assisted *Operando* Self-Healing of Cu_2O Photocathodes Teresa Gatti; Politecnico di Torino, Italy

The ongoing problems in western countries connected to the global energy supply urgently forces the research community to strive in finding new methodologies for boosting the functional properties of earth-abundant raw materials, for example the largely available cupreous oxide. In this work, we focus on the surface sensitization of this metal oxide semiconductor with an argon plasma treatment, that promotes, during photoelectrochemical hydrogen evolution, the formation of metallic copper nanostructures. Interestingly, these copper-based hierarchical nano-branches, having inherent plasmonic properties, are at the origin of the improved shelf-life of the modified Cu_2O photocathode, as we demonstrate by advanced structural and photophysical analyses. Our proposed photophysical mechanism for an *operando* electrode stabilization suggests that a self-healing process can occur within the Cu_2O/plasmonic Cu heterostructure. These findings pave the way to the implementation of new, easy-to-make strategies to improve the properties of low-cost, low-toxicity energy materials.

11:30 AM NM03.01.04
Plasmon-Enhanced Electrochemical Oxidation of Alcohol Molecules Jingjing Qiu, Daniel Boskin and Zachary W. Ragan; San Francisco State University, United States

Plasmon-mediated electrocatalysis, i.e., the application of plasmonic nanostructures as electrodes/catalysts or both, has emerged as a promising approach to facilitate electrochemical reactions. We have investigated the electrochemical oxidation of 4-(hydroxymethyl)benzoic acid (4-HMBA) on different metallic working electrodes in alkaline electrolytes, including gold (Au), nickel (Ni), and platinum (Pt) metal. Au shows the lowest onset potential for catalyzing the electrooxidation of 4-HMBA among the three metals in base, whereas Pt does not catalyze the electrooxidation of 4-HMBA under alkaline conditions. The products of electrochemical oxidation of 4-HMBA catalyzed on Au working electrode are 4-carboxybenzaldehyde and terephthalic acid analyzed by high-performance liquid chromatography. The electrodeposited Au nanostructures on indium tin oxide (ITO)-coated glass is further utilized as the working electrode and catalyst for the 4-HMBA electrooxidation by introducing the plasmonic effects of the Au nanostructures. With the broad absorption of the Au nanostructures anchored on the ITO substrate in the visible and near-infrared range, we show that they could enhance the electrochemical oxidation of 4-HMBA under green and red LED light illuminations. The plasmonic effects of the Au nanostructures are proposed to contribute to the enhancement of the reaction and the photothermal effect is excluded based on electrolyte-temperature-dependent measurements. A possible reaction mechanism is proposed for the electrochemical oxidation of 4-HMBA on Au working electrodes in an alkaline electrolyte. Ongoing work focuses on investigating the electrochemical oxidation of electronically unique aromatic substituents of 4-HMBA and the plasmonic effects from the Au nanostructure electrodes in assisting other electrochemical reactions.

Reference:
J. Chem. Phys. 157, 081101 (2022)

11:45 AM NM03.01.05
Utilizing Interband Transitions in Non-Noble Metal Nanoparticles for Sustainable Photocatalysis Son C. Nguyen; University of California, Merced, United States

When moving from noble to non-noble metals, the localized surface plasmon resonances of metallic nanoparticles become less distinctive, but the photo-induced interband transitions are strong and accessible in the visible region. Interband transitions in metallic nanoparticles have recently gained more attention for photocatalysis due to the unique properties of the corresponding hot carriers. It is desirable to explore interband transitions in non-noble metal nanoparticles for photocatalysis. It is also important to transition from utilizing precious (such as Au, Pd) to affordable (Co, Bi) metals for their cost effectiveness, strong light absorption, reasonable stability, and interesting electronic properties for photocatalysis. In this talk, I will share some promising photocatalytic activities of Co-B alloy and Bi nanoparticles in some model reactions and compare their peformance to Au and Pd nanoparticles.

SESSION NM03.02: Nanostructure/Ferroelectricity
Session Chairs: Klaus Boldt and Greta Patzke
Tuesday Afternoon, April 11, 2023
InterContinental, Fifth Floor, Ballroom A

1:30 PM *NM03.02.01
Manipulating Atomic Structures at the Au/TiO_2 Interface for O_2 Activation Wei David Wei; University of Florida, United States

The metal/oxide interface has been extensively studied due to its importance for heterogeneous catalysis. However, the exact role of interfacial atomic structures in governing catalytic processes still remains elusive. Herein, we demonstrate how the manipulation of atomic structures at the Au/TiO2 interface significantly alters the interfacial electron distribution and prompts O2 activation. It is discovered that at the defect-free Au/TiO2 interface electrons transfer from Ti3+ species into Au nanoparticles (NPs) and further migrate into adsorbed perimeter O2 molecules (i.e., in the form of Au-O-O-Ti), facilitating O2 activation and leading to a ca. 34 times higher CO oxidation activity than that on the oxygen vacancy (Vo)-rich Au/TiO2 interface, at which electrons from Ti3+ species are trapped by interfacial Vo on TiO2 and hardly interact with perimeter O2 molecules. We further reveal that the calcination releases those trapped electrons from interfacial Vo to facilitate O2 activation. Collectively, our results establish an atomiclevel description of the underlying mechanism regulating metal/oxide interfaces for the optimization of heterogeneous catalysis

2:00 PM NM03.02.02
One-Step Synthesis of Cu_xO_y/TiO_2 Photocatalysts by Laser Pyrolysis and Their Application for Selective Ethylene Production from Propionic Acid Degradation Juliette Karpiel[1,2], Pierre Lonchambon[1], Frédéric Dappozze[2], Chantal Guillard[2] and Nathalie Herlin-Boime[1]; [1]CEA Saclay, France; [2]Université Lyon 1, IRCELYON, France

Ethylene C_2H_4 is an essential organic molecule for chemical industries and is needed in ton quantities. However, its current synthesis pathways require high temperatures and/or pressures, leading significant energy consumption. In this context, we aim to use photocatalysis as an alternative method to produce ethylene at ambient temperature and pressure. Literature shows that photo-decarboxylation of propionic acid (PA) mainly produces CO_2, H_2 and ethane[1–4]. In addition, ethylene traces were also detected with Pt/TiO_2 or TiO_2 P25 catalysts[3,4]. In this work, we show how the use of copper-modified TiO_2 nanoparticles (NP) applied for the first time to PA degradation allows promoting high selectivity towards ethylene photo-production under UV light without noble metals.
TiO_2 and Cu_xO_y/TiO_2 photocatalysts were successfully synthetized by laser pyrolysis technique. This one-step method consists on an interaction between a CO_2 laser beam with gaseous and/or aerosolized liquid precursors. Such process offers great flexibility. Pure TiO_2 were synthesized from TTIP (Titanium Tetra Isopropoxide) precursor. Addition of Cu(acac)$_2$ in TTIP allowed obtaining copper-modified TiO_2 powders (Cu = 2 wt%). Besides the addition of Cu, only the effect of the atmosphere (He or Ar) during the synthesis was investigated in the present case. Samples were labelled TiO_2-X and Cu/TiO_2-X (X = He, Ar) depending on the atmosphere of synthesis.
The samples consist of a mix of anatase and rutile phases, with a higher rutile proportion in powders elaborated under Ar. XPS analyses reveal co-existing various Cu chemical states in both Cu/TiO_2 samples. Cu/TiO_2-He particularly favors the reduced Cu^0 and Cu^+ species at the expense of Cu^{2+}. STEM-HAADF coupled to EDX chemical analysis revealed copper species in Cu/TiO_2-He sample homogeneously dispersed on TiO_2 surface of ~10 nm diameter whereas Cu/TiO_2-Ar sample presented distinct copper species NPs of 1-3 nm on bigger TiO_2 support (~30 nm diameter). Such marked differentiation in terms of morphology between Cu/TiO_2-He and Cu/TiO_2-Ar samples are attributed to a change of flame intensity inducing different synthesis temperatures depending on the working atmosphere during laser pyrolysis.
Photocatalysts were tested for PA degradation under anaerobic conditions. Concerning pure TiO_2, the main products were CO_2 and C_2H_6. C_2H_4 (C_2H_4/CO_2 = 1%) and H_2 were found in trace amounts. Surface modifications with copper/copper oxides to TiO_2 photocatalysts lead to drastic changes in terms of levels of photo-generated products. Apart from CO_2, Cu/TiO_2-He mostly produced C_2H_6, but significantly enhanced C_2H_4 formation (C_2H_4/CO_2 = 11%) up to 200 minutes. From this time, C_2H_4 production slows down, when on the contrary H_2 production considerably takes off. This phenomenon was attributed to the reduction of highly dispersed copper species on TiO_2 surface in Cu/TiO_2-He. When Cu is reduced to Cu^0, H_2 production improves at the detriment of C_2H_4. With Cu/TiO_2-Ar, C_2H_4 was the major hydrocarbon product (C_2H_4/CO_2 = 85%), evolving linearly at the expense of C_2H_6 and H_2. In this latter case, Cu_xO_y is present as particles of 1-3 nm in diameter and is not so easily fully reduced, therefore the pathway to C_2H_4 production is enhanced. Production of ethylene at 260 ppmv/h exceeded 130 times the production rate obtained from of pure titania.
This study shows the laser pyrolysis flexibility in synthetizing Cu/TiO_2 photocatalysts with various morphologies, but also the possibility of using Cu_xO_y species to enhance the selectivity from C_2H_6 to C_2H_4 during PA decarboxylation, with a ratio C_2H_4/CO_2 as high as 85%.

References

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2:15 PM NM03.02.03
Tethering Catalytic Nanoparticles to Supramolecular Nanostructures for Improved Recyclability Yukio Cho, Kiera Y. Tai and Julia Ortony; Massachusetts Institute of Technology, United States

Nano-sized catalysts are promising due to their high catalytic activity originating from ultra-large surface-to-volume ratios. However, nanoscale suspensions are also inseparable, hampering the reusability and recyclability of nano-sized catalysts. While depositing the nano-sized catalysts on supporting materials offers an approach to overcome this challenge, the surface of supporting materials often has little flexibility to harness the surface chemistry, which leads to limited loading ratios and uncontrolled nucleation growth of the catalysts on the surface. Here we show that nano-sized catalysts may be anchored to self-assembled nanostructures, offering tunable surface chemistry which can be harnessed to promote affinity with and recyclability of catalysts. In this study, we use sub-10nm gold nanoparticle (AuNP) catalysts and L-cysteine-functionalized aramid amphiphile nanotubes which exhibit a strong affinity with AuNPs, as a model system. We observe that sub-10nm AuNPs bind evenly on the surface of the nanotubes without precipitation. We confirm that the AuNP-CysAA system is capable of reducing 4-nitrophenol. Unlike only AuNPs suspension, the reacted mixture of the AuNP-CysAA system can be easily separated by filtration to reuse due to the high-aspect-ratio of the nanotubes.

2:30 PM NM03.02.04
Ferroelectric-Photocatalyst Nanocomposite Thin Films for Enhanced Photoelectrocatalytic Activity Joe Briscoe[1], Adriana Augurio[1], Qian Guo[1], Alberto Alvarez Fernandez[2], Vishal Panchal[3], Bede Pittenger[3], Peter Dewolf[3], Stefan Guldin[2] and Ana Jorge Sobrido[1]; [1]Queen Mary University of London, United Kingdom; [2]University College London, United Kingdom; [3]Bruker Corporation, United Kingdom

Low-cost, oxide-based photo-electrocatalysts (PEC), such as Fe_2O_3, $BiVO_4$, $CuWO_4$, are gaining increased attention to achieve unassisted water splitting to produce solar fuels. Although they possess ideal bandgaps in the range of 2-2.5 eV, they suffer from a high level of surface recombination and low carrier mobility[1]. Ferroelectric polarization has emerged as a new strategy in photocatalysis to induce opposite band bending at material surfaces facilitating increased charge separation and promoting selective redox reactions[2]. However, most ferroelectric have wide bandgaps, and therefore do not absorb visible light, and are insulating therefore cannot transport photogenerated charges. Therefore, herein, we combine ferroelectric $BaTiO_3$ with the photocatalyst Fe_2O_3 in parallel at the nanoscale to combine the benefits of ferroelectrics and photocatalysts in a nanocomposite film.

To produce this structure, porous $BaTiO_3$ (pBTO) thin films were synthesized by the soft template-assisted sol-gel method. Using different concentrations of organic template, the porosity of pBTO was controlled to obtain suitable thin films for photocatalyst integration. The overall porosity and surface area of the pBTO thin films is determined by SEM analysis and ellipsometry.

The ferroelectric phase of pBTO is confirmed by XRD analysis and Raman spectroscopy. The switching of spontaneous polarization of pBTO by an electric field is verified by Piezoresponse Force Microscopy (PFM). The alignment of polar dipoles to the ferroelectric surface (P_{up} or P_{down}) is evaluated by testing the PEC performance of pBTO after electrochemical (EC) poling at ±8V, which show that the photoanode performance is improved for P_{down}.

Lastly, the pBTO/Fe_2O_3 thin film shows an enhancement of the photocurrent density compared to either the bare Fe_2O_3 (by ~2 times) and pBTO thin films (by ~20 times), which could be correlated to the upward band bending induced by the ferroelectric polarization of pBTO. The PEC response in pBTO/Fe_2O_3 is accordingly regulated by EC poling without altering the Fe_2O_3 layer chemically (as confirmed by XPS), leading to further enhancement of the photocurrent. This research work shows a facile and low-cost approach for the development of novel ferroelectric/photocatalyst photoanodes with switchable control of their PEC performance, which possess a great potential for photoelectrochemical applications.

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2:45 PM NM03.02.05

Assisted Enhanced Photocatalysis by the Addition of a Ferroelectric Component to Copper-Doped TiO_2 Nanotubes Gilles D. Berhault[1], Nouf Al-Aqeel[2], Wadha Alrashedi[2], Mohammad Yunas[3], Nuhad Abdullah Alomair[2], Fathi Jomni[4] and Hafedh Kochkar[2]; [1]Research Institute on Catalysis and Environment, France; [2]Imam Abdulrahman Bin Faisal University, Saudi Arabia; [3]King Fahd University of Petroleum and Minerals, Saudi Arabia; [4]University Tunis El Manar, Tunisia

Introduction

Titanium dioxide is the most used semiconductor in photocatalysis due to its good chemical stability and suitable band edge potentials for H_2 production. However, its large band gap (3.2 eV for anatase) restrains its use to photoexcitation under UV illumination. TiO_2 also presents a high recombination rate of electron-hole pairs limiting its intrinsic activity. Different strategies have been envisaged to decrease recombination including change of morphology, formation of heterojunctions, doping with cations or combination with carbon allotropes. Even if successful, these strategies rely on the consumption of part of the excitons to keep others available for reaction. In this respect, ferroelectric polarization can modify band structures and charge transport performance in adjacent semiconductors without consumption of part of the excitons. Among ferroelectrics, $SrTiO_3$ offers favourable conditions for photocatalysis with a conduction band only 200 meV more negative than TiO_2 while it is also a metastable paraelectric compound becoming ferroelectric under optical excitation. Therefore, herein, the interest of using $SrTiO_3$ with Cu-doped TiO_2 nanotubes was here considered.
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Materials and Methods

TiO_2 nanotubes (TNT) were synthesized using a hydrothermal procedure under strong alkaline conditions. TiO_2 nanotubes were impregnated with $Cu(NO_3)_2.3H_2O$ (0.5 wt% Cu) before drying and calcination. The resulting material was then doped with strontium (0.2 to 1.0 wt %). Photocatalytic tests were performed under UV and visible irradiations for the formic acid photodegradation.

Results and Discussion

Deep structural characterization was performed. First, UV-vis DRS emphasizes the role of plasmonic properties following the Cu addition making these materials active under visible irradiation. Second, Raman shows the formation of surface Sr-O-Ti entities up to 0.8 wt% Sr.
XPS analysis also reveals a net modification of the Ti, O and Sr species with increasing addition of strontium resulting from the progressive replacement of surface oxygen vacancies by Sr-O-Ti entities. PL and EIS also show that incorporating strontium decreases the recombination rate of electron-hole pairs and stabilizes photogenerated charges increasing their lifetime by 75%.
Combined together, limited recombination and higher stabilization of photogenerated charges leads to an increase of the photocatalytic activity under UV irradiation by 50% at the optimum Sr loading for in situ $SrTiO_3$ formation (0.8 wt% Sr) and by an impressive higher activity under visible irradiation (initial rate: 0.6 $\mu mol.L^{-1}.min^{-1}$ without Sr, 109 $\mu mol.L^{-1}.min^{-1}$ at optimum Sr loading).
Extension of this study was also made to Cu-doped systems comprising graphene oxide. Once again, the Sr addition results in a strong increase of the photocatalytic response. Modelization of the kinetics of photodegradation including diffusion phenomena was performed and compared to dielectric properties. A perfect correlation was observed between the increase of activity and the propensity to charge polarization induced by Sr addition confirming the role played by the ferroelectricity induced by in situ $SrTiO_3$ entities on the enhanced photocatalytic properties.

Conclusion

Assisted photocatalysis by addition of a ferroelectric component to semiconductor systems was herein demonstrated as a promising alternative for enhancing the photocatalytic performance of commonly used semiconductors like TiO_2 through stabilization of photogenerated charges while limiting recombination processes. Application made using Sr addition to Cu-doped TiO_2 nanotubes can be extended widely to other semiconductor systems allowing better yields in pollutant abatement or in green energy production.

3:00 PM BREAK

SESSION NM03.03: Porous Material
Session Chairs: Prashant Jain and Maria Wächtler
Tuesday Afternoon, April 11, 2023
InterContinental, Fifth Floor, Ballroom A

3:30 PM *NM03.03.01

Tuning Surface States as Performance Parameters for Water Oxidation on Metal Oxide Photoanodes Hang Chen[1], Jingguo Li[2], Carlos A. Triana[1], Yonggui Zhao[1] and Greta Patzke[1]; [1]University of Zurich, Switzerland; [2]Uppsala University, Sweden

During the past decades, photoelectrochemical strategies have attracted increasing interest for the direct conversion of solar energy into sustainable chemical fuels. Generally, surface states generated from the water oxidation process by photogenerated holes are recognized as a key parameter for tuning the performance of photoanodes in water splitting setups, but their behavior and precise chemical nature remains to be explored for many prominent materials.

This applies specifically for hematite Fe_2O_3 photoanodes, for which we recently investigated fundamental questions associated with its two different types of surface states (referred to as S1 and S2) and their interaction.[1] While S1 has long been identified as an iron-oxo species through operando spectroscopy and related rate law investigations, the precise nature and behavior of S2 with lower oxidative energy has been controversially discussed. Photoanodes with hematite nanorods were prepared via published protocols and the dynamic interaction of their surface states was evaluated concerning the influence of oxidative potentials, illumination intensity, and electrolyte pH. We tentatively assigned S2 to an iron-peroxo intermediate of the water oxidation process via photoelectrochemical impedance spectroscopy (PEIS) measurements, which were complemented with transient photocurrent spectroscopy (TPS) results. Our assignment was based on the following key observations: Potential-dependent rate law analyses revealed a transition of 1st order reaction kinetics for surface holes with low densities to 3rd order kinetics at higher hole density for higher applied potentials (1.3 V vs. RHE). At lower potentials (0.9 V vs. RHE) a transition from zero to 3rd order kinetics was observed. Further, the lifetime of S2 was rather long with >3 min, and it was generated from the accumulation of shorter-lived S1 states. In strongly alkaline media, S1 states became more mobile to be transformed into S2 states which displayed 3rd order reaction kinetics. Near the point of zero charge, a unique three-stage transformation of the reaction mechanism was unraveled. The quick migration and reaction of oxo species under intense illumination or surface deprotonation conditions can give rise to longer-lived peroxo species and higher reaction orders. This model paves new ways to optimize photoanode performance through tuning the accumulation and migration of oxo species.

In a parallel study, we enhanced the efficiency of bismuth vanadate $BiVO_4$ photoanodes through introduction of a reduced catalytic layer on TiO_2 protected $BiVO_4$.[2] The surface of the resulting R-TiO_2@$BiVO_4$ photoanodes was enriched in oxygen vacancies and their performance was clearly superior to pristine $BiVO_4$. Our PEIS studies revealed the presence of two surface states on $BiVO_4$ photoanodes (S1 around 0.45 V and S2 near the water oxidation potential around 1.05 V), while R-TiO_2@$BiVO_4$ displayed only S2 with S1 being passivated. Moreover, the hole densities in S2 were notably increased for R-TiO_2@$BiVO_4$ as the accumulation of intermediates was promoted with rapid water oxidation kinetics, which identifies S2 as reaction centers related to oxygen vacancies. Our R-TiO_2 surface coating strategy was furthermore investigated with a wide range of analytical methods, showing that the excellent water oxidation activity of R-TiO_2@$BiVO_4$ photoanodes arises from a simultaneous enhancement of S2 reaction centers and suppression of adverse VO_2+/VO^{2+} recombination processes. Therefore, our surface engineering strategy not only stabilizes $BiVO_4$ photoanodes but also highlights the essential role of surface states in their performance optimization.

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4:00 PM NM03.03.02
Reactor Design for Nanoparticle-Based 3-Dimensional Photocatalysts Markus Niederberger and Fabian Matter; ETH Zurich, Switzerland

Multiscale nanoparticle assembly is at the heart of efforts to integrate nanoparticles into macroscopic materials and devices [1]. The idea of arranging nanoparticles in a modular and defined way to larger entities is extremely appealing, because in such a way a nearly indefinite number of different architectures is accessible from a limited set of building blocks. Among the many geometries, 3-dimensional structures like aerogels are unique in the sense that the size-specific properties of the nanobuilding blocks are fully preserved in the macroscopic material [2]. With their extensive porosity and large surface areas aerogels are particularly attractive for applications in gas-phase photocatalysis [3]. Moreover, if they can be produced in monolithic form with sizes in the centimeter range, completely new possibilities and challenges open up, which are also associated with interesting scientific and technical questions. In particular, gas flow through and the penetration of light into the macroscopic bodies represent important parameters that must be taken into account in the development of suitable photoreactors [4-7]. Only if the macroscopic shape of the aerogel and the reactor design are perfectly matched can the full photocatalytic performance of the aerogel be exploited [7]. Based on photocatalytic methanol reforming as a model reaction, this presentation will show how all these aspects are interrelated and how they have to be optimized to increase the hydrogen production rate.

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4:15 PM NM03.03.03
Photocatalytic Activity and Electron Storage Capability of TiO_2 Aerogels with Adjustable Surface Area Anja Hofmann[1], Alexandra Rose[2], Pascal Voepel[2], Barbara Milow[2] and Roland Marschall[1]; [1]University of Bayreuth, Germany; [2]German Aerospace Center, Germany

Aerogels are a group of nanostructured materials which offer the possibility for tailoring the surface area and crystallinity in a wide range. TiO_2 aerogels are suitable candidates for photocatalytic applications due to this high surface area with presumably high amount of reactive sites and improved charge separation.[1,2] Additionally, TiO_2 in general is known for the trapping of electrons close to the surface with the formation of Ti^{3+} states, showing a characteristic broad absorption at a maximum of 650 nm with dark blue coloration.[3] These stored electrons can be used for different reduction reactions, such as the reaction with different metal ions to metal nanoparticles.[4,5] The nitrogen reduction reaction to ammonia in the dark is another very promising reaction which was reported the first time by Bahnemann *et al.* in 2011 for TiO_2 colloids.[6] This reaction can pave the way to a decentralized, energy efficient production of ammonia, which is commonly produced *via* the extremely energy intensive Haber-Bosch process.

Herein, mesoporous TiO_2 aerogels with varying properties were investigated for their electron storage capability and photocatalytic activity. These aerogels were synthesized *via* a novel modified acid catalyzed sol-gel synthesis with subsequent supercritical drying.[7] The surface area could be tailored in a range of 92 up to 600 $m^2 g^{-1}$ by variation of the heat treatment conditions. Absorption measurements and quantification experiments revealed an increase in the storage of photogenerated electrons in water-methanol mixtures with decreasing calcination temperature and increasing surface area. At the same time, the sacrificial hydrogen evolution rate decreased. It could be further shown, that the electron storage capability depends on the concentration of the hole scavenger. Beside the reduction reaction of Pt ions in the dark using the photogenerated electrons in the TiO_2 aerogels, a nitrogen reduction reaction to ammonia in the dark, using these stored electrons could be performed and verified by salicylate test.

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4:30 PM NM03.03.04
Effects of Periodic Pore Ordering on Photocatalytic Hydrogen Generation with Mesoporous Semiconductor Oxides Tobias Weller[1] and Roland Marschall[2]; [1]Justus-Liebig-Universität Giessen, Germany; [2]University of Bayreuth, Germany

Since the first reports on periodically ordered mesoporous silica materials by the Kresge group[1,2] and some earlier works, scientist all over the world have been fascinated by the crystalline (periodic) pore ordering in such materials. Since then, long-range periodically ordered mesopores with a number of geometries have been reported, including two-dimensional (2D) hexagonal, three-dimensional (3D) cubic, 3D continuous gyroidal and others, for a range of different materials including a vast number of (crystalline) oxides and hybrid materials.[3–5]
Scientists have been using such ordered mesoporous materials for a range of different applications including in catalysis, since the large surface area, e.g. of periodically ordered mesoporous oxides, can exhibit a higher number of active sites. The advantage of large surface area has been utilized in a number of other applications including sensing, proton conduction and batteries.[6] In many cases where periodically ordered mesoporous materials have been achieved, the authors were inclined to link the improved performance with the degree to which the material displayed porosity and associated increased surface area.
But since a review by Rolison[7] suggesting that periodic pore ordering in catalysis is not required, no systematic study has been reported on how periodic pore order in mesoporous materials affects hydrogen generation in photocatalysis. The most probable reason for the lack of such studies is that it is experimentally challenging to vary solely the degree of periodic pore order, e.g. of a mesoporous semiconductor, without changing other important material parameters, like the crystallite size, pore wall thickness, surface area, pore diameter or pore wall surface chemistry, the latter being easily affected by using different types of templates (e.g. using polymer or silica spheres as templates).
Motivated by this challenge, we showed that the triblock terpolymer poly(isoprene-*b*-styrene-*b*-ethylene oxide) (PI-*b*-PS-*b*-PEO; ISO) can be used for the preparation of a phase-pure and three-dimensionally (3D) co-continuous periodically ordered mesoporous quaternary $CsTaWO_6$ semiconductor for photocatalytic hydrogen generation with cubic alternating gyroid morphology.[8]
By varying the amount of templating polymer ISO relative to inorganic precursors, as well as adjusting other synthetic parameters, we are now able to control major physicochemical characteristics of the resulting mesoporous network. We show the preparation of mesoporous $CsTaWO_6$ powders that differ mainly in the degree of long-range periodic mesopore ordering, without significantly changing crystallite size in the pore walls or accessible surface area. Utilizing the resulting oxides as photocatalysts for sacrificial hydrogen evolution reaction (HER), we experimentally demonstrate that the degree of pore connectivity in mesoporous photocatalysts is the main factor controlling liquid phase photocatalytic HER when other parameters are kept non rate-limiting.[9]

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SESSION NM03.04: Poster Session I
Session Chairs: Lilac Amirav, Klaus Boldt, Matthew Sheldon and Maria Wächtler
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM NM03.04.01
Detonation Synthesis of TiO_2-TiC Photocatalyst for NO_x Oxidation under Visible Light Ahmed Al Mayyahi, Shusil Sigdel, Christopher M. Sorensen and Placidus B. Amama; Kansas State University, United States

Nucleation of TiO_2 on TiC is a promising strategy to design narrow band gap anatase-rutile junction TiO_2 supported on TiC with visible light photocatalytic activity. However, the lack of a facile and scalable approach for the synthesis of TiO_2-TiC has impeded its application in photocatalysis. This study reports a scalable, low-cost, reliable, and green approach for producing TiO_2-TiC. The approach is based on detonating a mixture of hydrocarbon (C_7H_8) and titanium precursor ($TiCl_4$) with O_2 in a multi-liter chamber to produce scalable amounts of TiO_2-TiC per day. Results show that the band gap of TiO_2-TiC is sensitive to the molar ratio of $TiCl_4$ to C_7H_8 used in the detonation. TiO_2-TiC with a band gap of 2.7 eV is produced when the molar ratio of $TiCl_4$ to C_7H_8 is 0.73. The TiO_2-TiC produced exhibits high performance in the oxidation of NO_x to nitrates with minimal release of NO_2 under blue light and shows limited activity under green light. Also, the same TiO_2-TiC ($TiCl_4/C_7H_8 = 0.73$) exhibits noticeable photocatalytic activity in NO_x oxidation under high humidity, a condition that simulates the environment in urban cities. The high photocatalytic activity is attributed to (1) the narrow band gap of TiO_2-TiC enabling visible light absorption; (2) the synergy between anatase and rutile in the hybrid structure allowing effective electron-hole separation and subsequently increasing the number of active radicals on the catalyst surface; and (3) the presence of TiC providing a non-photocatalytic domain to store NO_x photooxidation products on the catalyst surface and hindering their release to the atmosphere in the form of nocuous NO_2.

5:00 PM NM03.04.03

Ferroelectric $Bi_{1+x}FeO_3$ Thin Film for Enhanced Photoelectrochemical Water Splitting Performance Haozhen Yuan, Joe Briscoe, Subhajit Pal and Chloe Forrester; Queen Mary University of London, United Kingdom

$BiFeO_3$ thin films have been widely studied for photoelectrochemical water splitting application because of its narrow bandgap and good ferroelectricity which can promote the separation of photo-generated charges. Bismuth is well known as volatile and excess bismuth is usually added into the precursor to compensate the loss of bismuth during heat treatment. However, the exact quantity of excess bismuth and how excess bismuth affects its PEC performance have not been studied. Herein, self-doped $Bi_{1+x}FeO_3$ (x from 0 to 0.3) thin films are prepared via simple chemical solution deposition method. The grain size of films increases firstly and then decrease with increasing x. The loss of bismuth after annealing is confirmed by EDX and it estimates that a stoichiometric $BiFeO_3$ thin film can be achieved between x=0.05 and 0.1. Enhanced photocathodic photocurrent density is observed in slightly bismuth-rich films (x=0.15 and 0.2) which can be ascribed to the co-existence of rhombohedral and orthorhombic crystal structures. Moreover, the switching of ferroelectric domains in BFO thin films is observed using piezoresponse force microscopy, confirming the ferroelectric polarization. In addition, the PEC performance can be controlled via the ferroelectric polarization using electrochemical (EC) poling. Our work offers a simple and low-cost approach to enhance the photocathodic current density, which could help the further development of $BiFeO_3$-based thin films for PEC water splitting application.

5:00 PM NM03.04.05
Fabrication and Characterization of TiO_2 Nanotube Array for Seawater Splitting Electrode Prepared by Anodization Han-Sol Yoon[1], Kyeonghan Na[2,2], Jae-Yoon Kim[1], So-Hyeon Lee[1] and Won-Youl Choi[1,2,2]; [1]Gangnueng-Wonju National University, Korea (the Republic of); [2]Gangneung-Wonju National University, Korea (the Republic of)

Among the technologies for hydrogen production, water splitting is a technology that attracts much attention that doesn't cause carbon emissions. But there is a limitation in using highly purified fresh water for hydrogen production through water splitting. Only 2.5 vol% of the water on Earth is fresh water and the other is seawater, and freshwater has many uses, so applied research for the use of seawater is necessary for the dissemination of water-splitting technology. To splitting seawater, the oxygen evolution reaction (OER) electrode requires some unique properties such as high catalytic activity for seawater and chlorine corrosion resistance. To improve these properties, methods for the fabrication of various nanostructures have been suggested and among them, anodization is a method that can be growing aligned nanotube arrays on the surface of a TiO_2 plate. In this study, the TiO_2 OER electrode was fabricated by anodizing to improve catalytic activity and resistance to chlorine corrosion. Morphological and electrochemical properties of TiO_2 OER electrode were characterized using field emission scanning electron microscopes, X-ray diffraction, cyclic voltammetry, and Ultraviolet-visible spectroscopy. Among the anodized electrodes, the sample fabricated in electrolyte using NH_4F-H_2O-$C_3H_8O_2$ was shown the most hydrogen evolution, and the best resistance to chlorine corrosion was measured for the sample in which the H_2SO_4 electrolyte was used. The average pore diameter of the nanotubes was measured to be below 114 nm using FE-SEM image analysis, and the layer thickness was observed to be more than 10μm.

5:00 PM NM03.04.06
Ultra-stable, 1D TiO_2 Lepidocrocite for Photocatalytic Hydrogen Production in Water-Methanol Mixtures Hussein Badr and Michel Barsoum; Drexel University, United States

Water and sunlight are the cleanest, renewable, and most abundant resources on Earth. Developing inexpensive, scalable photocatalysts that are long-stable, for hydrogen, H_2, production has long been a cherished dream of humanity. Herein we report on one dimensional lepidocrocite-based nanofilaments, NFs, $\approx 5\times5$ Å^2 in cross-section - that generate H_2 from 80:20 vol.% water/methanol mixtures, when exposed to Xe-lamp radiation that simulates the solar spectrum. The NFs were stable in the mixtures for times > 4,300 h, 300 h of which were under irradiation, whilst being stirred. Apparent quantum yields as high as 12.6% were obtained. Based on deuterated water results we conclude that water is the H_2 source. No carbon dioxide nor oxygen is produced. Since our NFs do not produce CO_2, their green credentials, and their economic prospects for large scale-up suggest new lines for developing cheap and ultra-stable materials able to produce H_2 photochemically for long times.

5:00 PM NM03.04.07
Solar Energy Conversion Using Multinary Complex Oxides Prepared by Arc-Synthesis Nadia G. Macedo, Jessica C. Alvim, Leonardo C. Soares, Márcio Sangali, Rubens Caram Jr, Luelc Costa, Miguel T. Galante and Claudia Longo; University of Campinas, Brazil

Semiconductor oxides have been used as photocatalysts for conversion of solar energy in different applications of technological interest. Compared to binary oxides, the multinary oxides can exhibit improved sunlight harvesting; also, the conduction and valence band edges can be modulated, that can enhance the selectivity for some photoelectrochemical (PEC) reactions. Recently, our research group used the arc-melting of Cu_2O and WO_3 precursors for synthesizing Cu_2WO_4, a p-type semiconductor. Ongoing studies revealed that Cu_2WO_4 particles immobilized on gas diffusion electrodes produced ethanol from PEC CO_2 reduction reaction (PEC-CO_2RR). Electrodes prepared with particles of the composite containing $CuFeO_2$ and copper oxides, obtained by arc-synthesis from of Cu_2O and Fe_2O_3 precursors, also behave as p-type semiconductor electrodes and have been evaluated as photocathodes for PEC-CO_2RR and in-situ H_2O_2 production from PEC O_2 reduction reaction. On the other hand, electrodes containing ilmenite ($FeTiO_3$) particles synthesized by arc-melting of TiO_2 and Fe_2O_3 precursors behave as n-type semiconductor; ongoing studies revealed that ilmenite electrodes exhibited high efficiency and excellent long-term stability for application as photoanodes for PEC oxygen evolution reaction (PEC-OER). PEC properties of n-type semiconductor electrodes were also observed for the multiphasic α-$AgVO_3$/Fe_2O_3/Ag synthesized by arc-melting. Scanning electron microscopy and energy dispersive spectroscopy revealed that this composite consisted of Ag nanoparticles decorating micrometric Fe_2O_3 and nanostructures of the metastable α-$AgVO_3$. The performance of such photoanode for PEC OER and for removal of contaminants of emerging concern from water is under investigation. These results revealed that arc-melting can be used as a time-efficient methodology for synthesizing multinary complex oxides for application in PEC reactors for water decontamination and for solar fuels production from CO_2RR.

5:00 PM NM03.04.08
Enhanced Photocatalytic Activity of TiO_2 Brookite Phase by Sono-Reduction Method Seyyedmohammadhossein Hejazi[1,2], Mahdi Shahrezaei[1], Alberto Naldoni[1], Stepan Kment[1,2] and Hana Kmentova[3]; [1]Czech Advanced Technology and Research Institute (CATRIN), Czechia; [2]Nanotechnology Centre, Centre of Energy and Environmental Technologies, Czechia; [3]Palacky University Olomouc, Czechia

The reduction of TiO_2 has been proven to enhance its photocatalytic activity by extending its light absorbance from UV to the visible part of the light spectrum and by optimizing the amount and position of defects that can act as co-catalytic sites. Traditional reduction method at elevated temperatures in contact with a reductant gas like hydrogen, has some disadvantages like phase transformation, sintering and even introducing impurities because of the harsh reaction conditions. In this contribution, we used the sono-reduction method in mild conditions at room temperature and aqua media under Ar atmosphere, to input defects at the surface of brookite as the most photoactive TiO_2 phase and to produce so-called "black TiO_2". We have shown that this strategy, without using a noble metal co-catalyst, could increase the H_2 evolution rate up to 3 times (from 19.3 to 58.5 $\mu mol.g^{-1}.h^{-1}$) in comparison with the pristine (white) sample.

5:00 PM NM03.04.09
Multidimensional Ternary Heterostructured Self-Precipitated Ag Nanoparticles on TiO_2@$SrTiO_3$ for Photoreforming of Plastics Face Mask to Hydrogen Ting-Han Lin, Jia-Mao Chang and Ming-Chung Wu; Chang Gung University, Taiwan

Solar-to-hydrogen via the photocatalytic reaction has been considered a promising way to obtain sustainable green energy in this generation. In the past three years, the COVID-19 pandemic changed our life habits and led people produce waste of personal surgical masks daily. Photoreforming of plastics waste to hydrogen contributes to lowering the environmental load and provides another route of sustainable energy acquirement. In this study, we prepared the ternary photocatalysts with heterostructure construction of zero-dimensional $SrTiO_3$ nanocubes ($SrTiO_3$ NC) and one-dimensional TiO_2 nanofibers with self-precipitating Ag nanoparticles (AT NFs). AT NFs synthesized by hydrothermal method showed the unique Ag NPs on the surface of TiO_2 NFs, increasing the absorption. Via in-situ hydrothermal growth reaction of $SrTiO_3$ NC, we precisely manipulate the distribution of $SrTiO_3$ NC on AT NFs by tuning the proportion of strontium titanate. As a high proportion of $SrTiO_3$, the one-dimensional structure of AT@$SrTiO_3$ gradually weakened, and the self-precipitated Ag nanoparticles were covered as dopants in the AT@$SrTiO_3$. From the morphology observation and the study of XPS and XAS spectra to investigate interface bonding information, we noticed that several $SrTiO_3$ NC covered the silver particles, and partial Ag NPs were retained on AT@ $SrTiO_3$ with specific concentration, maintaining the excellent photoresponse due to surface plasma resonance of Ag NPs. The photocatalytic hydrogen production rate in a mixture of water/ethanol under xenon lamp irradiation can reach 320.8 $\mu mol \bullet g^{-1} \bullet h^{-1}$. In addition, for the photoreforming of the surgical mask to hydrogen production, we carried out the hydrolysis pretreatment in an alkaline solution and then used UV ozone to activate PP and PE molecules. Both pretreatments were beneficial to the hydrolysis and polarity that showed the hydrogen production to 316.9 $\mu mol \bullet g^{-1} \bullet h^{-1}$.

5:00 PM NM03.04.10
Cu_2O/Mo:$BiVO_4$ PN Junction Photoelectrode for Solar Water Oxidation Hervin Errol T. Mendoza, Zongkai Wu, Samutr Assavachin, Chengcan Xiao and Frank E. Osterloh; University of California, Davis, United States

Semiconductor-based solar water splitting for renewable fuel generation is one of the practical means of addressing the increasing global energy demand. Cu_2O (p-type, $E_g = 2.0$ eV) is earth-abundant and inexpensive while $BiVO_4$ (n-type, $E_g = 2.4$ eV) is preparable using scalable methods, making these two materials suitable choices for cost-efficient and sustainable energy production. A Cu_2O/$BiVO_4$ structure with a theoretical solar-to-hydrogen efficiency of 9.2% can potentially exhibit unassisted water splitting, but very few studies have been carried out to investigate this system (Wu, Z. et al., Chem. Comm., 2018, 54(65), 9023-9026). In this work, bilayer photoelectrodes were constructed from Cu_2O and Mo-doped bismuth vanadate (Mo:$BiVO_4$) and characterized. Cu_2O was electrodeposited onto a F-doped tin oxide (FTO) substrate and Mo:$BiVO_4$ nanoparticles were prepared by solution phase synthesis. The bilayer was then obtained through electrophoretic deposition of Mo:$BiVO_4$ on Cu_2O followed by argon annealing at 550^{o}C for 8 hrs. X-ray diffraction data indicated the formation of new phases in the film after annealing. Photoelectrochemical experiments in 0.1 M Na_2SO_4 solution at pH 7 showed anodic photocurrent with onset potential of ~0.6 V vs. reversible hydrogen electrode (RHE). Surface photovoltage spectroscopy suggests formation of a pn junction between Cu_2O and Mo:$BiVO_4$, likely causing the device to work only under applied bias conditions. Use of oxygen evolution cocatalysts and charge selective contacts had been explored in an attempt to mitigate the issue.

5:00 PM NM03.04.11
Transition Metals and Stainless Steel for Low Cost Direct Water Splitting Stefan L. Schweizer[1], Haojie Zhang[2] and Ralf B. Wehrspohn[1]; [1]Univ of Halle-Wittenberg, Germany; [2]Max Planck Institute of Microstructure Physics, Germany

The research on materials for the water splitting reactions is in focus for several years...
the Oxygen evolution reaction (OER) and the Hydrogen evolution reaction (HER),
We review the recent process of the global research on transition metal phosphide (TMP) based heterostructures for efficient water splitting.

To reduce the cost of electrochemical water splitting, two strategies to prepare robust and abundant 3D electrodes:
a) the design and preparation of highly active catalysts, and
b) the use of a cheaper substrate stainless steel for the preparation of 3D electrodes.

Both strategies have promising potential for the further design and preparation of abundant and robust 3D electrodes for efficient electrochemical water splitting as well as for other electrochemical areas.

For the first strategy, we prepared a heterostructure by combining two different catalysts, namely NiFe LDH (*layered double* hydroxides) nanosheets and NiCoP nanowires.
The resulting 3D NiFe LDH/NiCoP@NF (nanofoam) electrodes demonstrated a better bifunctional activity for both the HER and the OER when compared to its counterparts.
A new recipe for preparing TMP by the ALD process was also explored and optimized for the first time. The CoP ultrathin films prepared with our ALD recipe show a higher HER activity than CoP films prepared by the traditional post-phosphorization method.

The heterostructure with a strong synergistic effect is an effective approach to improve the catalytic activity of prepared catalysts and a novel strategy to design and prepare bifunctional electrocatalysts for efficient water splitting. However, the related reaction mechanisms happening on the surface of the heterostructure are still not understood.
For the second strategy, we used carbon nano tubes (CNT) as the interface material to combine a stainless steel (SS) mesh with highly active catalysts to improve the activity of SS-based 3D electrodes for efficient water splitting. The CVD process for growing CNTs on the surface of SS was optimized, and the as-prepared CNT/SS electrodes were successfully modified with the state-of-the-art catalysts Pt and RuO2. The resulting 3D Pt/OxCNT/SS and RuO2/OxCNT/SS exhibited a better HER and OER activity, respectively, than the reference of 20 wt% Pt/C/SS and RuO2/SS.

Employing CNT as an interface material can make extremely stable SS become more suitable to the decoration with highly active electrocatalysts for the preparation of SS-based 3D electrodes towards efficient water splitting. The possibility of modifying CNT/SS with abundant and efficient catalysts to further enhance the performance of 3D SS-based electrodes is still needed to be investigated further.

The TMP-based catalysts deposited by ALD show a promising application potential for designing and preparing 3D electrodes for (photo)electrochemical water splitting as well as other electrochemical areas by depositing TMP on various 3D structures. Our work explored and improved the ALD process to obtain the controllable deposition of highly pure and stable CoP, but other TMP, such as Ni-based, Fe-based and Mo-based phosphides as well as their bi-/trimestral phosphides can also be prepared by the ALD approach.

5:00 PM NM03.04.12
Photopolymerized Superwettable Coatings Enabled by Dual-purpose ZnO for Liquid/liquid Separation Chenxuan Li and Lei Fang; Texas A&M

University, United States

Low-cost and scalable superwettable coating methods provide viable approaches for energy-efficient separation of immiscible liquid/liquid mixtures. A scalable photopolymerization method is developed to functionalize porous substrates with a hybrid coating of tetrapodal ZnO (T-ZnO) and polymethacrylate, which exhibits simultaneous superhydrophobicity and superoleophilicity. Here, T-ZnO serves dual purposes by (i) initiating radical photopolymerization during the fabrication process through a hole-mediated pathway and (ii) providing a hierarchical surface roughness to amplify wettability characteristics and suspend liquid droplets in the metastable Cassie—Baxter regime. Photopolymerization provides a means to finely control the conversion and spatial distribution of the formed polymer, whilst allowing for facile large-area fabrication and potential coating on heat-sensitive substrates. Coated stainless-steel meshes and filter papers with desired superhydrophobic/superoleophilic properties exhibit excellent performance in separating stratified liquid-liquid mixtures as well as water-in-oil emulsions. The hybrid coating demonstrates desired mechanical robustness and chemical resistance for their long-term application in large-scale energy-efficient separation of immiscible liquid/liquid mixtures. The integration of photopolymerization features, superwettability, and excellent durability renders this hybrid coating approach a highly promising platform technology for various applications.

5:00 PM NM03.04.13
Selective Photocatalytic Conversion of Benzyl Alcohol to Benzaldehyde or C-C Coupling Products over Ion Exchanged CdS Hyun Sung Kim[1,2] and Hangil Lee[3]; [1]Pukyong National University, Korea (the Republic of); [2]Core Research Institute, Korea (the Republic of); [3]Sookmyung Women's University, Korea (the Republic of)

In this study, visible light absorbing CdS nanoparticles were partially modified with Au_2S and Ag_2S via a simple cation exchange process to prepare heterostructure photocatalysts (Au_2S@CdS and Ag_2S@CdS) for the conversion of aromatic alcohols to valued-added products, such as benzaldehyde and C-C coupling products. When Au_2S@CdS was used as the photocatalyst, benzaldehyde was obtained as the main product with a selectivity of 99%, and when Ag_2S@CdS was used as the photocatalyst, deoxybenzoin and hydrobenzoin were obtained as the main products with a selectivity of 95%. The critical photogenerated electron and hole transfer occurring during the photocatalytic reaction was systemically investigated by carrying out various control experiments and using in-situ high-resolution X-ray photoelectron spectroscopy. We believe that our study makes a significant contribution to the literature it provides a feasible approach for the formation of complex heterostructures via a simple ion exchange process. Further, we believe that this study provides a novel strategy for the preparation of catalyst complexes for the conversion of aromatic alcohols into value-added compounds.

5:00 PM NM03.04.15
Effect of Doping on Optical and Photocatalytic Properties of TiO_2-$Ti_3C_2T_x$ Hybrid Ahmed Al Mayyahi and Placidus B. Amama; Kansas State University, United States

The light absorption of TiO_2 can be extended from ultraviolet to visible region via structure disorder, chemical and physical doping, but with the trade-off of photocatalyst deactivation due to the short lifetime of photoexcited charge carriers. In this study, we report the simultaneous reduction and carbon doping of TiO_2 through refluxing with titanium carbide MXene ($Ti_3C_2T_x$) in the presence of a reducing agent (ethanol or hydrazine) to shift TiO_2 absorption to the visible region and allow visible light activity without compromising the lifetime of charge carriers. Carbon doping and defects (oxygen vacancies and Ti^{3+} ions) in TiO_2 enable visible light absorption by allowing sub-band transition while MXene hinders the consumption of charge carrier and promotes the formation of active radicals on TiO_2-$Ti_3C_2T_x$ by accepting the photoexcited electrons. UV-Visible spectroscopic measurement reveals absorption of TiO_2-$Ti_3C_2T_x$ in the visible region with an indirect band gap of ~2.85 eV. The effective charge carrier separation and subsequent formation of active radicals in TiO_2-$Ti_3C_2T_x$ are confirmed by photoluminescence and electron paramagnetic resonance spectroscopy. Multiple spectroscopic techniques are used to investigate the chemical interaction between TiO_2 and $Ti_3C_2T_x$ in the hybrid structure and evaluate carbon doping in TiO_2, as well as correlate the density of defects in TiO_2-$Ti_3C_2T_x$ with photocatalytic activity.

5:00 PM NM03.04.16
Heating Influence on Atomic Site Structural Changes of Mesoporous Au Supported Anatase Nanocomposite for Photocatalytic Progression Adil Alshoaibi; King Faisal University, Saudi Arabia

Semiconductor nano photocatalysis has considered a promising methodology for polluted water remediation. The electrons and holes' high recombination rate and low reaction rate have obstructed their large-scale applications. Thus, heterogeneous nano photocatalysts are needed for promoting their practical applications. Herein, anatase nanoparticles (ANPs) are synthesized and heat-treated within two-time intervals of 1 h and 2 h at 300 °C by sol-gel method and doped with gold nanoparticles (AuNPs) at room temperature (29 °C) owing to photocatalytic application. Vapor pressure scanning electron microscopy (VPSEM) shows the porous and granular localized homogeneous surface of Au-ANPs before and after heat treatment. The average nanoparticles diameter is calculated as 4.7 nm and after 2 h heat treatment it increased up to 4.9 nm. Atomic force microscopy (AFM) and Brunauer-Emmett-Teller (BET) method show that the Au-ANPs possessed low average surface roughness (Ra) ~ 3 nm, large surface area (SA) ~ 288 m2/g, and pore size distribution (PSD) 1.81 nm, respectively. Whereas Au-ANPs/2 h revealed Ra around 5 nm, SA ~ 145 m2/g, and PSD ~ 2.37 nm. All three nano photocatalysts exhibited thermal stability at ≤400 °C by thermogravimetric analysis. The Au-ANPs/2 h exhibited high photocatalytic activity with degradation of PR dye of 94% ($k = 0.01$ min−1, under ultraviolet radiation) after 280 min of reaction.

5:00 PM NM03.04.17
Controlling the Photoelectrochemical Water Oxidation Reaction Pathway via Surface Amorphous Overlayer Jaekyum Kim, Seung Hun Roh and Jung Kyu Kim; Sungkyunkwan University, Korea (the Republic of)

Hydrogen peroxide (H_2O_2), regarded as a green fuel and powerful oxidant, has represented high attention in the energy and environment field recently. Also, H_2O_2 is attracting attention in that it can be used as an energy carrier since it has an energy density of 2.1 MJ kg^{-1}, which is comparable to compressed hydrogen (3.5 MJ kg^{-1}). Over 95% of H_2O_2 is produced by Anthraquinone process, which needs high pressure of hydrogen, requires expensive catalyst, and consumes lots of energy during whole process. Therefore, it is vital to develop an alternative method for H_2O_2 production that is eco-friendly and economical. In this regard, photoelectrochemical (PEC) synthesis of H_2O_2 via 2-electron water oxidation is an alternative route. The water-oxidation process follows two pathways: oxygen evolution reaction (OER) at 1.23 V vs. reversible hydrogen electrode (RHE), and H_2O_2 production reaction at 1.76 V vs. RHE. Unfortunately, the two-electron pathway must compete with the four-electron pathway, which generates O_2. Due to these competitive pathways, the reaction kinetics become sluggish, and intense degradation of electrode occurs. To date, studies have demonstrated that the free energy change of adsorbed OH radicals is a key factor in H_2O_2 evolution. Therefore, it is challenging to design efficient, selective, and stable photoanode materials for efficient H_2O_2 production from H_2O.

For PEC water splitting photoanode materials, semi-conductive metal oxides such as Fe_2O_3, ZnO, $BiVO_4$, WO_3, SnO_2 and TiO_2 have been widely studied. Among various metal oxides for PEC water oxidation, titanium dioxide (TiO_2) is the most extensively studied and numerous efforts have been conducted to enhance the PEC activity of TiO_2. However, TiO_2 itself is OER favorable because of native defects derived surface oxygen vacancies. Moreover, TiO_2 has an unsatisfactory Faraday efficiency (FE) in water-oxidation reaction (WOR)-mediated H_2O_2 evolution, since TiO_2 has a higher OH adsorption energy compared with $BiVO_4$, WO_3, and SnO_2, which leads to the undesirable four-electron pathway and O_2 evolution. Since H_2O_2 production by WOR is a competitive reaction with the oxygen evolution reaction (OER), it is crucial and highly challenging to control the reaction pathway toward our goal, H_2O_2. In this study, we demonstrated the incorporation of amorphous titanyl phosphate (a-TP) overlayer on TiO_2 nanoparticles (TiO_2 NP) is conducive to modulate the WOR pathway and results in highly selective PEC H_2O_2 production. The ultrathin (*ca*. 2 nm) a-TP was conformally overlaid by *in-situ* surface reforming via lysozyme-molded mineralization. The a-TP overlayer manipulates the surface adsorption energies for the reaction intermediates to promote the WOR for H_2O_2 production, instead of the competing O_2 evolution reaction. Moreover, the a-TP overlayer conformally passivated the surface trap states, which eventually generated an efficient charge transfer. Consequently, a-TP/TiO_2 shows 3.7-times higher Faraday efficiency (63%) at 1.76 V vs. RHE under 1 sun illumination comparing to bare TiO_2 (17%), which is the highest performance among TiO_2 based catalyst. To sum up, the introduction of the a-TP overlayer is a promising strategy for steering the reaction pathway and achieving efficient solar-to-chemical energy conversion. We believe that introducing an overlayer on photoanodes to manipulate the reaction kinetics provides alternative and environmentally friendly PEC H_2O_2 production method, instead of the conventional anthraquinone process.

SESSION NM03.05: Semiconductors
Session Chairs: Klaus Boldt and Masaru Kuno
Wednesday Morning, April 12, 2023
InterContinental, Fifth Floor, Ballroom A

8:30 AM *NM03.05.01
The Relationships Between Excited State Dynamics and Photocatalysis of Nanoscale Semiconductors Gordana Dukovic; University of Colorado Boulder, United States

The synthetic tunability of electronic structure and surface chemistry of semiconductor nanocrystals make them attractive light absorbers for light-driven chemistry. A variety of architectures have been constructed where nanocrystals are coupled with multielectron redox catalysts to drive reactions like H_2 generation, CO_2 reduction, N_2 reduction, and water oxidation with light. In these systems, light absorption in nanocrystals is followed by charge transfer to catalysts, which then use them for redox transformations, and/or to sacrificial carrier scavengers. Interfacial charge transfer between the nanocrystal and the catalyst and its competitiveness with other relaxation pathways in nanocrystals are of paramount importance to the overall photochemical reactivity. In this talk, I will focus on our efforts to elucidate both the kinetics of charge transfer and the kinetics and mechanisms of the competing photophysical pathways in nanocrystal-based systems for light-driven multielectron chemistry. This work entails transient absorption spectroscopy measurements, extensive kinetic modeling to extract rate constants of relevant processes in these heterogeneous systems, and, for some systems, contributions from theory.

9:00 AM NM03.05.02
Doped III-V Quantum Dots for Enhanced Light Harvesting Forrest Eagle, Samantha Harvey, Ryan Beck, Xiaosong Li, Daniel Gamelin and Brandi Cossairt; University of Washington, United States

As demand for value added chemicals ever increases with population growth, new methods must be established to perform the complex chemical reactions required to create said products. Photocatalysis is a potential avenue to perform these reactions, using photoexcited materials to serve as a source of high energy electrons involved in more complex processes. However, creating efficient photosenitizers is a non-trivial task and must be painstakingly designed for high efficiency.
Shelled semiconducting nanocrystals (also known as shelled quantum dots) have two the main characteristics required for efficient light harvesting/photosensitization. These qualities are high absorption coefficients (up to 10^5 cm^{-1} M^{-1}) and robust photostability. However, the shell that imparts the increased absorption coefficient and photostability also traps charge carriers in the core. This leads to charge carriers with high overlap, leading to short excited-state lifetimes on the scale of tens of nanoseconds. This disadvantage can be mitigated by the introduction of a dopant such as Ag^+ or Cu^+ which causes the excited state lifetime to increase to hundreds of nanoseconds. We can measure electron transfer from these quantum dots to molecular acceptors via photoluminescence and transient absorption spectroscopies. In doing so, we see that the doped quantum dots exhibit enhanced electron transfer by up to a factor of 10. Finally, we use examine the electronic structure of these materials *in silico* to determine why the charge transfer is so greatly increased upon doping.

9:15 AM NM03.05.03
Scavenger-Dependent Hole Removal Dynamics in Pt-Tipped CdSe/CdS Dot-in-Rod Nanohybrids Soenke Wengler-Rust[1], Yannic U. Staechelin[1], Holger Lange[1,2] and Horst Weller[1,3,2]; [1]Universität Hamburg, Germany; [2]The Hamburg Centre for Ultrafast Imaging, Germany; [3]Fraunhofer IAP-CAN, Germany

Combining the light-absorbing properties of semiconductors with the catalytic activity of noble metals, Pt-tipped CdSe/CdS dot-in-rods are perfectly suited for photocatalytic applications including light-driven hydrogen generation in water.[1-3]
We conducted a systematic study, investigating the influence of the choice of hole (h^+) scavenger and pH value on the quantum yield of the hydrogen evolution reaction and combined this with investigations on the charge carrier dynamics, using time-resolved transient absorption (TA) spectroscopy from the femtosecond- to the microsecond-time scale. While the fs-TA spectroscopy enabled us to investigate the charge carrier movement within the semiconductor domain and onto the metal tip, in the µs-TA measurements the h^+ transfer onto the h^+ scavengers was observable. Contrary to expectations, the charge carrier dynamics did not follow the observed trend of the scavenger-dependent performance in hydrogen production. Instead, it was possible to distinguish exclusively between “surface-active” and “diffusion-controlled” scavengers, based on the charge carrier dynamics. These results reveal that it is not the h^+ transfer onto the scavenger, that is the efficiency-limiting step of the photocatalytic process and therefore represent an important insight on the way towards optimizing this nanoscopic photocatalytic system.

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9:30 AM NM03.05.04

Single-Nanoparticle Measurements of Charge Transport in $SrTiO_3$:Rh and $BiVO_4$ Photocatalysts for Z-Scheme Water Splitting Brian T. Zutter[1], Zejie Chen[2], Luisa Barrera[3], Aliya Lapp[1], Austin Bhandarkar[1], William Gaieck[2], Kenta Watanabe[4], Akihiko Kudo[4], Daniel Esposito[5], Rohini B. Chandran[3], Shane Ardo[2] and A. A. Talin[1]; [1]Sandia National Laboratories, United States; [2]University of California, Irvine, United States; [3]University of Michigan–Ann Arbor, United States; [4]Tokyo University of Science, Japan; [5]Columbia University, United States

Solar-powered water splitting using nanoparticle photocatalyst suspensions is a promising route to economical, clean hydrogen production. In the Z-scheme approach, hydrogen and oxygen-evolving photocatalysts, such as $SrTiO_3$:Rh and $BiVO_4$, are coupled with a redox mediator to improve light absorption compared to single-photocatalyst systems. A key step in the water-splitting process is the separation and transport of photo-excited electrons and holes to the photocatalyst surface. Here we characterize charge transport in individual $SrTiO_3$:Rh and $BiVO_4$ nanoparticles using a nanoprobe within a scanning electron microscope, and directly map photocarrier diffusion lengths with electron-beam induced current. Charge transport in $SrTiO_3$:Rh particles is space-charge limited by bulk Rh^{4+} defect states within the nanoparticle, in contrast to nearly Ohmic (band) conduction in $BiVO_4$ nanoparticles. Photogenerated e-h pairs diffuse less than 10 nm before recombining within $SrTiO_3$:Rh particles due to the high concentration of Rh traps (1%), whereas band conduction in $BiVO_4$ particles allows for photocarrier diffusion lengths in excess of 400 nm. Inefficient charge transport explains why the H_2-evolving $SrTiO_3$:Rh nanoparticles are the limiting component within this Z-scheme system.

9:45 AM NM03.05.05

Liquid Surface Photovoltage Spectroscopy Analysis of Quasi Fermi Level Splitting and Minority Carrier Electrochemical Potential at $BiVO_4$ /Liquid Junctions under Illumination Sahar Daemi, Chengcan Xiao, Sherdil Khan, Hervin Errol T. Mendoza and Frank E. Osterloh; UC-Davis, United States

$BiVO_4$ is an important photoanode material for water oxidation, but its photoelectrochemical properties with regard to other redox couples have not yet received much attention. Here, we use a combination of open circuit potential measurements, photoelectrochemical scans, and surface photovoltage spectroscopy (SPS) to evaluate the factors that control the oxidation of aqueous oxygen/hydrogen peroxide, sulfate/sulfite and hexacyanoferrate (III)/(II) redox couples with $BiVO_4$. Here, a vibrating Kelvin probe is used to measure the quasi Fermi Level splitting (qFLS) of each $BiVO_4$-liquid junction under illumination. For instance, the sulfate/sulfite couple yields SPV of 0.186 V under 45.9 mW/cm^{-2} (400 nm LED) illumination, comparable to the photovoltage from PEC (0.142 V) and suggests that photovoltage is limited by standard reduction potential of the SO_4^{2-}/SO_3^{2-} couple. For hexacyanoferrate (III/II), on the other hand, both photovoltage from SPV and photovoltage from PEC are zero, which suggests charge carrier recombination at $BiVO_4$/hexacyanoferrate interface. Using this information together with majority carrier potential (E_{Fn}), the electrochemical potentials of the minority carriers can be calculated. For instance, $E_{Fp} = 0.26$ V vs RHE under 45.9 mW/cm^{-2} for the $BiVO_4$ - sulfate/sulfite junction and $E_{fp} = 1.19$ V vs RHE under 51.6 mW/cm^{-2} for the oxygen/hydrogen peroxide junction. This shows that $BiVO_4$ can photoelectrochemically oxidize both redox couples, without applied bias. Generally, we find that the built-in voltage at the $BiVO_4$-liquid junctions controls the photovoltage, i.e. the maximum possible energy conversion efficiency. Lastly, the SPS measurements also provide information about the reversibility of the redox processes occurring in front of the $BiVO_4$ electrode. Overall, this work provides new insight into the factors that control the energy conversion efficiency of metal oxide photoanodes.

10:00 AM BREAK

SESSION NM03.06: Spectroscopy
Session Chairs: Robert Godin and Maria Wächtler
Wednesday Morning, April 12, 2023
InterContinental, Fifth Floor, Ballroom A

10:30 AM *NM03.06.01

Widefield Infrared Photothermal Imaging and Spectroscopy Masaru Kuno; University of Notre Dame, United States

Infrared Photothermal Heterodyne Imaging (IR-PHI) is now a well-established, chemical and morphological characterization technique widely applicable to environmental and material science applications. Examples include studying micro- and nanoplastics in spectrally complex, chemical environments as well as monitoring cation migration in hybrid lead halide perovskites. These successes portend future applications of IR-PHI to studying chemically heterogeneous processes such as those involved in catalytic reactions. Traditional IR-PHI possesses a spatial resolution of ~300 nm and works in a point-by-point scanning fashion. Time-expensive, single-point data acquisition limits image collection and subsequent chemical characterization. Consequently, we introduce here a widefield modality to IR-PHI where photothermal IR images are acquired using a high-speed CMOS camera. The approach parallelizes data collection and makes possible hyperspectral imaging of chemical specimens. Widefield image resolution and detection limits are established and compared with those of traditional IR-PHI.

11:00 AM NM03.06.02

Inherent Photosensitization Efficiency of TiO_2-Bound RuP Chromophores in Natural Sunlight Thomas Cheshire and Frances Houle; Lawrence Berkeley National Laboratory, United States

Photoabsorbers such as those in the RuP (phosphonated and methyl-phosphonated tris(2,2-bipyridine)ruthenium(2+)) dye family enable wide band-gap nanomaterials such as TiO_2 to absorb visible light, enabling their use in porous photoanodes that can convert sunlight directly into electricity or drive reduction-oxidation reactions for generation of chemical products from water and CO_2. The core physical process is electronic excitation of the dye followed by charge injection into the nanoparticle, the efficiency of which is a key factor in the overall efficiency of these energy conversion systems. It has been estimated in the literature that the charge injection frequency from these dyes into TiO_2 nanoparticle-based electrodes under continuous solar excitation is about 1 s^{-1}, however by performing quantitative simulations of photoexcitation and charge injection kinetics we have determined that the charge injection frequency is actually in the range of 50-60 s^{-1}. In this presentation the computational mechanistic framework for the dye-nanoparticle photophysics, validated using ultrafast transient absorption spectroscopic techniques, will be described. The framework includes the influence of light scattering in the nanoparticle film on dye excitations, and is adapted to simulate photosensitized water oxidation by dye-catalyst diads. The prediction that these dyes are capable of far higher photoconversion efficiency than estimated previously points to unrecognized sources of inefficiencies in these systems. The calculations show that the inefficiencies do not involve simple recombination losses, revealing that there may be opportunities for improvements of dye sensitized solar cells and photoelectrochemical systems through improved optical and materials designs. The computational framework has been developed for the Ru dyes but is readily extendable to other metal-centered dyes whose metal-to-ligand charge transfer excitations result in charge injection.

11:15 AM NM03.06.03
Quantum Effects in Nanoparticles of TiO_2, WO_3, and Y_2O_3 Sergey Mamedov; HORIBA Scientific, United States

Metal oxide nanoparticles are attractive for many applications but have recently become an essential part of highly efficient catalysis materials. The material's efficiency depends on size, shape, and surface chemistry, which critically determine their properties and interaction.
Raman spectroscopy is a powerful method to investigate nanoparticles' vibrational properties, as the Raman band's peak and width are very sensitive to the local structure. Besides, phonons' behavior at the nanoparticle boundary strongly depends on the particle size and is a critical factor in creating a highly efficient material. It was shown that the Raman peak of TiO_2 at 142.9 cm^{-1} shifted with a decrease in the nanoparticles' size due to the quantum confinement. However, nanopowders of WO_3 and Y_2O_3 were not investigated yet. The samples of TiO_2, WO_3, and Y_2O_3 with a mean size ranging from 5 to 40 nm were investigated by Raman spectroscopy in the broad spectral range. The model of phonon confinement was used to describe the experimental data. The correlation length of the phonons calculated from the spectra of nanoparticles shows a good correlation between grain sizes obtained from Raman spectra and XRD. Raman spectra are more sensitive to nanoparticles' structural motive compared to XRD. The Raman spectra may differ even if X-ray diffraction shows the same particle size. It reflects the differences in the surface structure of nanoparticles.

11:30 AM NM03.06.04
Visualizing Ultrafast Structural Deformations in Photoexcited Nanocrystals Burak Guzelturk; Argonne National Laboratory, United States

In the last decades colloidal nanocrystals have become ubiquitous materials in optoelectronic and solar energy applications ranging from light-emitting diodes to artificial photosynthesis. Pushing performance limits in these applications beyond the state of the art requires understanding and controlling microscopic electronic and structural responses in the ensembles of photoexcited nanocrystals. Particularly, understanding the origins of nonradiative losses such as carrier trapping and hot carrier relaxation is critical to increase the utilization of excited electronic states for efficient energy transport and conversion. In this talk, I will highlight the use of pump-probe electron diffraction and X-ray scattering approaches to unravel electron – phonon couplings in colloidal nanocrystals to investigate the atomistic origins of nonradiative relaxation and associated transient lattice deformations. I will present our recent work resolving dynamic lattice responses in photoexcited II-VI, IV-VI and metallic nanocrystals which reveales dynamic structure - property relationships key to manipulating photocatalytic functionalities in these nanomaterials.
[1] B. Guzelturk, B. Cotts. D. Jasrasaria, J. Philbin, et al., Nature Communication 12, 1860 (2021)
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11:45 AM NM03.06.05
Photocatalytic Activity Enhancement of Iron Oxide in Structural Engineered Anodic Aluminum Oxide Photonics Crystals Carina Hedrich[1], Anna R. Burson[1], Silvia González-García[2], Víctor Vega[3], Victor M. Prida[2], Abel Santos[4], Robert H. Blick[1] and Robert Zierold[1]; [1]Center for Hybrid Nanostructures, Universität Hamburg, Germany; [2]Physics Department, School of Sciences, University of Oviedo, Spain; [3]Laboratory of Nanoporous Membranes (STSs), University of Oviedo, Spain; [4]School of Chemical Engineering and Advanced Materials, The University of Adelaide, Australia

Over the last decade, iron (III) oxide (Fe_2O_3) has increasingly come into focus as a promising photocatalyst since it is abundant on earth and its' electronic band gap is located in the visible region of the electromagnetic spectrum. Thus, solar light can be used to excite iron oxide and thereby induce photocatalytic reactions such as oxidative water purification. However, Fe_2O_3 photocatalysts often suffer from inefficient charge carrier generation or fast recombination of them. One well-studied approach to overcome this limitation is to combine Fe_2O_3 with other semiconductors, generating heterojunctions which facilitate the charge separation. Alternatively, the charge carrier generation can be enhanced by tuning the light-matter interaction, for instance, by utilizing the so-called slow photon effect which appears in photonic crystals (PhCs).
PhCs are periodical arrangements of materials with different dielectric constants and possess photonic stopbands (PSBs), also known as photonic band gaps, wherein photons of the respective wavelengths cannot exist in the structure – similar to electrons in a semiconductor band gap. At the PSB edges, the group velocity of incoming photons is strongly reduced and thereby the interaction probability between photons and the PhC material increases. This slow photon effect can improve the charge carrier generation in semiconductor-based PhCs when the PSB edge is aligned with the electronic band gap of the semiconductor.
Realization of two-dimensional PhCs is possible by tailoring the anodization of aluminum. In general, anodic aluminum oxide (AAO) membranes feature self-organized, highly ordered pores with distinct geometrical characteristics. Modifying the electrochemical anodization parameters and applying pulse-like anodization profiles allow to adjust the pore morphology from straight towards modulated structures, e.g., distributed Bragg reflectors or gradient index filters.
Herein, such AAO-PhCs are conformally coated with Fe_2O_3 thin films by atomic layer deposition (ALD) which is based on sequential, self-limiting gas-solid surface reactions allowing for conformal material deposition in high aspect ratio nanostructures. The PSB position of the AAO template can be precisely tuned across the whole visible region and will be aligned with the semiconductor band gap to take advantage of the slow-photon effect. The influence of the Fe_2O_3 thickness (1-6 nm) on the photocatalysts' performance is systematically investigated by studying the photodegradation of methylene blue as a model pollutant of water.
Optimizing and combining AAO-PhC templates with ALD functionalization of cheap and abundant semiconductors, i.e., iron oxide, might pave the way to wavelength-selective, effective photocatalytic nanostructures.

SESSION NM03.07: Water Splitting

Session Chairs: Gordana Dukovic and Matthew Sheldon
Wednesday Afternoon, April 12, 2023
InterContinental, Fifth Floor, Ballroom A

1:30 PM *NM03.07.01
Development of Particulate Photocatalysts for Water Splitting Kazunari Domen[1,2]; [1]Shinshu University, Japan; [2]The University of Tokyo, Japan

Sunlight-driven water splitting has been studied as a means of producing renewable solar hydrogen. Overall water splitting using particulate photocatalysts has been attracting growing interest, because such systems can be spread over wide areas by potentially inexpensive processes [1]. In fact, a solar hydrogen production system based on 100-m^2 arrayed photocatalytic water splitting panels and an oxyhydrogen gas-separation module was built, and its performance and system characteristics including safety issues were reported recently [2]. Nevertheless, it is essential to radically improve the solar-to-hydrogen energy conversion efficiency (STH) of particulate photocatalysts and develop suitable reaction systems. In my talk, recent progress in photocatalytic materials and reaction systems will be presented.

The author's group has studied various semiconductor oxides, (oxy)nitrides, and (oxy)chalcogenides as photocatalysts for water splitting [3]. $SrTiO_3$ is an oxide photocatalyst that has been known to be active in overall water splitting under ultraviolet irradiation since 1980. Recently, the apparent quantum yield (AQY) of this photocatalyst in overall water splitting has been improved to more than 90% at 365 nm, equivalent to an internal quantum efficiency of almost unity, by refining the preparation conditions of the photocatalyst and the loading conditions of cocatalysts [4]. This quantum efficiency is the highest yet reported and indicates that a particulate photocatalyst can drive the endergonic overall water splitting reaction at a quantum efficiency comparable to values obtained in photon-to-chemical and photon-to-current conversion processes by photosynthesis and photovoltaic systems, respectively.

For practical solar energy harvesting, it is essential to develop photocatalysts that are active under visible light irradiation. Recently, Ta_3N_5 [5], $Y_2Ti_2O_5S_2$ [6], TaON [7], and $BaTaO_2N$ [8] were reported to be active in photocatalytic overall water splitting via one-step excitation under visible light irradiation. In these achievements, the synthesis of well-crystallized semiconductor particles and the loading of composite cocatalysts were important for improving the photocatalytic activity. Nevertheless, further improvements in the preparation of cocatalyst/photocatalyst composites are still required to achieve a sufficient STH value.

It is possible to combine hydrogen evolution photocatalysts (HEPs) and oxygen evolution photocatlaysts (OEPs) and decompose water into hydrogen and oxygen via two-step excitation. Such a process is recognized as Z-scheme widely. Particulate photocatalyst sheets consisting of La- and Rh-codoped $SrTiO_3$ as the HEP and Mo-doped $BiVO_4$ as the HEP immobilized onto Au and C layers split water into hydrogen and oxygen with STH values exceeding 1.0% [9,10]. Some other (oxy)chalcogenides and (oxy)nitrides with long absorption edge wavelengths are also applicable to Z-schematic photocatalyst sheets and hold the promise of realizing greater STH values.

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2:00 PM NM03.07.02
Immobilization of Cobalt-Based Polyoxometalate on Titanium Dioxide Nanorods for Photoelectrochemical Water Oxidation Boon Chong Ong, Teik Thye Lim and Zhili Dong; Nanyang Technological University, Singapore

The production of hydrogen from water as a source of renewable energy is a crucial technology to overcome the energy crisis and world pollution issues. However, there are challenges due to its non-thermodynamically favorable reaction and the complex electron transfer process. Titanium dioxide (TiO_2) has been widely used as a photocatalyst due to its high stability and activity towards light radiation. It is considered one of the promising types of catalysts that can catalyze the water oxidation reaction under light radiation, but its performance is often hampered by the fast recombination of photogenerated electron-holes pairs. Polyoxometalates (POMs), a class of transition metal oxides, with good redox properties, tunable structure and high durability could act as an effective hole scavenger layer to enhance the activity of TiO_2 towards water oxidation. In this study, a nanocomposite film, consisting of TiO_2 and cobalt-based POMs, was synthesized by the growth of TiO_2 on a conductive fluorine-doped tin oxide (FTO) substrate *via* the hydrothermal technique. This step was followed by layer-by-layer deposition of POMs. The photoelectrochemical water oxidation test showed that the onset potential of POMs coated TiO_2 photoanode was lower. The induced photocurrent at the applied potential of 1.23 V *vs.* reversible hydrogen electrode (RHE) was approximately two times that of pristine TiO_2. POMs layers would reduce the recombination rate of electron-hole pairs by extracting and transporting the generated holes, thus improving the overall PEC performance. The photoelectrochemical response was further enhanced with increasing POMs layers, but there was an optimal number beyond which the produced current density began to decline owing to light penetration limitation. In term of durability, the generated photocurrent density remained relatively stable throughout the test period with minor fluctuations that could be caused by the formation and evolution of oxygen bubbles. This work provides a facile layer-by-layer deposition method to immobilize layers of POMs on TiO_2 to promote PEC water oxidation under neutral conditions, which is attractive for long-term applications.

2:15 PM NM03.07.03
Photocatalytic Water Oxidation of WO3 Nanoparticles with Regenerative Redox Couple Noyoung Yoon[1,2], Sang Youn Chae[3], Oh-Shim Joo[1] and Eun Duck Park[3]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Yonsei University, Korea (the Republic of); [3]Ajou University, Korea (the Republic of)

Photocatalytic water splitting is one of the promising ways to produce green hydrogen with zero CO_2 emission. However, current stage, solar to hydrogen conversion efficiency (~1%) is much lower than industrial meets. for visible light utilization, the band gap of semiconductor photocatalyst is limited to less than ~3 eV, however, water splitting reaction requires a large driving force due to its high overpotential for each hydrogen evolution and oxygen evolution reaction and also due to fast electron-hole recombination at the semiconductor photocatalyst surface. Therefore, sacrificial agents such as Ag+, persulfate, and O_2 were used to facilitate the photoelectrochemical reaction and fast carrier extraction from the semiconductor. However, only a half-reaction of water splitting occurs in presence of the sacrificial agent. Moreover, the sacrificial agent is also an energy-contained chemical resource, therefore consuming the sacrificial agent is not the regenerative pathway for water splitting or green hydrogen production. Lastly, some sacrificial agents can lead to the poisoning of photocatalysts. Therefore it is better to use regenerative redox couple as electron or hole donner for photocatalytic reaction. with redox coupled in a water medium, the photocatalysts successfully store solar energy via half-reaction, then the redox couple can be regenerated by the counterpart reaction. In this study water oxidation of WO_3 was carried out with an electron-accepting sacrificial agent, Ag^+, and redox couples such as Io_3^-/I^-, $Co(phen)_3^{2+/3+}$, $Fe^{2+}/^{3+}$. To improve the kinetics of both the electron acceptor reduction reaction and water oxidation reaction, the PtRu alloying nanoparticle co-catalyst was introduced. The ratio of Pt and Ru was controlled for the best activity, and also confirmed the PtRu co-catalyst is active for both redox couple reduction and water oxidation reaction. This study shows that the PtRu cocatalyst is useful for tandem photocatalyst systems with a redox mediator or other tandem system for photocatalytic full water splitting systems.

2:30 PM NM03.07.04
Mechanisms Governing Solar-to-Hydrogen Conversion Efficiency in Multijunction Silicon Nanowire Photocatalysts Samantha R. Litvin, Taylor Teitsworth, Samuel Bottum and James Cahoon; University of North Carolina-Chapel Hill, United States

In the nearly 50 years since the first demonstration of photoelectrochemical water-splitting, solar fuels such as hydrogen have yet to become a practical source of alternative energy in large part due to the high cost and low efficiency of solar fuel systems. Si-based particle suspension reactors (PSRs), which consist of light-absorbing photocatalytic particles in solution that can individually split water, are a simple and potentially low-cost paradigm to generate hydrogen and enable solar fuel generation on a large scale. Multijunction silicon nanowires (MJ SiNWs) can absorb light across the visible spectrum, have p-n junctions that facilitate charge separation, and have recently demonstrated the ability to split water. Here, we present the bottom-up vapor-liquid-solid synthesis of single nanowires with multiple p-i-n junctions consisting of degenerately-doped segments and abrupt dopant transitions <10 nm. MJ SiNWs are functionalized for water-splitting with oxygen and hydrogen evolution co-catalysts via a spatioselective photoelectrodeposition process. Photovoltaic and electrochemical characterization of single-nanowire devices show tunable photovoltages exceeding 10 V under 1-sun illumination and water splitting activity at infrared wavelengths up to ~1050 nm. Experimental techniques and finite-element modeling have allowed us to systematically isolate and investigate aspects of STH including light absorption and charge carrier activity. Our studies indicate that photocatalyst performance and efficiency is dictated by nanowire dopant profile and surface composition, as well as the photonic characteristics of the sub-wavelength nanowire diameter. Unlike wider bandgap oxide and chalcogenide particles previously studied for PSRs, MJ SiNWs bring the photonic advantages of a tunable, mesoscale geometry and the cost and environmental advantages of Si to the PSR design, providing a new approach for water-splitting reactors.

2:45 PM NM03.07.05
Growth of $MoSe_2$ Nanosheets Around ZnO-SnO_2-$ZnSnO_3$ Hollow Nanofibers (h-ZTO) for Effective CO_2 Photoreduction Hazina M. Charles and Caroline Sunyong Lee; Hanyang University, Korea (the Republic of)

Hazina Charles, Rajendra C. Pawar, Haritham Khan, Jin-Goo Park, Caroline Sunyong Lee*
Department of Materials and Chemical Engineering,
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Solar-driven semiconductor photocatalysts, especially photocatalysts with multi-heterojunctions, have gained a lot of interest as a potential solution to the world energy crisis and environmental pollution. In this study, simple electrospinning followed by solvothermal technique were used to synthesize h-ZTO/$MoSe_2$ hybrid photocatalysts with multiple heterojunctions. Hybrid photocatalysts were fabricated by adjusting the h-ZTO/$MoSe_2$ ratio, which demonstrated outstanding photocatalytic activity than that of pure h-ZTO, due to its double growth of $MoSe_2$ nanosheets on h-ZTO hollow nanofibers. To understand morphology, microstructure, phase composition, and functional characteristics of the synthesized photocatalysts, different techniques were employed including FE-SEM, TEM, XRD, XPS, PL, TR-PL, and PEC. Optimal h-ZTO/$MoSe_2$ hybrid photocatalyst exhibited efficient photocatalytic transformation of CO_2 into CO, $H_{2,}$ and CH_4, with yielding rates of 140, 64, and 33 $\mu molg^{-1}h^{-1}$, respectively. Moreover, the optimal hybrid photocatalyst showed the highest CO_2 photoreduction selectivity of 93%. This remarkable activity could be driven by the homogeneous growth of $MoSe_2$ in/on the hollow nanofibers walls, which improved their capacity for light scattering and offered a significant number of active sites to activate and desorb CO_2 throughout the reaction. This study indicated that hollow nanofibers well coated with MoSe2 nanosheets can provide bright insights on how to design a catalyst with high product selectivity.
Keywords: Hybrid photocatalyst, hollow (h-ZTO) nanofiber, $MoSe_{2,}$ CO_2 photoreduction, Multiple heterojunctions.
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3:00 PM BREAK

SESSION NM03.08: Carbon Nitride
Session Chairs: Lilac Amirav and Kazunari Domen
Wednesday Afternoon, April 12, 2023
InterContinental, Fifth Floor, Ballroom A

3:30 PM *NM03.08.01
Time-resolved Optical Spectroscopy to Accelerate the Development of Particulate Carbon Nitride (CN_x) Photocatalysts Robert Godin; The University of British Columbia, Canada

Polymeric photocatalysts made of Earth-abundant elements have been extensively developed over the past decade to take advantage of their synthetic tunability.[1] Within this family, carbon nitrides (CN_x) are emerging as exciting photocatalysts because of their high photocatalytic performance combined with good stability and facile synthesis. However, significant gaps remain in our knowledge of the photophysical properties of these organic polymeric materials. Determining the pathways and mechanism of photoinduced processes will greatly aid our efforts to engineer better CN_x photocatalysts for solar fuel production.[2]
Time-resolved spectroscopies, particularly transient absorption spectroscopy (TAS), enable us to determine the nature of short lived photoexcited states and determine the kinetics of competing processes. We utilize TAS to shed light on leading strategies followed in the pursuit of improved photocatalytic activities: 1) morphological modifications, 2) heterojunction formation, and 3) CN_x precursor blends.
CN_x possesses a 3D morphology resulting from π–π stacking of 2D sheets composed of condensed heptazine units, which gives insoluble particles with low surface area. Nanostructured CN_x can show improved efficiency by allowing for fine-tuning of properties such as length, diameter, and polymer backbone conformation. However, there are contradictory reports in the literature the on the relationship between surface area and photocatalytic efficiency. To address this question, we devised a method to tune the morphology of CN_x after polymerization occurred, thus limiting the potential for uncontrolled chemical changes during the high temperature polymerization step. Using water-soluble CN_x nanosheets as the building block, we observed unique CN_x morphologies using mesoporous silica as the template.[3] Our spectroscopic investigations identified that residual CN_x nanosheets caused charge trapping and the loss of photocatalytic activity, possibly counteracting any gains from reducing the size of features.
Forming a heterojunction is a common strategy to promote charge separation and charge carrier lifetime to improve the efficiency of CN_x photocatalysts, though the distinct molecular interface formed are not well-understood.[4] A highlighted example is the case if organic-organic CN_x heterojunctions with carbon nanodots (CDs). Despite the similarity in material compositions, different CN_x/CD heterojunctions show that the flow of charges is dependant on the type of CDs incorporated.[5] Segregation of opposite charges across the two different materials leads to impressive chemical selectivity methanol formation from CO_2.

Incorporation of other small molecules into the framework of CN_x in a copolymerization process provides a handle to regulate the intrinsic framework of CN_x and optimize electronic band structures, optical absorption, and the overall photocatalytic performance of CN_x.[6] We carried out the systematic synthesis of CN_x prepared through copolymerization at various precursor ratios. Our optical spectroscopy and material characterization investigations highlight the complex interconnections between chemical structure, electronic structure, physical properties, photophysics, and photoactivity.

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4:00 PM NM03.08.02
Light-Driven *sp*^{3}-*sp*^{3} Cross-Coupling of Carboxylic Acids and Alkyl Halides over a Ni Single-Atom Catalyst Mark A. Bajada[1], Giovanni Di Liberto[2], Vincenzo Ruta[1], Sergio Tosoni[2], Alessandra Sivo[1], Gianfranco Pacchioni[2] and Gianvito Vile[1]; [1]Politecnico di Milano, Italy; [2]University di Milano Bicocca, Italy

The coupling of two *sp*^{3} hybridized fragments remains a challenging protocol for organic synthesis. Although visible light-driven metallaphotoredox catalysis, a method that combines photoabsorbers and transition metals, has become a powerful tool to conduct such transformations, resource economical and scalability issues persist, due to the use of catalysts and light absorbers which exploit critical raw materials (e.g., iridium complexes) and are homogeneous in nature. Here we report the first synergistic merger of metallic single-atom and photoredox catalysis, in the form of a Ni atom-supported carbon nitride material, for decarboxylative *sp*^{3}-*sp*^{3} cross-coupling between carboxylic acids and alkyl halides. This operationally straightforward system, comprised of only earth abundant components, works with chloro-, bromo-, and iodoalkanes, and exhibits a wide functional group tolerance in terms of both the coupling partners, *i.e.* the alkyl halide and carboxylic acid. Further still, since the metal and photoredox catalytic cycles were essentially combined within one single-atom material, we were able to easily recover and re-use the heterogeneous system for several times, preserving its activity between individual trials. With the help of computational studies, we have elucidated the active site of the Ni single-atom material, analyzing both the metal coordination with the carbon nitride support and binding of the substrates to the active site, thus proposing a plausible reaction mechanism. The reaction time is 83% shorter than the reported homogeneous procedure, making the method highly attractive for industrial applications. We thus further exemplify the versatility of our system through the synthesis of an API precursor, and the adaptation of our single-atom catalytic system within a continuous flow photoreactor device.

4:15 PM NM03.08.03
Nitrogen-deficient Carbon Nitride Photocatalyst for Selective Oxidation of HMF Coupled with Hydrogen Evolution Dai-Ling Tsai, Hsing-Ting Liu and Jih-Jen Wu; National Cheng Kung University, Taiwan

Two-dimensional polymeric carbon nitrides composed of earth-abundant elements have been known to be the potential visible-light-driven photocatalysts for solar energy conversion and environmental remediation. Intrinsic defect engineering in carbon nitrides has drawn substantial attention because it provides a promising approach to boost the photocatalytic performance of carbon nitrides without introducing heteroatom in the basic unit. In this work, melon-based carbon nitrides are prepared by thermal polycondensation of supramolecular complexes of various nitrogen-rich organic compounds. Solid-state nuclear magnetic resonance characterizations reveal that defect-modified carbon nitride can be obtained by varying the composition of supramolecular complexes. Nitrogen-deficient carbon nitride is produced by thermal polycondensation of the supramolecular complex of melamine, cyanuric acid, and triaminopyrimidine. The nitrogen-deficient carbon nitride with the exceptional photocatalytic performance for simultaneous biomass valorization and H_2 evolution compared to the pristine melon carbon nitride is demonstrated in this work. The simultaneous H_2 evolution from water splitting coupled with selective oxidation of 5-(hydroxymethyl) furfural (HMF) to 2,5-diformylfuran (DFF) is achieved over the nitrogen-deficient carbon nitride photocatalyst with activities of 70 mmol g^{-1} h^{-1} and 94 mmol g^{-1} h^{-1} under AM 1.5G (100 $mWcm^{-2}$) illumination with a UV filter. The photophysical properties of carbon nitrides are tunable by modifying the microstructure towards efficient photocatalytic activities. The influences of chemical and electronic structures on the photocatalytic activity of nitrogen-deficient carbon nitride will be discussed in this presentation.

SESSION NM03.09: Poster Session II
Session Chairs: Lilac Amirav, Klaus Boldt, Matthew Sheldon and Maria Wächtler
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM NM03.09.01
Graphitic Carbon Nitride Films with Biomimetic Structure for Photocatalytic Conversion of Carbon Dioxide I-Hsiang Tseng[1], Yu-Hsuan Liu[1], Yu-Cheng Tsai[1] and Ta-I Yang[2]; [1]Feng Chia University, Taiwan; [2]Chung Yuan Christian University, Taiwan

A hydrothermal method was developed to synthesize carbon-modified graphitic carbon nitride (gCN). Meanwhile, natural leaves with hierarchical surface structure were introduced to homogeneously graft gCN and to improve light absorption. The modification resulted in the exfoliation of graphitic stacking and formation of defects for better charge transfer. The addition of glucose and the presence of hierarchical structure improved the photocatalytic activity. Carbon monoxide and methanol were main products from the photoreduction of gaseous carbon dioxide and water vapor under visible light illumination. By tuning the type and concentration of hole scavengers, the photocatalytic activity and product selectivity could be further enhanced.

5:00 PM NM03.09.02
Z-Schematic Artificial Leaf-like Structure for Biosolar Oxyfunctionalization of C-H Bonds Lee Chung Hyun; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The natural Z-schematic photosynthesis is a promising catalytic system for biocatalytic solar-to-chemical production. Here, we construct a Z-schematic, wireless photoelectrocatalytic (PEC) system (i.e., artificial leaf) for biocatalytic oxyfunctionalization reactions. The monolithic leaf structure consists of a tandem photoanode-photocathode configuration that uses sunlight as the sole energy source to drive redox reactions. Under solar light, inorganic oxide photoanode extracts electrons from H_2O electron feedstock and transfers the electrons to the organic photocathode. Meanwhile, the conjugated thiophene based organic photocathode absorbs photoanode-filtered light for O_2 reduction to H_2O_2 with a high faradaic efficiency (76 %) even in neutral pH environments. The *in situ* generated H_2O_2 activates biocatalytic enzyme to drive C-H oxyfunctionalization (e.g., ethylbenzene oxyfunctionalization) with an excellent enantioselectivity (enantiomeric excess > 99%). Furthermore, we solve hydroxyl radical mediated inactivation of biocatalyst using a membrane, which increases enzymatic productivity with a benchmark total turnover number of about 100,000 among PEC and photocatalytic platforms that trigger biocatalyst mediated synthesis. This work presents the first artificial leaf architecture for enzymatic oxyfunctionalization of C-H bonds.

5:00 PM NM03.09.03
Photocatalytic Gold Deposition on Titanium Dioxide Templates Mimicking Axonal Growth Fatemeh Abshari, Moritz Paulsen, Jan Schardt, Blessing Adejube, Salih Veziroglu, Alexander Vahl and Martina Gerken; Christian-Albrechts-Universität zu Kiel (CAU), Germany

Nanoionic memristive devices that are based on the field driven migration of metal cations and oxygen vacancies have gathered high interest in the scientific community for their capability to technically mimic synaptic connections. Less attention has been given to long-range global plasticity in artificial neuronal networks. The aim of our research is to use light-stimulated growth of gold metal lines to technically mimic the growth of long-range axonal connections for neuromorphic computing architectures. To mimic the growth of axons we investigate the formation of metal lines by UV-light-stimulus-driven photocatalytic deposition of gold on titanium dioxide layers. The growth process is conducted in a beaker by reduction from aqueous gold chloride precursor ($HAuCl_4$) and is observed by transmission optical measurements in an inverted-microscope setup. Surface properties are analyzed by 3D laser interference microscopy and scanning electron microscopy (SEM) and electrical conduction measurements are taken.
We fabricated the photoactive titanium dioxide layers with the thickness of 40-100 nm on quartz glass by DC sputtering. The substrates were then heat treated for 1h at 300°C and subsequently cooled on a metal plate to achieve the photocatalytically active anatase phase of titanium dioxide. In the growth process the substrates are placed in a beaker containing 15 ml of the precursor. The solution is obtained by dissolving 15 mg of $HAuCl_4$ crystalline powder in 60 ml of deionized water. We utilize a UV LED with the wavelength peak of 365 nm to illuminate the sample in the beaker. The illumination time and UV-intensity are crucial for this dynamic process. Here we illuminated for 3h and replaced the solution every hour. Furthermore, we repeated this experiment by adding a surfactant to the solution to achieve faster growth and better surface coverage as proposed by literature.
In-situ characterization of the growth process is possible by placing the beaker in an optical microscope with transmission configuration. While the sputtered titanium dioxide and the quartz glass substrate show high transparency, the grown gold will absorb and reflect the transmitted light and thus yield an observable change in transmission. We also analyzed the morphology of the grown gold layers by 3D laser interference microscopy and scanning electron microscopy (SEM) after the growth procedure. The measurements show the formation of gold clusters on the surface of the titanium dioxide layers. Sufficient growth time is needed to reach the percolation threshold and attain a conductive gold layer which is crucial for our aim of mimicking axonal connections. We recorded electrical current-voltage characteristics to investigate the electrical conductivity of the grown gold. Our measurements revealed a value of electrical conductivity ��=0.015 S for areas with high surface coverage. It is obvious from 3D laser interference microscopy that the thickness of gold clusters is not uniform throughout the surface of titanium dioxide. Therefore, the conductivity across the 2D surface of the TiO_2/Au composite varies. With its potential capability to locally control the growth of long-range metallic connections, photocatalysis is a promising approach towards mimicking the dynamic formation of long-range axonal connections in neural networks.

5:00 PM NM03.09.05
Photocatalytic Degradation of Perfluoroalkyl Substances in Water by Using a Duo-Functional Tri-Metallic-Oxide Hybrid Catalyst Junjie Niu; University of Wisconsin--Milwaukee, United States

Abstract
Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the most typical poly- and perfluoroalkyl substances (PFASs) compounds. PFOA is detected in surface water, groundwater, sediment, sludge, and municipal wastewater. In recent years, various adsorbents such as activated carbon, polymer-supported carbon, anion exchange metal-organic framework, and beta-cyclodextrin have been used for the removal of PFASs. The recalcitrant nature of PFASs urges scientists to discover solutions to permanently remove PFAS contaminations from water with less energy in contrast to incineration. Here we present a duo-functional tri-metallic-oxide (*f*-TMO) hybrid photocatalyst, which displayed both high adsorption capacity and high defluorination rate of a series of PFASs including PFOA, PFOS, PFHpA, PFHxA and PFBA due to the generated holes/electrons (h^+/e^-) and multi-radicals (Samuel, Shang, Niu. ***Chemosphere***, 293 (2022) 133568). Particularly the Langmuir adsorption capacities up to 827.8 and 714.5 mg g^{-1} along with the adsorption efficiency of 99.8% and 99.4% for PFOS and PFOA were respectively achieved, which are more than two times higher than the most used activated carbons. A defluorination ratio of as high as 74.8% with PFOA and a ratio up to 67.6% with PFOS were respectively achieved. Over 98% PFOA molecules were degraded within as fast as 15 min, which demonstrates an excellent degradation kinetics. After degradation, the PFOA residuals were as low as 10 ng L^{-1} in industrial wastewater with an initial concentration of 1 ppb. As for the more recalcitrant sulfonic acid of PFOS, an as high as 95.5% degradation efficiency was obtained within 300 min. It was found the most high-F molecules such as $C_7F_{15}COOH$ were gradually degraded into low-F molecules such as CF_3COOH within 60 min before they were completely decomposed into non-toxic F^-. In parallel, the *f*-TMO photocatalyst still exhibited a >96.2% degradation efficiency after eight regeneration cycles. The high physical adsorption capacity and high defluorination rate make this *f*-TMO catalyst a promising candidate in removing various PFASs from a broad range of residential and industrial water systems.

Keywords: Adsorption; Perfluoroalkyl substances (PFASs); Photocatalytic degradation; Water treatment

5:00 PM NM03.09.06
Heterostructured Photocatalysts of Ni^{2+} Doped CdS Quantum Dots and β-$Pb_{0.33}V_2O_5$ Nanowires: Towards Selective CO_2 Reduction Karoline E. García-Pedraza and David Watson; University at Buffalo, The State University of New York, United States

Solar photocatalytic reduction of carbon dioxide (CO_2) to valuable products such as carbon monoxide, methane, and ethanol has become an appealing approach to mitigate the deleterious impact of the combustion of fossil fuels. Quantum dots (QDs), visible light-sensitive nanomaterials, have been widely studied for converting solar energy into chemical energy due to their light-harvesting properties, compositional tunability, and size-dependent energetics. However, bare QDs suffer from low selectivity toward the reduction of CO_2. To improve their catalytic activity, we have doped QDs with nickel(II) cations and interfaced them with ternary metal-intercalated vanadium oxide nanowires (NWs). Within the resulting heterostructures, QDs act as a charge donor, and the NWs exhibit intercalative mid-gap states functioning as a charge acceptor. Although our collaborative team has previously studied this type of heterostructure for hydrogen evolution and water splitting, they remain unexplored for CO_2 photoreduction. This presentation will cover the preparation and characterization of heterostructures consisting of cysteine-capped nickel(II)-doped CdS QDs (cys-NiCdS QDs) interfaced with β-$Pb_{0.33}V_2O_5$ NWs. The heterostructures are envisioned as a system to selectively reduce CO_2 under white-light illumination. This presentation will highlight recent results from materials synthesis and characterization, photophysical and photoelectrochemical assessment of excited-state charge transfer, and photocatalysis using gas chromatography (GC) for product characterization.

5:00 PM NM03.09.07
Perovskite-Type Oxynitride Nanofibers Performing Photocatalytic Oxygen and Hydrogen Generation Anja Hofmann and Roland Marschall;

University of Bayreuth, Germany

In times of ever-growing energy demand, the finiteness of fossil carbon reserves, and the rise in CO_2 emissions, solar-light induced photocatalytic water splitting for the generation of clean and renewable hydrogen as an alternative energy carrier becomes increasingly important. For this, photocatalysts with suitable band positions for solar water splitting and with high absorption of light in the visible light range are crucial. One promising candidate for this is $BaNbO_2N$ with an absorption edge up to 740 nm and suitable band positions.[1-4] Nanostructuring can be used to further enhance the photocatalytic activity by an increase of the surface area and presumably the number of reaction sites in the photocatalysis.
Herein, we are presenting a novel approach for complex nanostructured oxynitrides.[5] (111)-layered perovskite $Ba_5Nb_4O_{15}$ nanofibers with tailored fiber diameter were prepared *via* electrospinning and subsequent calcination, [6-8] and were then converted to cubic perovskite oxynitride nanofibers by ammonolysis.[5] Most importantly, the nanofiber morphology retains during the ammonolysis, and the nanofiber diameter can be tailored as well. A thorough characterization including Rietveld refinement revealed the formation of a novel $BaNbO_2N$-Ba_2NbO_3N oxynitride composite. The conversion resulted in visible-light absorption with a decrease of the band gap from 3.9 eV for the $Ba_5Nb_4O_{15}$ layered perovskite nanofibers to 1.9 eV for the converted oxynitride nanofibers. Diameter-dependent hydrogen and oxygen evolution activities of the converted oxynitride nanofibers decorated with Pt or $CoNbO_4$, respectively, with an optimum nanofiber diameter will be presented.

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5:00 PM NM03.09.08
Surface Structural Change Investigations of Modified Fe_3O_4 Nanoparticles Concerning Efficient Reusability and Enhanced Photocatalytic Activity Hangil Lee[1] and Hyun Sung Kim[2]; [1]Sookmyung Women's University, Korea (the Republic of); [2]Pukyong National University, Korea (the Republic of)

As interest in energy efficiency increases, research on various types of catalyst materials is being actively conducted. However, the indiscriminate use of photocatalyst nanoparticles (NPs) can cause environmental pollution. Therefore, the recovery rate of photocatalyst NPs used to efficiently decompose organic pollutants is as important as photocatalytic efficiency. In this study, we focused on improving the recovery rate of MO NPs with improved photocatalytic properties via the modifications. For this purpose, we achieve our objective by modulating the pH after doping the Fe_3O_4 NPs with Co ions as we focus on verifying the change of surface structure of the modified Fe3O4 NPs. Interestingly, the predominant species on the surface of the Co@Fe_3O_4 NPs fabricated under basic conditions was similar to $CoFe_2O_4$ structure with an enhanced magnetic property and photocatalytic activity. In order to confirm the changes in the oxygen vacancy according to the modulation of Fe_3O_4 NPs, we tried to identify them through various surface analysis methods such as scanning transmission electron microscopy in conjunction with electron energy-loss spectroscopy and X-ray absorption spectroscopy. We further investigated the photocatalytic oxidation of 2,5-hydroxymethylfurfural (HMF) and the magnetic properties using VSM for the modified Fe_3O_4 NPs to maximize the reuse for minimizing the water pollution. As a result, we found that the base treated Co@Fe_3O_4 NPs can be enhanced by improving their photocatalytic and by increasing the recovery rate owing to enhanced magnetic property. In addition, it was confirmed that the doped Co ion showed a Co^{2+} state from XAS result. The structure of Co@Fe_3O_4-B NPs that can be predicted from these experimental results is $Co^{2+}Fe_2{}^{3+}O_4$. Therefore, we can reasonably predict that the surface structure of Co@Fe_3O_4-B NPs can be similar to that of $CoFe_2O_4$ because it is well known that the magnetic properties of $CoFe_2O_4$ are better than that of Fe_3O_4. Furthermore, the abundant defect structures formed during Co doping under alkaline conditions improved the photocatalytic properties of the Co@Fe_3O_4-B NPs. Therefore, biomass were effectively decomposed using modified Co@Fe_3O_4-B NPs, which exhibited remarkable reusability.

5:00 PM NM03.09.09
Effect of Material and Shape of Nanoparticles on Hot Carrier Generation Ly Thi Minh Huynh, Seokheon Kim and Sangwoon Yoon; Chung-Ang University, Korea (the Republic of)

Nonradiative decay of photoexcited plasmons generates energetic nonthermal charge carriers. These hot charge carriers play a major role in plasmonic photocatalysis and photovoltaics. Therefore, establishing the relationship between the hot carrier generation efficiency and the structural and chemical parameters of nanoparticles is crucial for developing highly efficient plasmonic catalysts and photovoltaic materials. In this study, we compare the quantum efficiency of hot carrier generation between gold (AuNPs) and silver nanoparticles (AgNPs), and spherical (AuNSs) and cubic gold nanoparticles (AuNCs). We construct nanoparticle-on-mirror (NPoM) systems where reactant molecules are positioned in the nanogaps between the nanoparticles and gold films. Excitation of the NPoM at 785 nm, followed by the detection of products using surface-enhanced Raman spectroscopy allows us to measure the plasmon-driven reaction yields. Dividing the reaction yield by the calculated absorption cross section at the excitation laser wavelength provides the efficiency of hot carrier generation per absorbed photon. We reveal that AgNPs are more effective at generating hot carriers than AuNPs, which is consistent with the higher electron-surface scattering rate of AgNPs. The hot carrier generation of AuNCs is marginally better than that of AuNSs, which can be attributed to the enhanced electric fields inside the AuNCs in the nanogap region. This study contributes to a rational design of plasmonic catalysts or photovoltaic materials of higher efficiencies.

5:00 PM NM03.09.10
Plasmon-Assisted Photocatalytic Conversion of Carbon Dioxide – A Demonstration by Two Case Studies Ken Elen[1,2,3], Daria Burova[1,2,3], Jordi Volders[1,2,3], Pascal Buskens[4,1], An Hardy[1,2,3] and Marlies Van Bael[1,2,3]; [1]Hasselt University, Belgium; [2]Imec - Imomec, Belgium; [3]EnergyVille, Belgium; [4]TNO, Netherlands

Emissions of carbon dioxide are widely viewed as the leading cause of climate change. To achieve the necessary emission reductions, measures must be taken in various areas by concentrating on sustainable energy sources, energy efficiency, and materials recycling. Carbon dioxide utilization can be realized by multiple complementary technologies, such as thermocatalytic, (photo-)electrochemical, and biochemical methods. Here we report on two plasmon-assisted photocatalytic processes that allow the conversion of carbon dioxide to methane or carbon monoxide.

Methanation of carbon dioxide, also known as the Sabatier reaction, involves the reduction of carbon dioxide with hydrogen gas to produce methane and water. Conventionally this is achieved using a heterogeneous catalyst at elevated temperatures (400-500°C) and pressures up to 100 bar. Conventional catalysts typically comprise metal oxide supported transition metals. In industrial plants, Ni usually serves as the preferred catalyst due to an optimal balance between low cost and high activity and selectivity towards methane. In analogy to catalysts used for the conventional thermal Sabatier reaction, plasmonic catalysts for the light-assisted methanation of CO_2 comprise metal oxide supports decorated with metal nanoparticles, primarily elements of group VIIIb, that act as the catalytic sites. Here, we present the preparation of silica- and alumina-supported Ru catalysts by deposition precipitation and subsequent chemical reduction. Our work demonstrates that these Ru-decorated catalysts can be used successfully for the light-assisted Sabatier reaction at near-to-ambient pressures ($p < 3{,}5$ bar) and at a catalyst bed temperature of approximately 220°C, realized via combined heating and illumination of the reactor. [1]

The catalytic conversion of carbon dioxide to CO can be achieved by the Reverse Water Gas Shift (RWGS) reaction. As carbon monoxide is the main reaction product, the RWGS reaction is considered a potential route for the renewable production of syngas, a mixture of CO and H_2, which can be used as a feedstock for the subsequent production of higher hydrocarbons. The RWGS reaction is endothermic and has a low equilibrium constant, even at high temperatures. In a conventional process, the RWGS reaction requires temperatures between 500°C and 800°C. The use of plasmonic metals is one of the most promising approaches to decreasing the reaction temperature. Here, we describe titania-supported Au catalysts that are suitable for the light-assisted production of CO under mild conditions ($T < 200°C$ and $p < 3{,}5$ bar). Additionally, we demonstrate that the selectivity towards CO can be improved by decreasing the size of the gold nanoparticles. We propose that illuminated plasmonic Au nanoparticles enhance the desorption of CO from the catalyst through photogenerated charge carriers, which ensures a highly selective production of CO. [2]

These two case studies demonstrate that nanoplasmonics can offer a convenient approach for activating chemical reactions by light. Furthermore, these examples illustrate that plasmon catalysis can be utilized to convert carbon dioxide to value-added chemicals with sunlight as a sustainable energy source.

[1] D. Burova et al. “Comparing the performance of supported Ru nanocatalysts prepared by chemical reduction of $RuCl_3$ and thermal decomposition of $Ru_3(CO)_{12}$ in the sunlight-powered Sabatier reaction” Catalysts (2022) 284
[2] J. Volders et al. “Sunlight-powered reverse water gas shift reaction catalyzed by plasmonic Au/TiO2 nanocatalysts: effects of Au particle size on the activity and selectivity” Submitted (2022)

This work received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement 101015960 (SPOTLIGHT). Part of this work also received financial support from the VLAIO network “Flanders Innovation & Entrepreneurship” through the Catalisti Moonshot project D2M.

5:00 PM NM03.09.11
Real Structure and Thermal Stability of Ag and Ag@X Core-shell Nanoparticles Prepared by Gas Aggregation Cluster Sources Tereza Kosutova, Lukas Horak, Jan Hanus, Ondrej Kylian, Hana Libenska, Zdenek Krtous, Amir M. Ahadi, Jaroslav Kousal, Miroslav Cieslar, Artem Shelemin, Pavel Pleskunov, Mykhailo Vaidulych, Pavel Solar, Andrei Choukourov, Hynek Biederman and Milan Dopita; Charles University, Czechia

In the presented work, we investigated homogeneous silver nanoparticles and silver nanoparticles wrapped in titanium oxide or plasma polymeric shell, so called core-shell nanoparticles.
Silver nanoparticles belong to plasmonic nanoparticles, in which it is possible to couple electromagnetic field with the collective oscillations of conduction electrons - plasmons. These nanoparticles have great application potential because, for Ag nanoparticles, the localized surface plasmon resonance is in the region of visible light. In combination with the titanium oxide shell, the silver cores could extend the active region to visible light for the photocatalytic properties of titanium dioxide. The conjunction of the Ag core and the plasma polymeric shell brings the possibility to tune the optical absorption by varying sizes of the cores just by changing the amount of the polymeric precursor added to the aggregation chamber.
All studied nanoparticles were prepared by gas aggregation cluster sources combined with magnetron sputtering of single metallic targets in different configurations. This physical preparation method is environmentally friendly, scalable to industry demands, provides high cleanness of the process and tunability of nanoparticles structure. The core-shell nanoparticles with varied thicknesses of TiO_x shell were prepared by the in-flight coating of primarily formed silver cores, whereas the Ag@ppHMDSO nanoparticles were created by plasma-enhanced chemical vapor deposition of hexamethyldisiloxane (HMDSO) simultaneous to the aggregation of silver cores.
This study focuses on the thermal stability of described nanoparticles as it is the critical property for applications where heat transfer occurs. The evolution of morphology, chemical and phase composition, size distribution and microstructure of Ag and both types of core-shell nanoparticles during the annealing was determined by the combination of in-situ/ex-situ x-ray scattering methods (XRD, SAXS), ex-situ transmission and scanning electron microscopies, and x-ray photoelectron spectroscopy. Optical properties were investigated by UV-Vis spectroscopy.
The measurements showed that Ag nanoparticles are not very thermally stable in the air atmosphere. Their coalescence starts around 100 °C. Contrary, both types of shells formed around nanoparticles act as protection against sintering up to 300 °C. After annealing, the size of crystallites increases and the density of structural defects is reduced for all types of nanoparticles. The evolution is the fastest for pure silver nanoparticles. On the heated samples of both types of core-shell nanoparticles, pure crystalline silver particles were observed.
The addition of secondary Ti magnetrons to the deposition chamber caused a narrowing of the size distribution of Ag cores and the formation of the covering shell [1]. The series of samples with different shell thicknesses was simply prepared by varying the magnetron current on the titanium targets.
For the second type of studied core-shell nanoparticles, the presence of HMDSO in the chamber leads to changes in the size distribution and the architecture of prepared nanoparticles [2]. The increasing amount of HMDSO induces the formation of individual core-shell nanoparticles, chains of core-shell nanoparticles and, for the highest concentration of HMDSO, the synthesis of multicore-shell nanoparticles. The size of crystallites in the silver cores of nanoparticles decreases with the addition of HMDSO, which prevents further aggregation.

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5:00 PM NM03.09.12
Functionalized Anodic Aluminum Oxide Photonic Crystals as Tailor-Made Photocatalysts Carina Hedrich[1], Anna R. Burson[1], Siew Yee Lim[2], Abel Santos[2], Robert H. Blick[1] and Robert Zierold[1]; [1]Center for Hybrid Nanostructures, Universität Hamburg, Germany; [2]School of Chemical Engineering and Advanced Materials, The University of Adelaide, Australia

Reusable, cheap, non-selective and decentralized water purification systems for chemicals are urgently needed to provide drinking water to everyone, especially with respect to the challenges humanity is facing these days, such as climate change, growing population, or overfertilization of the soil, just to name a few. Photocatalysts are promising materials for providing purified water by using sunlight to induce various chemical reactions, e.g., the decomposition of pollutants.
Electrochemical oxidation of aluminum results in the formation of anodic aluminum oxide (AAO) membranes which consist of aluminum oxide matrices that contain ordered cylindrical pores perpendicular to the surface. Pulse-like anodization profiles periodically modulate the pore diameter whereby photonic crystals (PhCs) – periodic arrangements of materials with different dielectric constants – are created featuring a photonic stopband (PSB) in which

the transmission of light within the structure is forbidden. The PSB position is defined by the PhC composition, namely the utilized materials, their thicknesses, and the sequence. Note, the group velocity of incoming photons is significantly decreased at the PSB edges enhancing the interaction probability of photons with the PhC material. This slow-photon effect can increase the degradation of chemicals whose absorption maximum is aligned with the PSB edge. However, to ensure the PSB position matching, this approach requires a specific PhC for each compound that should be decomposed. In contrast, we report a more general strategy by utilizing semiconductor-based PhCs to increase the charge carrier generation when the PSB edge is aligned with the semiconductor bandgap. As a consequence, the photocatalytic degradation performance is improved regardless of the pollutants' absorption properties and the same PhC structure can be applied for decomposition of various compounds at the same time.

Herein, we present the fabrication and characterization of tailor-made titanium dioxide (TiO_2) coated AAO-PhCs. First, AAO-PhC structures are prepared by pulse-like anodization with precise adjustment of the PSB position to match the semiconductor bandgap. Second, tailor-made AAO-PhCs are conformally coated with TiO_2 of different thicknesses (0.5-6 nm) by atomic layer deposition (ALD). ALD is a gas phase deposition technique based on sequential, self-limiting gas solid-surface reactions which enable conformal coating of high aspect ratio structures such as AAO. Finally, optical characterization of TiO_2-functionalized AAO-PhCs is correlated with their photocatalytic properties which are studied by degradation of organic dyes, specifically methylene blue, methyl orange, and rhodamine B.

We believe that tailor-made AAO-PhCs combined with semiconductors deposited by ALD can further improve the photocatalytic efficiency regarding the decomposition of several chemicals. Therefore, such structures might be utilized for water purification by filtration in combination with *in situ* photocleaning.

5:00 PM NM03.09.13
Facile Fabrication of Hierarchical Graded Structure to Maximize Photocatalytic Surface Area via Additive Manufacturing Heungseok Oh, Haritham Khan, Taehyeob Im, Jin-Goo Park and Caroline Sunyong Lee; Hanyang University, Korea (the Republic of)

TiO_2 hierarchical structure which has high surface area was demonstrated via additive manufacturing to maximize its exposed area from sunlight. Conventionally, structures are fabricated by electrospinning, hydrothermal and nanoparticle synthesis. Using these processes, complex shapes are not possible to make. In this study, we have adopted extrusion based additive manufacturing method which is one of the various additive manufacturing technologies to overcome existing problems to have no limitation in making complex shapes with great variety of materials. The hierarchical graded structure was fabricated by extrusion-based additive manufacturing machine using TiO_2 feedstock which is composed of Anatase-TiO_2 powder and polymeric binder system. Then, Hierarchical structure was debound and sintered to obtain porous ceramic structure. During sintering temperature ranging from 400 to 900 °C, anatase to rutile phase transformation occurs. Sintering conditions should be optimized to increase the weight percentage of anatase phase which shows much better photocatalytic efficiency than that of rutile phase. The amount of anatase phase tends to increase with deceasing sintering temperature. In order to find the optimized sintering temperature condition, the CO_2 selectivity based on CO_2 photoreduction result using each structure was measured and compared. Finally, it was confirmed that the extrusion-based additive manufacturing could be a potential fabrication route for photocatalytic application by making hierarchical structure with high surface area.

5:00 PM NM03.09.14
Hybrid Nanoparticles of Conjugated Polymers and Gold Nanocrystals for controllable energy and charge transfer Dabin Lee and Juhyun Park; Chung-Ang University, Korea (the Republic of)

We demonstrate how to make hybrid nanoparticles of conjugated polymers and gold nanocrystals using a film dispersion approach, and how to manipulate the paths for energy and charge transfer by varying the conjugated polymers used as the donor and acceptor. The conjugated polymers could be assembled with a phospholipid having a hydrophobically modified polar head to create conjugated polymer nanoparticles (CPNs) with an average diameter of about 60 nm and inner voids with a diameter of about 10 nm. It was discovered that when conjugated polymers and phospholipid were assembled in a film by solvent drying, nanowires with inside voids of 10 nm diameter were first formed. Upon ultrasonication in water dispersion, the nanowires were fragmented by Ralyleigh instability, resulting in a uniform conjugated polymer nanoparticle with an average diameter of 60 nm. By embedding gold nanocrystals inside the void regions of CPNs, the resulting hybrid nanoparticles had gold nanocrystals that were 3 nm apart, greatly improving the localized surface plasmon resonance and light-harvesting properties. We showed that charge transfer from hybrid nanoparticles to species in water medium was the main route when energy levels of conjugated polymers were well-matched with gold, whereas photothermal effect became a major energy dissipation route when hybrid nanoparticles comprised of a conjugated polymer with a mismatched energy level with gold. These findings point to the potential for hybrid nanoparticles based on conjugated polymer and gold to be used in photothermal or photocatalytic processes, depending on the alignment of energy levels.

5:00 PM NM03.09.15
Formation of TiO_2 Thin-Films Through Laser-Induced Oxidation of a TiS_2 Precursor Drake R. Austin[1,2], Brian M. Everhart[3], Morgen Smith[3], Susanna Post[4], Christopher Muratore[4], Placidus B. Amama[3] and Nicholas Glavin[1]; [1]Air Force Research Laboratory, United States; [2]UES Inc., United States; [3]Kansas State University, United States; [4]University of Dayton, United States

In this work, crystalline thin-films of anatase and rutile TiO_2 are formed within an amorphous TiS_2 precursor (400 nm thick) through laser-induced oxidation. This was achieved by scanning a continuous wave, 514 nm laser beam across the precursor film surface in the presence of oxygen (ambient air and pure O_2). The 20 μm ($1/e^2$ diameter) focal spot allowed for the oxidation of many localized regions at varying intensities and scan speeds. These regions were characterized under Raman and ultraviolet-visible spectroscopy to determine the crystalline phase and band gaps of the laser-oxidized regions. After identifying the conditions needed to produce varying anatase/rutile mixtures in the intensity/scan speed phase space, large regions of crystalline TiO_2 were then produced by raster-scanning the laser repeatedly. Raman mapping was used to determine the spatial variation in the crystallinity of these larger regions, while X-ray diffraction analysis was used to estimate the anatase/rutile mass fraction present. Multiple whole-sample (2 in^2 area) thin-films of varying antase/rutile mixtures were subsequently created in the same manner, with each sample produced using different laser-processing conditions. Finally, the photocatalytic activity of each sample was determined by measuring the relative change in concentration of various NO_x species in a flow reactor during exposure of the film to simulated sunlight. Mechanisms driving the reaction kinetics of the TiS_2 oxidation/crystallization as well as the photocatalytic activity of the films are discussed.

5:00 PM NM03.09.16
Photocatalytic Denitrification by Sensitized Electrospun Filters Jessica M. Andriolo[1], Erik M. Grumstrup[2], A. A. Talin[3] and Jack L. Skinner[1]; [1]Montana Technological University, United States; [2]Montana State University, United States; [3]Sandia National Laboratories, United States

Nitrogen-based fertilizers are critical to the production of successful crops for farmers, yet use of these supplements has led to nitrate contamination of surface and ground waters. Nitrate is a frequently occurring ground water pollutant that has significantly increased in concentration over the last century due to use of fertilizers. Nitrates in aquatic environments promotes biological growth and algal blooms, resulting in eutrophication and depleted oxygen. Lack of oxygen results in damage to aquatic ecosystems, causing death of aquatic animals and infiltration of nitrogen oxyanions that severely affect human health by reducing nitrate to nitrite in the human gut.

Several water treatment technologies have been examined to address nitrate pollution. While nitrate removal has been predominantly approached by traditional physicochemical and biological treatment processes, these methods have presented drawbacks including high operational and labor costs, large energy requirements, and residual waste production. Recently, more sustainable processes for denitrification of natural waters have been explored. Such technological approaches include use of nanomaterials that serve as catalysts to promote photocatalytic denitrification at a reduced fingerprint.

In this work, a catalytic electrospun filter was designed to use photons from natural sunlight to promote reduction of aqueous nitrate. The filter was designed to have a high surface area, presenting many photocatalytic sites for nitrate reduction and to improve catalytic efficiencies. Polymer fibers in the filter consisted of a coaxial structure with a polycaprolactone-poly(3-hexylthiophene-2,5-diyl) (PCL-P3HT) blend core (sensitizer layer to promote absorption and electron injection) and a PCL - polyethylene glycol (PEG) block copolymer shell. In the design used, PEG blocks would be dissolved from the shell structure and filled with zirconium oxide nanoparticles (ZrONPs) that exhibit an adequate reduction potential and provide stability. The ZrONPs would then be accessible by aqueous solution at the fiber surface while still making contact with the semi-conducting fiber core.

In past work, thin film versions of the photocatalytic fibers were fabricated to determine feasibility of the design. In the thin film version, a glass cover slip was spin coated with a PCL-P3HT blend. PCL-PEG block copolymer was then spin coated onto the PCL-P3HT layer. PEG blocks were subsequently dissolved and filled in with ZrONPs by sonication in an ethanol-ZrONP solution for 10 min. The resulting structure provided protection of the P3HT from water by the glass cover slip and PCL, and the edges of the material were sealed with glue. Using a Hepatochem PhotoRedOx Box system and a 540 nm LED source, nitrate reduction was monitored over 8 hr. Results showed a 22 % reduction of aqueous nitrate. The solution used also contained methanol as the electron shuttle during the reaction. In a simpler version of the thin film, excited state lifetimes of P3HT thin films were compared to P3HT thin films coated in ZrONPs using ultrafast pump-probe spectroscopy. Results showed that at 2 ns, the P3HT thin film had returned back to ground state, whereas the P3HT thin film coated in ZrONPs maintained excitation, possibly indicating a long-lived charge separated state. Conductivity characterization of PCL-P3HT thin films was also performed and showed typical semiconductor characteristics of the material on an I-V curve.

In this work, we will begin fabrication of the electrospun, sensitized photocatalytic denitrification filter. Our preliminary results showed a 60 % PCL / 40 % P3HT blend provided preferrable viscosities for electrospinning. The final filter will be tested for nitrate reduction efficiency in the Hepatochem PhotoRedOx system and characterized by electron microscopy.

5:00 PM NM03.09.18

Mesoporous Zinc Oxide Supported Silica-Titania Nanocomposite—Structural, Optical and Photocatalytic Activity Adil Alshoaibi; King Faisal University, Saudi Arabia

Sol-gel-based titania nanoparticles (TNPs), Silica-titania nanocomposite (STNC), and zinc supported silica-titania nanocomposites (Z/STNC) are synthesized at low temperature. FESEM/EDX shows that ZNPs are homogeneously distributed in the STNC. The STNC has average roughness (Ra) ~6 nm, surface area ~340 m2/g, pore volume ~0.24 cm3/g, and particle size 4 nm ± 0.3 nm, which decrease down to Ra ~5 nm, large surface area 351 m2/g, pore volume 0.4 cm3/g, and particle size 3 nm ± 0.4 nm due to filling of STNC pores by Zn species. STNC is revealed 94% transmission, refractive index 1.34 at 633 nm, and bandgap 2.7 eV, which decreased down to 80% transmission, large refractive index 1.38, and low bandgap 2.25 eV after ZNPs doping. The Z/STNC observed high photocatalytic activity 92%, R2 ~98%, and rate constant 0.011 min−1 in the photodegradation of phenol red under UV-light irradiation.

5:00 PM NM03.09.19

Effect of $BaTiO_3$ Polarisation on Photocurrent Generation and Charge Carrier Dynamics in Ferroelectric Photoanodes for Photoelectrochemical Water Splitting Chloe Forrester[1,2], Adriana Augurio[3], Joe Briscoe[1], James Durrant[2], Ji-seon Kim[2] and Charlie Henderson[2]; [1]Queen Mary University of London, United Kingdom; [2]Imperial College London, United Kingdom; [3]AO Research Institute Davos, Switzerland

Solar-driven photoelectrochemical water splitting can provide a sustainable source of hydrogen as a clean and renewable form of energy. Semiconductors employed in water-splitting photoanodes can have large rates of recombination which ultimately reduces the amount of oxygen evolved and limits the solar-to-hydrogen conversion efficiency. Ferroelectric materials possess a permanent internal electric field which has been shown to increase the lifetime of charge carriers by an order of magnitude and has the potential to reduce recombination in ferroelectric semiconductors[1].

Here, $BaTiO_3$ is studied as a wide-bandgap ferroelectric semiconductor and the effect of enhancing the ferroelectric properties by a method of poling is explored. The impact of the ferroelectric field on photocurrent generation and charge carrier dynamics is examined using steady state and transient spectroscopic techniques.

Comparing as-grown films with little ferroelectric alignment to poled films, an increase of photocurrent from 30 to 145 $uAcm^{-2}$ at 1.23 V vs RHE and an increase in IPCE from 3.5 to 34% at excitation wavelengths (325 nm) was observed after poling. Heating above the Curie temperature for $BaTiO_3$ to remove the polarisation was also shown to decrease the photocurrent in a reversible process. Transient absorption spectroscopy measurements demonstrate that the lifetime of probed electrons increases from $t_{50\%}$ from 0.1 ms to 4 ms after poling. Simultaneous transient photocurrent measurements show a corresponding increase in charge density extracted from 0.2 to 2 $uCcm^{-2}$, showing a link between electrons living longer and less recombination and more charge extraction. A model is suggested to explain how the orientation of ferroelectric dipoles and subsequent internal screening can influence surface band bending in a direction which favours the extraction of holes from the photoanode to the electrolyte. This study highlights the benefits of using ferroelectric fields to reduce recombination in photoanodes.

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SESSION NM03.10: Wastewater Decontamination
Session Chairs: Klaus Boldt and Christine Kranz
Thursday Morning, April 13, 2023
InterContinental, Fifth Floor, Ballroom A

9:00 AM NM03.10.01

Harvesting *C*lean Fogwater by Using Nanoengineered Photocatalytically Reactive Fog Harvesters Ritwick Ghosh[1,2], Adrien Baut[2], Giorgio Belleri[2], Michael Kappl[1], Hans-Jürgen Butt[1] and Thomas Schutzius[2]; [1]Max-Planck-Institute for Polymer Research, Germany; [2]ETH Zürich, Switzerland

The increasing mismatch in location of population density to the distribution of freshwater availability has aggravated the global freshwater stress. To handle this stress, researchers have looked into possibilities of tapping water from alternative resources like fog, dew, rain and desalination. Fog being a passive resource and is estimated to have a huge potential for supplying water, happens to be the most promising one. However, in many places the utility of fog as potable water becomes limited as air-borne contaminants (a major concern near urban areas) present in the surroundings get attached to the fog droplets and get collected. A possible passive way to mitigate the contaminants from being collected with fog will provide a sustainable solution for the different fog harvesting communities. The present study was focused to find such passive solution to this identified problem by leveraging the existing knowledge of both photocatalysis and fog harvesting. Photocatalysis is a process where metal oxides with semiconductor properties like titanium dioxide or zinc oxide get energized due to exposure to light in the ultraviolet wavelength and are capable of reducing organic molecules on their surface. We spray the fog harvester mesh fibers with the titanium dioxide nanoparticle coating and graft PDMS brush onto the nanoparticles after that. The coating thickness is optimized and is of the order of microns, thus not having any significant effect on the aerodynamic efficiency of the fog harvester. On the other hand, the PDMS brush helps in modulating the surface wettability of the coated fiber, besides imparting robustness to the surface coating. Later using inductively coupled plasma - optical emission spectrometry we confirmed that no additional concentration of titania or silica is found in the collected water, confirming the coating is safe for fog harvesting applications.
Two types of coated surfaces (varied by wettability i.e. superhydrophilic and hydrophobic) were prepared and tested against contaminated artificial fog, methyl orange dye was used as a contaminant surrogate. The concentration of organic contaminants were also varied and it was seen that for concentration at maximum allowable limit (referring to US EPA guidelines), the decontamination of the organic molecules leads to an impressive removal of 91% of the contaminants while dripping along the hydrophilic reactive surface. The best case for the hydrophobic reactive surface was at 76%, meaning the process takes longer timescale to decay on a hydrophobic surface than hydrophilic. To investigate this, a fundamental study was done using epifluorescence microscopy at micro-droplet scale to find the deciding factors driving the photocatalytic reduction reaction. It was found that the interplay between surface reactivity and the diffusivity of the molecules drive the photocatalytic decay reactions. Following the trends by finding lines of best fit and considering the operating conditions, a theoretical framework could be developed. The theoretical framework can predict the extent of decay expected at the given time depending on the concentration and the size of water droplets intercepted at the surface. It also predicts whether the reaction falls in the reactivity limited or the diffusion limited regime. Additionally, with the epifluorescence microscopy we developed a new process based on imaging the intensity to determine the rate of decay of contaminants in water droplets, an easy and scalable way to quantify the extent of cleaning of the water. The collection efficiency for the fog incidents were measured and the rate of collection was comparable to outdoor fog harvesting. These coated meshes were also tested outdoors, interestingly the decontamination was seen to even get enhanced on continuous UV exposure from the sun. Overall, the study may be considered as the first step towards understanding how to obtain drinkable water from contaminated fog.

9:15 AM NM03.10.02
Photosensitized Thermoplastic Nano-Photocatalyst for Potential Applications in Extraterrestrial Facilities Lidia Mezzina, Angelo Nicosia and Placido G. Mineo; University of Catania, Italy

Nowadays space colonization is one of the most popular topics, leading many space agencies to launch several space missions. However, considering that future space missions (such as NASA's Artemis Program) have the goal of settling humans on the Moon (and later on Mars) the presence of xenobiotic pollutants in closed environments could represent a health risk for organisms exposed to long-time exposure in a close environment. Indeed, the scarceness of primary resources such as air and water and the importance of their purification and recycling have determined the need to seek new low-energy depollution methods. Photocatalysis activated by solar light is a promising depollution method that uses reactive oxygen species (ROS) to mineralize organic pollutants. One of the most used photocatalysts is titanium dioxide in form of nanoparticles (TiO_2 NPs) [1]. However, the photocatalytic approach is unsuitable to be used in underground facilities and/or space environments (e.g., extraterrestrial facilities), because the photocatalytic mechanism of TiO_2 cannot be promoted by photons generated from the indoor lighting system, since they don't have enough energy to activate the photocatalysts [2]. Finally, recovery of the photocatalytic slurry from the depolluted solution is not easily feasible, particularly in low-gravity conditions.
To overcome the above issues, we produced different filmable nanocomposites using the *in-situ* radical copolymerization of an ad-hoc synthesized porphyrinic macromonomer (the photosensitizer) and methylmethacrylate directly into TiO_2 NPs. This approach aims to improve the photocatalytic performance of TiO_2 by ensuring intimate contact between the photocatalyst and the photosensitizer, also exploiting the PMMA waveguide effect [3].
The photocatalytic activity of the so-obtained nanocomposites was verified against both common dye probes and recalcitrant xenobiotic pollutants, employing light sources falling in the visible light range (λ>390 nm). The experimental data showed that the sensitized nanocomposites' photocatalytic performance is about double that of the unsensitized nanocomposite. This improved effect is due to the photosensitizer which could act both as an electron transfer and/or a dopant agent, boosting the TiO_2 photocatalytic efficiency. Thanks to their intrinsic properties (good filmability, thermal stability, wettability, etc), this new kind of thermoplastic nano-photocatalyst is suitable to be used in the form of thin films as an auxiliary system to the already employed depolluting systems in unconventional sceneries: underground or Low Earth Orbit laboratories, or (potentially) in future lunar shelters [4].

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9:30 AM NM03.10.04
Photocatalytic NO_x Mitigation Under Relevant Conditions Using Carbon Nanotube-Modified Titania Brian M. Everhart, Ahmed Al Mayyahi, Bade Tonyali, Umut Yucel and Placidus B. Amama; Kansas State University, United States

Although a majority of photocatalysts exhibit improved NO conversion to NO_2, the performance in the oxidation of NO_2, the more toxic form of NO_x, to nitrate remains a challenge; in addition, the performance of hybrid photocatalysts under practical conditions is unclear. This study demonstrates the use of carbon nanotube-TiO_2 (CNT-TiO_2) photocatalyst films for the effective transformation of NO_x into nitrates. Using the objective figure of merit for NO_x abatement, $DeNO_x$ index, the catalyst performance in a laminar-flow reactor was evaluated under simulated conditions that are relevant in abating NO_x. The conditions probed include relative humidity (RH), initial NO_x concentration, reactor geometry (headspace distance), and state of the catalyst (fresh vs. recycled). Our results reveal CNT-TiO_2 significantly outperforms P25 despite exhibiting comparable NO conversion at low RH. P25 experiences a 66% reduction in DeNOx at high RH compared to low RH while CNT-TiO_2 only incurs a 27% reduction. For recycled photocatalysts, this disparity becomes even more pronounced; CNT-TiO_2 experiences a 49% reduction in DeNOx at high RH, whereas P25 experiences a 134% reduction. In addition, mass transfer from the bulk airflow was found to limit NO conversion when the reactor headspace is too large (> 3 mm), due to limited diffusion of NO_x to the photocatalyst surface. Our findings highlight the importance of headspace distance, a parameter that has mostly been overlooked in reactor design for photocatalytic oxidation of NO_x, but is expected to dictate the optimal catalyst configuration for flue gas treatment. The remarkable $DeNO_x$ activity observed in CNT-TiO_2 over a wide range of RH levels is rationalized based on the ratio of physisorbed-to-chemisorbed water on the photocatalyst surface.

9:45 AM BREAK

SESSION NM03.11: Catalytic Mechanisms
Session Chairs: Lilac Amirav and Haimei Zheng
Thursday Morning, April 13, 2023
InterContinental, Fifth Floor, Ballroom A

10:30 AM *NM03.11.01
In Situ Liquid Cell Transmission Electron Microscopy Study of Nanoparticle Catalytic Reactions Haimei Zheng[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

Liquid cell transmission electron microscopy (TEM) has become a powerful tool for the real-time study of chemical reactions and dynamic phenomena at solid-liquid interfaces. Various advancements have been made. For example, UV light was introduced into a liquid cell which enabled the study of photocatalytic water splitting by TiO_2 nanoparticles. Interestingly, it was found that electron beam may serve as a “light” source for the investigation of pseudo-photocatalytic water splitting with rutile TiO_2 nanorods. The observation revealed the catalyst facet dependent water splitting behavior, for instance, the catalytic reactions generated hydrogen gas bubbles were found preferentially residing at the {110} facet of the rutile TiO_2 nanorod under a low electron dose rate. The electron beam effects were suppressed under the low dose imaging. Development has also been made for the study of other complex catalytic reactions, and catalytic nanoparticle restructuring has been found. Direct observation of catalytic nanoparticle structural evolution at the atomic level opens many opportunities to uncover the catalytic reactions mechanisms, and future design of novel catalysts.

11:00 AM NM03.11.02
Prediction of Excited-State Reaction Barriers in Heterogeneous Catalytic Systems with Many-Body Perturbation Theory Aaron Altman and Felipe H. da Jornada; Stanford University, United States

Excited-state catalysis encompasses a class of catalytic chemical reactions where the system of reactants adsorbed on a catalyst surface is in an excited electronic state, usually reached through light absorption or injection of a hot electron. Studies over the past decade have demonstrated the ability of illuminated nanoparticle catalysts to dramatically speed up reaction rates, selectivity amongst multiple products, and open new reaction pathways, leading to products that are otherwise not attainable in thermodynamic equilibrium. However, even with the large experimental effort, the theoretical understanding of these phenomena is still lagging. Despite substantial advances coupling non-adiabatic dynamics with excited-states, there are still few demonstrated formalisms that are able to map the rich phase space of excited-state energies in chemically complex and heterogeneous systems. Here, we present one of the first rigorously-computed excited-state potential energy surfaces (PESs) for an extended heterogeneous catalytic system, computed with the GW plus Bethe-Salpeter equation approach. In particular, using a mixed stochastic-deterministic method recently developed in our group to enable such large calculations, we compute the excited state PESs for the hydrogen adsorption/desorption reaction on a rutile TiO2 (110) surface including many-electron interactions. We find that the hydrogen desorption energy barrier in the first excited state is about half of the ground-state barrier, confirming the general expectation that lower barriers may be obtained when a catalytic system is in the electronic excited state. Additionally, we see that the primary cause of the decrease in excitation energy as a function of the reaction coordinate is the effective shift in bandgap of the system due to changing hybridization of the valence bands of TiO2 with the unoccupied H orbitals. These results confirm that barriers in the excited state PES can be significantly smaller than in the ground state and reveal that the excited state activation barriers are tunable via the hybridization of the catalyst’s surface states with the adsorbate.

11:15 AM NM03.11.03
Mediating Photoredox Cycloaddition Reactions of Enones Using Surface-Modified Metal Halide Perovskite Nanocrystal Catalyst Chen Wang and Jingheng Yuan; City University of New York, Queens College, United States

Cycloaddition reactions are employed to construct essential chemical motifs in multiple types of bioactive compounds. We utilize the excellent optical property of perovskite nanocrystals to efficiently sensitize these important reactions and explore surface chemistry approaches to control the chemo- and diastereoselectivity of reaction products. By modifying the surface ligand shell of cesium lead bromide perovskite nanocrystals ($CsPbBr_3$ PNCs), we obtained a stable photocatalyst that can effectively activate different cycloaddition reactions of enones. Time-resolved optical spectroscopic investigation reveals the reactions undergo a photoredox mechanism. The PNC sensitizes [2+2] cycloaddition resulting in a cyclobutyl motif by generating the triplet excited state of enones through photoinduced electron transfer followed by a charge recombination process. The kinetic information collected by transient absorption indicates that it is possible to preserve the anion radicals of enones by introducing appropriate sacrificial electron donors to compete with charge recombination from the PNC. Unlike the triplet excited state, these anion radicals serve as the intermediates for [1+4] cycloaddition and lead to products with cyclopentyl rings. In this specific scenario of photoredox reactions, the stability of our surface-modified PNCs surpasses conventional metal chalcogenide nanocrystals, such as CdSe, due to the fast hole removal ability. Our work demonstrates that metal halide PNCs are versatile photocatalysts for synthetic chemistry, and mediating photoredox processes can realize the selection of reaction pathways to yield different products.

SESSION NM03.12: Microscopy
Session Chairs: Lilac Amirav and Maria Wächtler
Thursday Afternoon, April 13, 2023
InterContinental, Fifth Floor, Ballroom A

1:30 PM *NM03.12.01
Scanning (Electrochemical) Probe Microscopy—Morphological and Activity Studies ofHeterogenized Photocatalytic Systems Eva Oswald, Andreas Hellmann, Giada Caniglia and Christine Kranz; Ulm University, Germany

Efforts towards carbon-neutral energy conversion and storage such as light-driven water splitting (*i.e.,* artificial photosynthesis), fuel cells, etc. require

understanding of processes that occur at interfaces. Usually, catalytic studies to determine the light-driven catalytic activity in homogenuous and heterogenous catalysis are performed at the bulk-level, *e.g.,* using head-space gas chromatography. Hence, insight into heterogeneities of molecule-in-matrix systems like active component distributions and with that information on variety in activity require spatially resolved measurements. Scanning electrochemical probe microcopy such as scanning electrochemical microscopy (SECM) and scanning electrochemical cell microscopy (SECCM) and hybrid SPM techniques are attractive not only in studying electrocatalysts [1,2] but also for activity screening of heterogenized molecular catalysts in light-driven water splitting [3]. Moreover, morphological changes associated with degradation processes can be studied.
In this contribution, an overview of the potential of SEPM techniques in light driven catalysis will be given ranging from nanoscale surface modifications like deposition of photocatalysts using SECCM to spatially resolved *in situ*determination of light-driven reaction intermediates and products such as hydrogen (H_2), oxygen (O_2) and hydrogen peroxide (H_2O_2) using miniaturized electrodes modified with electrocatalytic layers like as Prussian blue or Pd. Selected examples of heterogenized hydrogen evolution reaction (HER) and water oxidation catalysts (WOC) will be presented and challenges in these SEPM studies will be discussed.

Acknowledgement
Funding is acknowledged from the Deutsche Forschungsgemeinschaft (DFG – German Research Foundation) – project number 364549901 – TRR 234.

References
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[2] Y. Takahashi, et al., *Angew. Chemie Int. Ed.* **2020**, *59*, 3601-3608.
[3] E. Oswald et al, *Chem. Eur. J.* **2021**, *8*, 4475–4481.

2:00 PM NM03.12.02
Probing Surface Defects in Photocatalytic Materials Under Operando Conditions Raul Quesada-Cabrera[1,2]; [1]Universidad de Las Palmas de Gran Canaria, Spain; [2]UCL (University College London), United Kingdom

Vacancy engineering is widely explored as an efficient approach to drastically change the chemical and physical properties of functional materials. Oxygen vacancies (V_0) are perceived as some of the most reactive sites on a semiconductor surface, playing an important role in charge transport and charge trapping properties. Unfortunately, due to the inherent low concentrations and high reactivity of V_0, probing vacancy sites under *relevant* experimental conditions is challenging, with standard techniques requiring ultra-high vacuum conditions, cryogenic temperatures and/or ideal single-crystal surfaces. Such techniques are usually highly specialised and operate at the atomic scale, making it challenging to extrapolate any observation to microstructured materials for practical applications. It is thus critical to be able to gain information on the potential role and kinetics of V_0 in polycrystalline materials under *operando* conditions; particularly in areas where the formation of V_0 sites can greatly influence the material performance, such as photocatalysis and energy storage applications.

A few years ago, we developed a sensing technique based on surface-enhanced Raman spectroscopy, where the chemical contribution of semiconductor substrates was greatly enhanced upon formation of photon-induced surface V_0 sites (*photo-induced enhanced Raman spectroscopy* or PIERS). As a sensing tool, this effect relied on the interaction of plasmonic nanoparticles with V_0 sites at the semiconductor surface (**Nature Commun** 2016, 7, 12189). This discovery further allowed for the application of PIERS as a probing technique to evaluate atomic V_0 dynamics in metal oxide surfaces (**Adv. Sci.** 2019, 6, 1901841). In this case, we studied the formation and healing rates of surface-active V_0 in archetypical semiconductor photocatalysts, namely, TiO_2, WO_3, and ZnO. Contrary to conventional analytical tools, PIERS can provide intuitive and valuable information on the surface stability of atomic defects at ambient pressure and under operando conditions. Further insight into the charge transport properties on photon-induced defected metal-oxide surfaces has been recently sought using advanced time-resolved atomic force microscopy (AFM) techniques (**Nano Letters** 2021, 21, 19, 8348).

The implications of these results will be challenged and proposed as a lab-based approach to investigate the impact of defect sites in the photocatalytic performance of advanced materials with potential application in emerging (*solar*) technologies.

2:15 PM NM03.12.03
Real-Time Study of Surface-Guided Nanowire Growth by *In Situ* Scanning Electron Microscopy Amnon Rothman[1], Kristýna Bukvišová[2,2], Noya R. Itzhak[1], Ifat Kaplan-Ashiri[1], Anna E. Kossoy[1], Xiaomeng Su[1], Libor Novák[3], Tomáš Šikola[2,2], Miroslav Kolíbal[2,2] and Ernesto Joselevich[1]; [1]Weizmann Institute of Science, Israel; [2]Brno University of Technology, Czechia; [3]Thermo Fisher Scientific, Czechia

Surface-guided growth has proven an efficient approach for the production of nanowire arrays with controlled orientations and their large-scale integration into electronic and optoelectronic devices. Much has been learned about the different mechanisms of guided nanowire growth by epitaxy, graphoepitaxy and artificial epitaxy. A model describing the kinetics of surface-guided nanowire growth has been recently reported. Yet, many aspects of the surface-guided growth process remain unclear due to a lack of its observation in real-time. In this study we observe how surface-guided nanowires grow in real-time by *in situ* scanning electron microscopy (SEM). Movies of ZnSe surface-guided nanowires growing on periodically faceted substrates of annealed M-plane sapphire clearly show how the nanowires elongate along the substrate nanogrooves while pushing the catalytic Au nanodroplet forward at the tip of the nanowire. The movies reveal the timing between competing processes, such as planar vs nonplanar growth, catalyst-selective vapor-liquid-solid elongation vs nonselective vapor-solid thickening, and the effect of topographic discontinuities of the substrate on the growth direction, leading to formation of kinks and loops. Contrary to some observations for nonplanar nanowire growth, planar nanowires are shown to elongate at a constant rate and not by jumps. Decrease in precursor concentration as it is consumed after long reaction time, causes the nanowires to shrink back instead of growing, thus indicating that the process is reversible and takes place near equilibrium. This real-time study of surface-guided growth, enabled by *in situ* SEM, enables a better understanding of the formation of nanostructures on surfaces.

SESSION NM03.13: Virtual Session I
Session Chairs: Lilac Amirav, Klaus Boldt, Matthew Sheldon and Maria Wächtler
Wednesday Morning, April 26, 2023
NM03-virtual

8:00 AM *NM03.13.01
Modifying the Bi-Based Photocatalysts with Nanosized Metal Particles for Improved Catalytic Performances Ziyi Zhong[1], Yibing Song[2] and

Chenchen Zhang[1]; [1]Guangdong Technion Israel Institute of Technology, China; [2]Shantou University, China

Semiconductor photocatalysts have great potential applications in solar energy conversion and environmental purification [1-3]. However, most of them mainly work in the ultraviolet region due to their wide band gap. Bismuth oxyhalides, BiOX (X = Cl, Br and I), an important class of V–VI–VII ternary oxide semiconductors, show the improved property in separating photoinduced electron-hole pairs due to their layered structures [2]. However, their response is still limited to only ultraviolet (UV) in the solar spectrum, leading to low light utilization efficiency and, finally, low photocatalytic activity [4-5]. To address these issues, we modified the Bi-based catalysts with nanosized metal particles to improve their photocatalytic properties.
In the BiOI/TiO_2 system, we first generated metallic Bi nanoparticles in situ between the supported BiOI and TiO_2 support using the oxygen vacancies in the TiO_2 nanosheets. The theoretical and experimental results confirmed the reaction of the electron-rich oxygen vacancies in the 2D-TiO_2 nanosheets (TiO_2-NS) with the adsorbed BiO+ species, which broke the Bi-O bonds to form Bi0 nanoparticles in situ at the interface but still maintained the p-n heterojunction well. The existence of the Bi^0 nanoparticles allows electron transfer like that in the Z-scheme mechanism, enabling the effective separation and higher redox ability of photogenerated charge carriers. The formed BiOI/Bi/TiO_2 catalyst was used for Rhodamin B (RhB) photodegradation and achieved a much improved catalytic performance, i.e., duplicated apparent quantum yield (AQY) and triplicated reaction rate constant in the oxidation of Rhodamin B (RhB), was obtained [6].
For the 3D-BiOCl catalyst system, we modified the 3D-BiOCl hierarchical structure with Au particles (Au NPs) to obtain the Au/3D-BOC photocatalyst. The catalyst was used for CO_2 reduction, which was coupled with the selective benzyl alcohol (BA) oxidation to enhance the former reduction. After this modification, the reactive sites for photocatalytic CO_2 reduction changed from 3D-BOC to Au NPs, and the interaction between Au NPs and 3D-BOC could accelerate the electron transfer and the separation of carriers to prolong their lifetime further and adjust the band structure, which is beneficial to improve the redox ability of photogenerated carriers. Also, an enhanced light absorption efficiency was observed. As a result, the 1.0%Au/3D-BOC catalyst produced 94.2 µmol g^{-1} h^{-1} CO from CO_2 and converted 46.8% BA with a 99% selectivity to the high-value benzaldehyde (BAD) product.
These results provide new insights into the photocatalysis of Bi-based photocatalysts and feasible ways to improve their catalytic performances.

8:30 AM NM03.13.02

Hot Electron Driven Photocatalysis on Plasmon-Resonant Grating Nanostructures Steve Cronin; Univ of Southern California, United States

Understanding the relaxation and injection dynamics of hot electrons is crucial to utilizing them in photocatalytic applications. While most of the studies focused on hot carrier dynamics at various metal/semiconductor interfaces, we study the *in situ* dynamics of direct hot electron injection from metal to chemical adsorbates during photoelectrochemical reactions. Here, we report hot electron driven photocatalysis and ultrafast dynamics by exciting the localized surface plasmon resonance (LSPR) in Au grating photoelectrodes. *In situ* ultrafast pump-probe transient absorption (TA) measurements are used to study the dynamics of hot electrons when driving the hydrogen evolution reaction (HER). Here, a positive modulation of the absorption in the TA spectra corresponds to the interband transitions and a depletion peak results from LSPR-induced hot electrons. The extracted electron-phonon interaction time from LSPR bleaching decreases from 0.94 ps to 0.67 ps when the sample is immerged in 0.5 M Na_2SO_4 solution under -1 V applied potential due to extra energy dissipation channels. In aqueous electrolyte, the LSPR signal is red-shifted with delay time due to charge transfer between the metal surface and adsorbates' lowest unoccupied molecular orbital (LUMO) states and subsequent change of dielectric constant of nearby water environment. In contrast, when the grating is optically excited in air, the LSPR signal is blue-shifted with time, as the pump-induced hot electrons cool through electron-phonon scattering. Plasmon resonant enhancement of the photoelectrochemical current (up to 15.6X) was also observed on these gratings when irradiated on resonance, as produced by hot electrons generated from LSPR dephasing (i.e., damping). Here, hot electrons are transferred from metal surface states to adsorbates' LUMO states by chemical interface damping or chemical interface scattering, and no peak is observed when light is s-polarized (electric field parallel to grating lines), in which there is no coherent oscillation of electrons. By changing the polarization of the incident light, we can distinguish processes driven by hot electrons from those driven by interband transitions. Plateau-like peaks appear when exciting a 266nm-linewidth grating with monochromatic light between 3.6° and 9.0° incident angles, and a similar profile is observed in the measured absorptance. In addition, double peaks (6.7° and 8.4°) in the photocurrent measurement are observed when irradiating a 300nm-linewidth grating. The enhancement factor (i.e., reaction rate) is 15.6X between p-polarized (resonant) and s-polarized (non-resonant) light for 300nm-linewidth grating and 4.4X for 266nm-linewidth grating. Finite difference time domain (FDTD) simulations show two resonant modes for both grating structures, one corresponding to a dipolar LSPR mode at the Au/fused silica interface and the other on the metal surfaces away from the fused silica substrate.

1."In Situ Investigation of Ultrafast Dynamics of Hot Electron-Driven Photocatalysis in Plasmon-Resonant Grating Structures" Yu Wang, Yi Wang, Indu Aravind, Zhi Cai, Lang Shen, Boxin Zhang, Bo Wang, Jihan Chen, Bofan Zhao, Haotian Shi, Jahan M. Dawlaty, and Stephen B. Cronin. Journal of the American Chemical Society. 144, 8, 3517–3526 (2022)

2. "Hot Electron Driven Photocatalysis on Plasmon-Resonant Grating Nanostructures" Yu Wang, Indu Aravind, Zhi Cai, Lang Shen, George N. Gibson, Jihan Chen, Bo Wang, Haotian Shi, Boxiang Song, Ernest Guignon, Nathaniel C. Cady, William D. Page, Arturo Pilar, and Stephen B. Cronin. ACS Applied Materials & Interfaces, 12, 17459-17465 (2020).

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8:45 AM NM03.13.04

NIR-Responsive Metal-Free Multifunctional GQDs/Phosphorus-Doped g-C3N4 Composite for Starving Strategized Photodynamic Chain Therapy
Xichu Wang; University of New South Wales, Australia

NIR-responsive carbon nanocatalyst which combines glucose consumption and reactive oxygen species (ROS) generation is engineered to develop a chain reaction strategy for cancer starvation and photodynamic synergistic therapy. Graphene quantum dots and carbon nitride composite can cut off the energy supply by catalyzing glucose decomposition and producing H_2O_2 in response to NIR light at the targeted tumor area. Upon irradiation, visible light emitted by upconversion-functional GQDs part to carbon nitride, photolyzed glucose into H_2O_2, bursting the hydroxyl radical generation from the decomposition of hydrogen peroxide. The generated ROS serves as the cancer-killing weapon, resulting in excellent anticancer effects, as evidenced by in vitro and in vivo studies. For the first time constructed for cancer starving/photodynamic chain therapy, which yields a remarkable anticancer effect with minimum side effects at ultralow NIR light intensity.

9:00 AM *NM03.13.05

Nano-, Micro- and Macrostructuring of Multicomponent Aerogels from Nanocrystals Nadja C. Bigall[1,2]; [1]Leibniz Universität Hannover, Germany; [2]Cluster of Excellence PhoenixD (Photonics, Optics, and Engineering – Innovation Across Disciplines), Germany

Nanocrystal aerogels and solvogels are macroscopic assemblies which which exhibit extremely low densities and good accessibility of their large specific surfaces. When employing colloidally synthesized nanocrystals as building blocks, a high degree of control over size, shape and facets, as well as over the surface chemistry, composition, and hence, over the nanoscopic properties, can be exploited for such macroscopic gel materials. Additionally, depending on the nanoscopic and microscopic architecture of these networks, macroscopic gel monoliths with either the properties of the nanoparticles, or with even new collective properties can be yielded. Therefore, finding routes for nano- micro- and macrostructuring in especially multicomponent nanocrystal-based gels paves the way to distinct material properties.
As an example, gels from metal and semiconductors or from various semiconductors etc. benefit from controlling their network architecture which strongly influences the physicochemical properties with possible future applications in electrocatalysis and photocatalysis as well as in sensing, amongst others.
Here, we present our recent advances in structure-property-correlation as well as on synthetic approaches regarding nano, micro- and macrostructuring of nanocrystal-based gels.[1]

[1] Control over Structure and Properties in Nanocrystal Aerogels at the Nano-, Micro-, and Macroscale, Pascal Rusch, Dániel Zámbó, Nadja C. Bigall, Acc. Chem. Res. 2020, 53, 10, 2414–2424, https://doi.org/10.1021/acs.accounts.0c00463

SESSION NM03.14: Virtual Session II
Session Chairs: Lilac Amirav, Klaus Boldt, Matthew Sheldon and Maria Wächtler
Thursday Morning, April 27, 2023
NM03-virtual

8:00 AM *NM03.14.01
Harnessing Ultrafast Hot Carrier Dynamics in Perovskite Nanocrystals Peng Zeng[1], Xiaochun Liu[1], Xinjian Ren[1], Klaus Boldt[2], Trevor Smith[3] and Mingzhen Liu[1]; [1]University of Electronic Science and Technology of China, China; [2]Universität Konstanz, Germany; [3]The University of Melbourne, Australia

Rapid cooling of photoinduced carriers with excess energy above the bandgap, or hot carriers (HCs), is one of the major energy loss channels in current photovoltaics/photocatalysis applications. These processes are receiving intense interest following the triumph of the perovskite-based photoelectronic and photonic devices. The emergence of all inorganic $CsPbX_3$ (X=I, Br, Cl) perovskite nanocrystals (PeNCs) have again revived the hot-carrier-based applications for their relatively long hot carrier relaxation process. However there still remains demand for the longer hot-carrier relaxation process that is more favorable for maintaining a long time window for harvesting the excess energy from the hot electronc prior to being scattered by phonons. Concurrently it has been revealed that the relaxation is mostly mediated by the carrier-phonon coupling (CPC) interaction, in which hot carriers relax to band states mainly via emission of phonons. One straightforward approach is to suppress CPC in order to reduce longitudinal optical (LO) phonon emission that will slow the HC cooling accordingly. So far the PeNC community is still lacks an insightful investigation of a method for the direct control of the CPC and subsequently the HC cooling process. One may expect sizeor component-dependent CPC strengths, and indeed some works so far have revealed such a dependence in $CsPbX_3$ NCs. However, size- and/or component-control is not feasible for applications that require specified optical properties of NCs and usually either size or component need to be maintained. By thinking outside the (particle-in-a-)box, surface ligands in the NC system may provide a way by which the CPC can be tuned.
In this talk, we raise the question in what ways ligands affect the CPC interaction and subsequently the hot carrier relaxation. We model the ligand as a damper in an oscillation model that describes the electron-LO phonon coupling. The model predicts a mechanical damping effect on the CPC strength by the resistance of surface ligands against the lattice vibrations. Different capping ligands may possess different stiffness or rigidity that results in a varied damping effect. We accordingly applied (3-aminopropyl)triethoxysilane (APTES) ligands which form a thin polysiloxane layer wrapping $CsPbBr_3$ PeNCs. We find a significantly slowed HC cooling process (more than 3-fold slower) in the polysiloxane-capped $CsPbBr_3$ NCs in comparison to conventional long alkyl chain oleylamine (OAm) ligands (OAm-$CsPbBr_3$), using ultrafast transient absorption spectroscopy. We attribute the retarded HC cooling process to the suppressed CPC process caused by the cross-linked APTES, and provide evidence for the weak CPC strength in the APTES-$CsPbBr_3$ through cryogenic PL spectroscopy measurements. Our model also successfully rationalizes the linear temperature dependence and the difference of CPC strength in two samples.
Our work confirms the crucial role of the surface ligands in the CPC of perovskite NCs, and provides a way of controlling the HC cooling process. From a wider perspective, our fundamental understanding of the CPC will lead to both theoretical interest and practical inspiration to the perovskite community of future optoelectronic and photonic applications of the PeNCs.
This talk also summarizes our recent works on interfacial charge separation processes occuring for $CsPbBr_3$ PeNCs. We will also present an interesting finding of instaneous plasmonic-induced charge carrier transfer in bulk gold-$CsPbBr_3$-layered-heterostructures. This leads to efficient charge separation at metal/perovkite interface even using low photon energy excitation, which we believe is of great potentials in future hot-carrier applications.

8:30 AM NM03.14.02
Porous TiO_2 Fibres Loaded with Plasmonic Au Nanoparticles for Water Treatment Shiling Dong[1], George Tebbutt[1], Barbara Maciejewska[1] and Nicole Grobert[1,2]; [1]University of Oxford, United Kingdom; [2]Williams Advanced Engineering Limited, United Kingdom

Facing the global shortage of clean water, photocatalytic degradation is one of the greenest technologies to decompose the organic pollutants in wastewater. Over the past decades, TiO_2 has been the most popular photocatalytic material. Upon light irradiation, it generates highly reactive free radicals that can inactivate the microorganisms and mineralize the organic matter. However, there are factors limiting overall photocatalytic efficiency, mainly, the narrow visible-light photoresponse due to wide band gap, and the limited quantum yield due to the rapid recombination of charge carriers. More importantly, although TiO_2 nanopowder demonstrates high photocatalytic reactivity, it is difficult to be removed and recycled from water suspension, therefore, not suitable for applying in large-scale water treatment.
To address the identified issues, we developed highly porous TiO2 fibers coupled with plasmonic Au nanoparticles (NPs). We synthesized TiO_2 fibers by electrospinning from solution containing TiO_2 precursor and calcining the precursor fibres at high temperature. Cu ions were doped into TiO_2 lattice to reduce the bandgap from 3.22 eV to 2.89 eV, thus extending the photosensitive light wavelength from 385 to 430 nm. We are the first to engineer the porous structure by combining the previously reported strategies for producing mesoporous TiO2 fibers, e.g., use surfactant and control the crystallization, with a sacrificial polymer template method, in which the thermal decomposition of polymer particles creates homogenously distributed macropores. New science has been overserved in the synergetic effects of these two strategies in manipulating the porous structure of ceramic fibres.

The porous TiO_2 fiber is an ideal host for anchoring noble metal NPs to form Schottky heterojunctions. In our study, we create plasmonic Au NPs/TiO_2 fibres that show doubled photocatalytic efficiency in the photodegradation of two types of organic dyes, methyl blue and methyl orange, compared to bare TiO_2 fiber. We focus on understanding the localized surface plasmon resonance of Au NPs in enhancing the photocatalytic activities of TiO_2 fiber in terms of the overlapping of absorption band and the enhanced localized light intensity. Furthermore, our Au NPs/TiO_2 fibres could also be easily filtered out from water and reused for at least six times without losing the efficiency, therefore, showing great potential for degradation of organic pollutants in large-scale water treatment.

8:45 AM NM03.14.03
Hydrogenated Tantalum Nitride a Novel Photocatalyst for Enhanced Hydrogen Evolving Performance Mrinalini Mishra[1] and Tsong-Pyng Perng[2]; [1]Sustainability Science and Engineering Program International College, Tunghai University, Taiwan; [2]National Tsing Hua University, Taiwan

Solar-driven water splitting via semiconductor photocatalysts is a promising alternative in energy carriers in terms of clean, sustainable, and abundant energy sources. In recent times, tantalum-based (oxy-)nitride materials are being extensively explored due to their small bandgaps and favorable band edge positions for overall water splitting. The theoretical solar to hydrogen (STH) conversion rate for tantalum nitride (Ta_3N_5) is 16%. However, practically such high activity has not yet been reported. Previously, we investigated the photocatalytic efficiency of hydrogenated oxides like TiO_2 and ZnO. Hydrogenation induces surface and/or bulk defects depending on the condition of H_2 treatment. The surface defects act synergistically in improving the electrons and hole transport in oxide photocatalysts. However, the repercussions of hydrogenation on nitride semiconductors have seldom been studied.
In this work, Ta_3N_5 thin films were fabricated on Si wafer by 400 cycles of atomic layer deposition and were crystallized at 800 °C in NH_3. The crystalline films were hydrogenated at 300-500 °C under 20 bar H_2 for 30-120 min. Water splitting efficiencies of the treated and untreated Ta_3N_5 films were then evaluated under 300 W Xe lamp. Hydrogenation at 300 °C for 30 min resulted in a shift of X-ray diffraction (XRD) peaks towards higher angles, suggesting a contraction of the lattice and enhanced H_2 generation as compared to untreated Ta_3N_5. Whereas hydrogenation at 500 °C for 30 min exhibited XRD peak shift towards lower angles and the H_2 generation deteriorated severely. To further elucidate the effect of hydrogenation, the samples were also characterized by photoluminescence spectroscopy, ultraviolet photoelectron spectroscopy, valence band X-ray spectroscopy, atomic force microscopy, and Raman analysis

9:00 AM NM03.14.04
Synthesis and Characterization of a Carbon Nanodot-Cobalt Oxide Nanohybrid Anuoluwapo Anele[1], Sherine Obare[1,2] and Jianjun Wei[1]; [1]University of North Carolina, Greensboro, United States; [2]North Carolina A and T State University, United States

Carbon nanodots are a novel class of nanocarbons with fluorescent capabilities which conform to a size less than 10 nm. They have desirable properties such as their photoluminescence, solubility, electronic, photocatalytic, optical properties, and ease of functionalization. Cobalt oxide nanoparticles are metal oxides that have unique structural, chemical, physical, magnetic and optical properties making them useful for several applications such as energy storage, and catalysis. Synthesis of cobalt oxide and carbon nanodots include methods such as the arc-discharge method, laser ablation method, electrochemical method, thermal pyrolysis, hydrothermal method, casting, chemical reduction, co-precipitation, ionic liquid-assisted approach, irradiation, microemulsion, sol-gel approach, solvothermal approach, template method, and vapor deposition approach. Some of these methods of synthesis of carbon nanodots and cobalt oxide employ harsh temperatures and/or require longer reaction time for synthesis. The low toxicity of carbon nanodots coupled with its high solubility could also help improve on the same properties of cobalt oxide. In this research, we present a two-step microwave assisted synthesis of a novel cobalt oxide-carbon nanodot hybrid synthesized in reduced time and a cleaner way. This nanohybrid possesses enhanced optical properties compared to carbon nanodots alone. Structural properties of this nanohybrid are also presented. This nanohybrid could be applicable for several environmental and biological applications such as remediation, catalysis, bioimaging, sensor detection and drug delivery.

9:05 AM *NM03.14.06
Charge Transport Calculations Through Nanomaterial Interfaces Maytal Caspary Toroker; Technion-Israel Institute of Technology, Israel

Interfaces have long been studied for their fundamental importance in material microstructure as well as their broad applicability in electronic devices. However, the challenge involved in characterizing the relation between structure and electron transport of a large number of interface combinations inhibits the search for interfaces with improved functionality. Therefore, we develop a novel high-throughput screening approach that combines computational and theoretical techniques. We use a Density Functional Theory + U (DFT+U) quantum mechanical formalism to produce effective Schroedinger equations, which are solved by wave packet propagation to simulate charge transport across the metal/oxide interface. We demonstrate this method on nanomaterials, including molybdenum disulfide with vacancies interfacing with metals and dielectric materials.

This research is relevant for the activities in COST Action CA18234 titled “Computational Materials Sciences for efficient water splitting with nanocrystals from earther abundant elements”. This COST Action intends to focus on bridging the knowledge gaps between different theoretical methods and computer codes in order to facilitate the discovery of novel materials for energy conversion. The objectives of this challenge include building an organized network of European scientists working on achieving greater scientific understanding of water splitting and developing approaches for reliable and realistic multi-scale modelling of nano-oxides material architectures. I will display the networking activities and opportunities that are available by joining our COST Action.

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SYMPOSIUM

April 11 - April 26, 2023

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* Invited Paper
\+ Distinguished Invited

SESSION NM04.01: Advanced Manufacturing of 2D Materials at the Atomic Scale I

Session Chairs: Wenpei Gao and Chenglin Wu
Tuesday Morning, April 11, 2023
InterContinental, Fifth Floor, Ballroom B

10:30 AM *NM04.01.01
Towards Controlled Synthesis and Scalable Manufacturing of 2D Crystals Jun Lou; Rice University, United States

The emergence of two-dimensional (2D) materials has captured the imagination of researchers since graphene was first exfoliated from graphite in 2004. Their exotic properties give rise to many exciting potential applications in advanced electronic, optoelectronic, energy and biomedical technologies. Scalable growth of high quality 2D materials is crucial for their adoption in technological applications the same way the arrival of high-quality silicon single crystals was to the semiconductor industry. A huge amount of effort has been devoted to grow large-area, highly crystalline 2D crystals such as graphene and transition metal dichalcogenides (TMDs) through various methods.
While CVD growth of wafer-scale monolayer graphene and TMDs has been demonstrated, considerable challenges still remain. In this talk, we first advocate for the focus on the crystal growth morphology as an underpinning for understanding, diagnosing and controlling the CVD process and environment for 2D material growth. Like snowflakes in nature, 2D crystals exhibit a rich variety of morphologies under different growth conditions. The mapping of crystal shapes in the growth parameter space “encodes” a wealth of information, the deciphering of which will lead to better understanding of the fundamental growth mechanism and materials properties. However, the morphology pattern evolution of 2D crystals such as MoS_2 monolayers under a practical CVD growth condition is highly complicated due to the entanglement of multiple growth factors. The ability to directly monitor it in real-time would be substantial to provide first-hand data to lay the groundwork for most advanced tools such as machine-learning to unravel those threads. A customized system with the function of observing and recording the CVD growth of MoS_2 in a miniature furnace is developed in this work. Image processing techniques are utilized to convert the real-time growth footage into frame-wise digital numbers and machine-learning is deployed to uncover the importance of multiple controlling factors in the growth. The model successfully guides the discovery of experimental control parameters to grow ultra-large size MoS_2monolayers. The model also demonstrates the possibility to trace back experimental condition by analyzing the crystal morphology parameters. In a parallel effort, we also demonstrate that the widely used powder-processing technique of dry ball-mill, can be improved to produce high-quality 2D flakes in large scale and with low cost. Seventeen types of commonly seen polymers, including both artificial and natural ones, have been examined as additive to dry ball-mill of hexagonal boron nitride. The potential of polymer-assisted ball-mill exfoliation as a universal way to produce ultra-thin 2D nanosheets is also demonstrated.

11:00 AM NM04.01.02
Effect of Substitutional Oxygen on Properties of $Ti_3C_2T_x$ MXene synthesized from TiO_2 Precursor Aamir Iqbal[1], Hyerim Kim[2], Jung-Min Oh[3], Yury Gogotsi[4], Hanjung Kwon[5] and Chong Min Koo[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of); [3]Innomxene, Korea (the Republic of); [4]Drexel University, United States; [5]Jeonbuk National University, Korea (the Republic of)

MXenes are an emerging class of 2D materials with unique properties including excellent metallic conductivity, mechanical flexibility, hydrophilicity, and tunable surface functionality, which ensure their utility for diverse applications. However, the synthesis of stoichiometric MXenes with high quality in a low-cost process is still challenging because of the difficulty in controlling the oxygen substitution in the precursors and final products of MXenes. Here, we report a novel cost-effective method to synthesize $Ti_3C_2T_x$ MXene with controlled contents of substitutional oxygen by optimizing the amount of excess carbon in carbothermal reduction of TiO_2 precursor. The highest used content (2 wt.%) of excess-carbon yields TiC with minimal oxygen substitutes, which leads to Ti_3AlC_2 MAX phase with improved crystallinity and stoichiometry, and, finally, $Ti_3C_2T_x$ MXene with a high electrical conductivity (>11700 S cm^{-1}) and superior electromagnetic shielding effectiveness. Additionally, the effects of substitutional oxygen on the physical properties of TiC, and Ti_3AlC_2 are elucidated by density-functional theory calculations. This TiO_2-based method of synthesizing high-quality $Ti_3C_2T_x$ MXene substantially lowers the material cost and can facilitate large-scale manufacturing, thus accelerating global research on MXenes and their introduction into industrial products.

11:15 AM NM04.01.03
Synthesis of Quantum-Confined Borophene Nanoribbons Qiucheng Li[1], Luqing Wang[1], Hui Li[1], Maria K. Chan[2] and Mark C. Hersam[1]; [1]Northwestern University, United States; [2]Argonne National Laboratory, United States

Borophene refers to synthetic two-dimensional (2D) boron, which has attracted significant attention due to its anisotropic metallicity, correlated electron phenomena, and diverse superlattice structures.[1] Reducing the dimensionality of nanomaterials imposes additional quantum confinement effects that unlock new physical phenomena, such as one-dimensional (1D) confined plasmons, spin-polarized edge states, and Luttinger liquid behavior. However, the realization of quantum-confined borophene nanoribbons (BNRs) is hampered by limited boron precursor options for bottom-up synthesis. In this work, we present a substrate mediation strategy to synthesize quantum-confined BNRs on vicinal Ag(977) substrates. The resulting BNRs inherit the high degree of polymorphism present in borophene, resulting in $v_{1/5}$ and $v_{1/6}$-BNR lattice configurations in addition to phase intermixing.[2] Through atomic-scale imaging, spectroscopy, and first principles calculations, the edge structures of BNR polymorphs are shown to possess reconstructed armchair edges for $v_{1/6}$-BNRs and sawtooth zigzag edges for $v_{1/5}$-BNRs. The confined electron wave functions in 1D BNRs lead to the observation of energy level quantization and spatial nodes characteristic of quantum-well states.

Acknowledgement:
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11:30 AM NM04.01.04
Interlayer Coupling and Strain Localization in Twisted Bilayer 2D Materials Rui Huang[1], Ganbin Chen[1], Vahid Morovati[2] and Kenneth M. Liechti[1]; [1]The University of Texas at Austin, United States; [2]University of Connecticut, United States

Twisted bilayer 2D materials exhibit a wide range of intriguing physical properties, such as superconductivity, ferromagnetism, and superlubricity. Depending on the twist angle, periodic moire superlattices form in twisted bilayer graphene, with inhomogeneous interlayer coupling and lattice deformation. For a small twist angle, each moire supercell contains a large number of atoms (>10,000), making it computationally expensive for first-principles and atomistic modeling. In this work, a finite element method based on a continuum model is used to simulate the inhomogeneous interlayer and intralayer deformations of twisted bilayer graphene and MoS2. The van der Waals interactions between the 2D layers are described by a periodic potential energy function, whereas each 2D layer is treated as a continuum membrane with effective elastic properties. Our simulations show that structural relaxation and the induced strain localization are most significant at small twist angles, where the strain distribution is highly localized as shear strain solitons along the boundaries between neighboring domains of commensurate AB stacking. Moreover, it is found that there exist many metastable equilibrium configurations at particular twist angles, depending on the specimen size. The nonlinear mechanics of twisted bilayer 2D material is thus expected to be essential for understanding the strain distributions in the moire superlattices and the strain effects on other physical properties.

SESSION NM04.02: Advanced Manufacturing of 2D Materials at the Atomic Scale II
Session Chairs: Wenpei Gao and Chenglin Wu
Tuesday Afternoon, April 11, 2023
InterContinental, Fifth Floor, Ballroom B

1:30 PM *NM04.02.01
Direct Atomic Assembly and Physics Studies of Defects and Artificial Molecules in 2D Materials via Electron Beam Sergei Kalinin and Kevin Roccapriore; The University of Tennessee, Knoxville, United States

Direct fabrication of matter on atomic level is the North Star goal for areas spannign quantum computing, quantum communications, biological sensing, and fundamental physical research. Over the last decade, it has been shown that electron beams in Scanning Transmission Electron Microscopy can be used not only to probe structure and electronic properties of materials on atomic level, but also to modify materials on the atomic level. Harnessing electron beam changes for direct atomic farication however requires synergy between machine learning methods and microscope control. In this presentation, I will illustarte the progression of automated electron microscopy from real-time data analysis to physics discovery to atomic manipulations. Here, the applications of classical deep learning methods in streaming image analysis are strongly affected by the out of distribution drift effects, and the approaches to minimize though are discussed. The robust approach for real-time analysis of the scanning transmission electron microscopy (STEM) data streams, based on the ensemble learning and iterative training (ELIT) of deep convolutional neural networks, is implemented on an operational microscope, enabling the exploration of the dynamics of specific atomic configurations under electron beam irradiation via an automated experiment in STEM. Combined with beam control, this approach allows studying beam effects on selected atomic groups and chemical bonds in a fully automated mode. We demonstrate atomically precise engineering of single vacancy lines in transition metal dichalcogenides and the creation and identification of topological defects graphene. The ELIT-based approach opens the pathway toward the direct on-the-fly analysis of the STEM data and engendering real-time feedback schemes for probing electron beam chemistry, atomic manipulation, and atom by atom assembly. We further illustarte how deep kernel learning (DKL) methods allow to realize both the exploration of complex systems towards the discovery of structure-property relationship, and enable automated experiment targeting physics (rather than simple spatial feature) discovery. The latter is illustrated via experimental discovery of the edge plasmons in STEM/EELS. Jointly, these developments open the pathway for creation and characterization of designed defect configurations and artificial molecules in 2D materials.

2:00 PM NM04.02.02
A General Fruit Acid Chelation Route for Eco-Friendly and Ambient 3D Printing of Metals Soo Young Cho[1], Dong Hae Ho[2], Yoon Young Choi[3], Dong Gue Roe[1], Yonghyun A. Kwon[1], InCheol Kwak[1], Seonkwon Kim[1], Jung Woo Moon[1], Seonmi Eom[1], Sae Byeok Jo[4] and Jeong Ho Cho[1]; [1]Yonsei University, Korea (the Republic of); [2]Virginia Tech, United States; [3]University of Illinois at Urbana-Champaign, United States; [4]Sungkyunkwan University, Korea (the Republic of)

Recent advances in metal additive manufacturing (AM) have provided new opportunities for prompt designs of prototypes and facile personalization of products befitting the fourth industrial revolution. In this regard, its feasibility of becoming a green technology, which is not an inherent aspect of AM, is gaining more interests. A particular interest in adapting and understanding of eco-friendly ingredients can set its important groundworks. Here, we demonstrate a water-based solid-phase binding agent suitable for binder jetting 3D printing of metals. Sodium salts of common fruit acid chelators form stable metal-chelate bridges between metal particles, enabling elaborate 3D printing of metals with improved strengths. Even further reductions in the porosity between the metal particles are possible through post-treatments. A compatibility of this chelation chemistry with variety of metals is also demonstrated. The proposed mechanism for metal 3D printing can open up new avenues for consumer-level personalized 3D printing of metals.

2:15 PM NM04.02.03
Emergent Moiré Phonons Due to Zone Folding in WSe_2-WS_2 van der Waals Heterostructures Hsun Jen J. Chuang[1], Madeleine Phillips[1], Kathleen M. McCreary[1], Darshana Wickramaratne[1], Matthew R. Rosenberger[2], Vladimir P. Oleshko[3], Nicholas Proscia[1,4], Mark Lohmann[1,5], Dante J. O'Hara[1], Paul D. Cunningham[1], C. Stephen Hellberg[1] and Berend Jonker[1]; [1]Naval Research Lab, United States; [2]University of Notre Dame, United States; [3]National Institute of Standard and Technology, United States; [4]NRC, United States; [5]American Society for Engineering Education, United States

Bilayers of 2D materials offer unique opportunities for creating devices with tunable electronic, optical, and mechanical properties. In van der Waals heterostructures (vdWHs), where the constituent monolayers have different lattice constants, aligned bilayers foster a superlattice moiré length scale that is larger than the lattice constant of either constituent material. Here, we report new Raman modes in WSe_2-WS_2 vdWHs in the range of 240-260 cm^{-1}, which are absent in both monolayers and homobilayers of WS_2 and WSe_2. Using first-principles calculations and geometric arguments we show that these new modes are a consequence of the large moiré length scale, which results in zone-folded phonon modes that are Raman active. These modes are sensitive to changes in twist angle, but notably, they occur at identical frequencies for a given small twist away from either the 0-degree or 60-degree aligned heterostructure. Our measurements also show that the Raman intensity in the frequency range of interest, which includes both the new Raman modes and the WSe_2 A_{1g} peak, exhibits a markedly different dependence on excitation energy in near-0 vs. near-60 degree vdWHs. Temperature-dependent reflectivity measurements demonstrate the significant Raman intensity modulation arises from resonant Raman effects

2:30 PM NM04.02.04
Adhesive Matrix Transfer for Direct van der Waals Integration of Two-Dimensional Materials into Functional Devices Peter Satterthwaite[1], Weikun Zhu[1], Patricia Jastrzebska-Perfect[1], Melbourne Tang[1], Hongze Gao[2], Hikari Kitadai[2], Ang-Yu Lu[1], Qishuo Tan[2], Jing Kong[1], Xi Ling[2] and Farnaz Niroui[1]; [1]Massachusetts Institute of Technology, United States; [2]Boston University, United States

Pristine van der Waals (vdW) interfaces between two-dimensional (2D) and other materials are essential for emerging optical and electronic devices. Their fabrication is, however, challenged by weak vdW forces that are constrained by the intrinsic material properties and hence not readily tunable to accommodate formation of arbitrary heterostructures. Conventional techniques overcome this limitation by facilitating transfer using sacrificial layers, solvents and high temperatures, steps which could introduce damage and contaminants. In addition, often, post-transfer fabrication steps are required for device integration, which could further introduce damage. An ideal fabrication approach would accommodate a single-step 2D material-to-device integration.

To realize such a platform, here, we present the adhesive matrix transfer approach. This approach enables sacrificial layer-free, dry, and pristine fabrication of arbitrary vdW interfaces, and their integration into functional devices. Core to this approach is decoupling the vdW forces defining the interface of interest from the forces responsible for 2D material transfer. This is achieved by embedding the substrate of interest in a matrix whose surface adhesive forces can be independently tuned to allow for the transfer of arbitrary layers. With this approach we have demonstrated conventionally forbidden, direct vdW integration of diverse 2D materials, including MoS_2, WSe_2 and GaS, with bulk dielectrics (SiO_2, Al_2O_3), core building blocks of functional devices. We use this technique to then demonstrate single-step integration of 2D materials into devices, using an example of arrays of monolayer-MoS_2 transistors. With no exposure to polymers and solvents, our approach enables clean interfaces and pristine surfaces with reduced fermi-level pinning, which can be further engineered to demonstrate high-quality n- and p-type behavior. Beyond serving a platform to probe intrinsic properties of 2D and other sensitive nanomaterials without the influence of processing steps, our fabrication technique further allows efficient formation of devices with unconventional form-factors, here we discuss its application in 2D flexible electronics.

2:45 PM NM04.02.05
Spectroscopic Characterization of Buried 2D-3D Interfaces Enabled by Novel Polymer-Free Transfer Technique Christopher M. Smyth, John M. Cain, Alex M. Boehm, Stanley Chou, Taisuke Ohta and Tzu-Ming Lu; Sandia National Laboratories, United States

Two-dimensional (2D) materials have been studied for use in a variety of emerging electronic, optoelectronic, and photonic applications. Device fabrication often involves depositing various three-dimensional (3D) materials, such as metals or dielectrics, onto the 2D material, which creates a buried interface. Interfacing materials significantly affect the nature and homogeneity of the electronic and phononic structure in 2D materials. To date, spectroscopic studies of the doping and strain in supported 2D materials have mostly been limited to unrealistic cases where the 2D material is transferred or exfoliated onto a substrate of interest [1,2], with a few exceptions [3]. A polymer-free transfer technique capable of exposing any buried 2D-3D material interface would enable direct physical characterization of realistic heterojunction properties.

In this presentation, we present a new polymer-free transfer technique that allows direct characterization of the buried interface in almost any 2D-3D heterostructure. The method is enabled by employing a water soluble GeO_2 substrate and wafer bonding process. We demonstrate the diversity of the technique by fabricating various heterostructures on monolayer MoS_2, including inert and reactive metals and oxide dielectrics, and expose the initially buried interfaces for direct characterization. We also fabricate the same heterostructures by exfoliating MoS_2 onto metals and oxides to directly compare strain, doping, and chemistry in MoS_2 across fabrication techniques. We employ Raman spectroscopy to measure the strain and doping profile in MoS_2 heterostructures. The surface chemistry and band alignment (where applicable) are measured using X-ray photoelectron spectroscopy (XPS).

Reactively sputtered GeO_2 films exhibit a 2:1 O:Ge ratio according to XPS. After heterostructure fabrication and wafer bonding, the GeO_2 layer is completely dissolved in deionized H_2O within a few hours, exposing the buried interface. In general, peak shifts in MoS_2 Raman spectra indicate the degree of strain and doping imparted on MoS_2 significantly depends on the interfacing material and the fabrication method. When the interfacing material is directly deposited on MoS_2, the strain imparted on the MoS_2 is more significant than the degree of doping. Reactions between MoS_2 and reactive metals (Ti, Ni) are significant when the heterostructure is fabricated by direct deposition according to XPS and Raman spectroscopy. In contrast, when heterostructures are fabricated by exfoliating MoS_2 onto a substrate of interest, doping dominates over strain. Our novel method enables direct characterization of buried 2D-3D interfaces and expanded control over the strain profile in 2D materials, which could lead to new discoveries and functionalities.

This work was supported by a Laboratory Directed Research & Development program at Sandia National Laboratories. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government. This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science.

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[2] Y. Chen et al. ACS Nano 2018, 12, 2569-2579
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3:00 PM BREAK

3:30 PM NM04.02.06
From *h*-BN to Graphene: Understanding Electrical Conductivity of Single-Crystal Carbon-Doped *h*-BN through Its Structure Supawan Ngamprapawat[1], Tomonori Nishimura[1], Kenji Watanabe[2], Takashi Taniguchi[2] and Kosuke Nagashio[1]; [1]The University of Tokyo, Japan; [2]National Institute for Materials Science (NIMS), Japan

Hexagonal boron nitride (h-BN) is a promising ultrawide-bandgap semiconductor for emerging optoelectronic and high-power electronic devices. Nevertheless, ohmic current injection into h-BN remains a significant challenge in developing these current-driven devices. Interestingly, the hybridized two-dimensional structure containing boron, carbon, and nitrogen, which was reported to have modifiable electrical properties by controlling C concentration [1], is a potential material to overcome this challenge. It is thus possible that a small C concentration introduced to hybridize with h-BN could improve the electrical conductivity of h-BN.

In this study, the effect of C on the electrical conductivity of h-BN was investigated. To minimize the influences from other C-unrelated defects, the single-crystal h-BN synthesized under high pressure and high temperature (HPHT) was selected. C was introduced by post-growth diffusion with two different conditions: at 2.5 GPa and 3100°C for 30 minutes and at 1 atm and 2000°C for 4 hours. The former condition results in gray-colored h-BN and the latter one gives yellow-colored h-BN. According to SIMS profiles, the gray C-doped h-BN (h-BN:C) shows ~10 at.% C, which is ~100 times higher in C concentration than the yellow h-BN:C. The transverse dielectric breakdown of both h-BN:C is comparable to that of undoped h-BN. Raman spectra show the apparent differences between these two types of h-BN:C. At 3 K, the E_{2g} vibrational mode of h-BN is observed at ~1368 cm^{-1} for both h-BN:C, while the peaks corresponding to G and 2D modes in graphene are detected only in the gray h-BN:C, indicating the existence of C–C bonds. It can be expected that C and h-BN domains coexist in the gray h-BN:C. The electrical conductivity was investigated by forming metal contact following the method described in Ref. 2. The I-V characteristic of the gray h-BN:C initially exhibited nonohmic conduction within an applied voltage of ±100 V at 298 K and transformed to ohmic conduction after the breakdown-like behavior at 598 K. The surface topology change of the h-BN channel can be seen in most of the devices with ohmic conduction after the high-T measurements. On the other hand, the yellow h-BN:C requires at least ±50 V to inject current with nonohmic conduction for all T, and no breakdown-like behavior nor topology change in the channel is observed. After the T-dependent I-V measurements, the devices were characterized by electron-beam-induced current (EBIC) mapping, cross-sectional TEM, and EELS. The EBIC results indicate the formation of a conductive path in the gray h-BN:C channel. The EELS mapping and its energy loss spectra reveal the existence of discrete graphite/graphene layers and randomly distributed C domains in the gray h-BN:C, which is consistent with the Raman spectra. These results suggest the possibility that C structures existing in h-BN induced the local breakdown of h-BN, which functions as a conductive path. Therefore, to enable the development of h-BN:C-based high-power electronics, the formation of randomly distributed C domains and graphite/graphene layers must be controlled.

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3:45 PM NM04.02.07
High-Performance Monolithic Tellurene CMOS Through Polarity Engineering Mingyi Wang and Wenzhuo Wu; Purdue University, United States

Tellurene is an emerging 2D p-type semiconductor. By contact engineering and post-metallization annealing process, the ambipolar Te-FETs were fabricated in this study. Interestingly, thinner Te flakes tend to have a p-type characteristic while thick Te possesses n-FET property. Here, based on experiments and simulations, we propose a new transport model for 2D Te FETs. This model helps us understand the thickness-polarity dependence. Such phenomena in other 2D semiconductors were previously interpreted using the theory of band structure in different thicknesses. However, the subtle change in the band structure of Te is not capable of tuning the polarity from p-type to n-type. In other similar p-type 2D materials like BP, the role of surface native oxide was often ignored in FET transport. We further demonstrated for the first time a monolithic CMOS inverter based on tellurene, leveraging the symmetric operation of p- and n-type tellurene FETs. Our results not only demonstrate robust and high-performance tellurene CMOS inverters, but also provide a new transport model to similar 2D semiconductors, shedding light on high-performance 2D electronics and CMOS design.

4:00 PM NM04.02.08
Autonomous Beam Fabrication of 1D-2D Nano Hetero-structures within 2D Materials Matthew G. Boebinger[1], Kevin Roccapriore[1], Ayana Ghosh[1], Panchapakesan Ganesh[1], Maxim Ziatdinov[1], Sergei Kalinin[2] and Raymond R. Unocic[1]; [1]Oak Ridge National Laboratory, United States; [2]The University of Tennessee, Knoxville, United States

One of the central goals of nanotechnology is to directly fabricate nanoscale architectures with atomic-scale precision. With recent advancements in aberration corrected scanning transmission electron microscopy (STEM), the sub-Å sized electron beam can be used to manipulate the atomic structure of materials. Previous work has shown the electron beam is capable of locally and controllably creating defect structures within 2D materials such as nanopores and atomic edge configurations that have enhanced electronic, magnetic, optical and catalytic properties. In the model MoS_2 materials system, several such defect structures can be fabricated through the localized irradiation of sulfur sites within the lattice through the knock-on process. In this work, an emphasis was placed on the controlled fabrication and characterization of two distinct defect structures. First, the sulfur vacancy line (SVL) defect structure, composed of a line of single sulfur vacancy sites, that has previously been shown to conglomerate together to form a local metallic MoS area within the MoS_2 monolayer. Second, the metallic Mo_6S_6 (MoS-NW) nanowire-type defect structure that forms along the edge of nanopores within the MoS_2 monolayer. Initial work has demonstrated that these MoS-NW form preferentially along the zig-zag sulfur terminated direction within the lattice. Through precise control over the electron beam irradiation of S sites along this direction, edge decorated nanopores can be fabricated. To increase the reliability of this fabrication method, Python-based codes have been developed that allow for *in situ* data acquisition, decoding and automated beam control in-line with the electron microscope workflow following the ensemble learning iterative training (ELIT) approach for deep convolutional neural networks (DCNNs). Using ELIT DCNNs, during fabrication, the image is decoded in real time into the atomic coordinates and identities allowing for precise targeting of atomic species and locations. In this regard, automated electron beam manipulation experiments have been developed that can form these beneficial defect structures that can lead to direct bandgap engineering.

Microscopy research was performed at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory, which is a US Department of Energy (DOE), Office of Science User Facility.

4:15 PM NM04.02.09

High Throughput 2D Materials Fabrication with a Fully Mechanized Platform Suji Park, Houk Jang, Kevin Yager, Gregory S. Doerk, Aaron Stein, Jerzy Sadowski and Charles Black; Brookhaven National Laboratory, United States

Quantum Information Science (QIS) is an emerging research area that promises to revolutionize computing, communication, and sensing. Two-dimensional (2D) materials are one of the most versatile motifs for generating new QIS materials since one layer in arbitrary stacks forms heterostructures unconstrained by epitaxy. Since manual mechanical exfoliation, or "tape exfoliation," produced mono and few-layered graphene in 2004, researchers have made tremendous progress in 2D material research. However, it has been challenging to study and utilize 2D materials because of a time- and labor-consuming fabrication process that highly depends on the hands-on experience of researchers. Here, I present the ongoing development of a high throughput 2D material fabrication platform, Quantum Material Press (QPress), an integrated cluster tool including three custom machines: an exfoliator, cataloger, and stacker. The exfoliator is a fully automated machine for tape exfoliation using commercial pressure-sensitive adhesive (PSA) tape and a roller assembly. The mechanism of the exfoliator is the same as that of the manual tape exfoliation. However, the PSA tape is compressed onto a substrate by a press roller and peeled off by a tape rewinder instead of human hands. After the exfoliation, the cataloger detects and classifies the exfoliated flakes, and makes a data library for users. Finally, we use the fully motorized stacker to stack selected flakes into heterostructure, with 3-axis and 6-axis manipulation stages for a substrate and a stamp, respectively. These machines allow us to investigate underlying mechanisms of 2D material fabrication. We believe that QPress will help us to provide a more reliable method of 2D material fabrication by developing optimum conditions for higher yield and reproducibility.

SESSION NM04.03: Advanced Manufacturing of 2D Materials at the Atomic Scale III
Session Chairs: Fatemeh Ahmadpoor and Mohammad Naraghi
Wednesday Morning, April 12, 2023
InterContinental, Fifth Floor, Ballroom B

8:30 AM *NM04.03.01
Layer-number Dependency of Phase Transitions in 2D Layered Materials Revealed by Cryogenic Scanning Transmission Electron Microscopy Miaofang Chi; Oak Ridge National Laboratory, United States

Two-dimensional (2D) van der Waals (vdW) materials and their heterostructures provide excellent platforms for exploring fascinating physical phenomena and implementing intriguing applications. One of the most attractive features of this family of materials is the tunability of their quantum behavior depending on the layer number. Different exotic physical properties, such as magnetic, electronic, and optoelectronic properties, were observed in samples with different thicknesses, especially in a thickness range from monolayer through several nanometers. It is recognized that lattice structural transformations often accompany electronic and spin structural changes that provoke exotic quantum phenomena. It is however unclear whether the same structural transformation as bulk material occurs in thin flake samples. Indeed, a consistent result is often missing regarding the structure-property relationship in several-layer thick 2D vdW materials. In this talk, we reveal the thickness dependency of low-temperature phase transformation and exciton state change in several model 2D vdW materials by utilizing cryogenic atomic resolution scanning transmission electron microscopy (STEM) and monochromated electron energy loss spectroscopy (EELS). Our results allow a precise understanding of relevant layer-number-dependent properties, information critical to harnessing unique quantum characteristics in thin layer 2D vdW materials for device applications.

9:00 AM *NM04.03.02
***In Situ* Imaging of Phase and Twist Boundaries in 2D Materials** Yichao Zhang[1], Chia-Hao Lee[1], Ji-Hwan Baek[2], Huije Ryu[2], Gillian Nolan[1], Gwan-Hyong Lee[2] and Pinshane Y. Huang[1]; [1]University of Illinois at Urbana-Champaign, United States; [2]Seoul National University, Korea (the Republic of)

Scanning transmission electron microscopy (STEM) provides uniquely powerful tools to study the interfacial structure and transformations of 2D materials up to atomic resolution. Here, we utilize 2D multilayer stacks to create nanoscale laboratories for studying the atomic structure, structural transformations, and properties of 2D interfaces inside the STEM. We utilize graphene encapsulation in combination with a MEMS-based heating holder to conduct in-situ studies of solid-solid phase transformations and interfacial restructuring in 2D transition metal dichalcogenides. The graphene encapsulation protects the 2D materials from the vacuum environment of the STEM, enabling high temperature studies up to 1000°C. We use these structures to directly visualize the layer-by-layer phase transformation of $MoTe_2$ and the lattice reconstruction of 2D moirés.

First, we study the interfacial reconstruction mechanisms of twisted bilayer transition metal dichalcogenides ($MoSe_2$ and WSe_2) using *in situ* aberration-corrected STEM and dark-field transmission electron microscopy (DFTEM). We discover a new mechanism of local reconstruction from moiré patterns to parallel (3R) and/or antiparallel (2H) domains in twisted bilayer 2D transition metal dichalcogenides (TMDCs). Unlike previous reports, where the twist angle is altered by the rotation of a whole flake, we observe the nucleation and growth of commensurate domains through the formation and migration of grain boundaries. We capture the dynamic nucleation and growth of the aligned structure through a series of atomic resolution STEM images combined with atom-tracking analysis. These results provide new insights into the mechanisms of interlayer rotation at the atomic scale and potential method into engineering the structure of moiré superlattices.

Second, we examine the atomic mechanisms of phase transitions of $MoTe_2$. $MoTe_2$ exhibits multiple structural and electronic phases at room temperature (2H, 1T', and T_d) that can be easily manipulated with different stimuli, making it a promising candidate for phase-change memories, high-performance transistors, and broadband photodetectors. In order to capture the dynamics of the T_d-to-2H phase transition, we apply heat pulses as short as 0.5s to "freeze" the growth front of the 2H phase at different temperatures. Next, we combine dark-field TEM and aberration-corrected STEM to image the phase transitions of few-layer $MoTe_2$ *in situ* from the micro- to atomic scales. We find that T_d-to-2H phase transitions initiate at the phase boundary at temperatures as low as 200-225 C, much lower than previously thought. We individually measure the phase front of each layer and find that the linear growth rate of the 2H phase at 275^{o}C varies from 5 to 14 nm/sec between different layers, which suggests that factors such as strain and local defect densities affect the energy barrier of the phase transition. In addition, the 2H-T_d interfaces propagate primarily along the b-axis of the T_d grain, producing an anisotropic, layer-by-layer phase transformation. These results should lead to new methods to manipulate the quantum and electronic properties within individual atomic layers.

9:30 AM DISCUSSION TIME

9:45 AM BREAK

10:15 AM NM04.03.04

MOCVD Grown MoS_2 and WS_2 Characterized With Tip-Enhanced Raman Spectroscopy and Kelvin Probe Force Microscopy Michael Curtis[1], Patrick El Khoury[2], Chen Chen[3,4], Joan M. Redwing[2,4] and David Estrada[1,5]; [1]Boise State University, United States; [2]Pacific Northwest National Laboratory, United States; [3]The Pennsylvania State University, United States; [4]2D Crystal Consortium, United States; [5]Center for Advanced Energy Studies, United States

For decades Silicon based field-effect transistors (FETs) have been the foundation of modern semiconductor technology. Advancements in device fabrication have reduced the size of FETs down the nanoscale while improving performance and efficiency. Silicon however has reached its scaling limit and is no longer suitable for next generation devices due to inadequate carrier mobility, heat generation, and atomic scale thickness limitations. Transition metal dichalcogenides (TMDs) are intrinsic semiconductors that transition from indirect to direct band gaps in the near infrared to visible spectrum, making them excellent candidates for optoelectronic applications. However, the synthesis of these materials is not a trivial exercise, and the method of mechanical exfoliation, that jumpstarted the field, is not well suited for deeper research into the properties of these materials. Additionally, mechanical exfoliation has the potential to degrade the crystalline structure of the layers and is the source of significant defects. Interface quality and layer integrity are of vital importance when producing heterostructures, which is a key step in the functionalization of next-generation devices. To this end, direct epitaxial growth techniques such as metal oxide chemical vapor deposition (MOCVD) facilitates improved control of growth conditions by precise delivery of precursor gases at consistent reactor temperature and pressure, which enables the modulation of material properties. In this study, we demonstrate wafer scale growth of MoS_2 and WS_2 in a horizontal MOCVD reactor as part of the National Science Foundation's 2-dimensional Crystal Consortium. We use molybdenum hexacarbonyl, tungsten hexacarbonyl, and hydrogen sulfide precursors and grew MoS_2 at 9, 10, and 11 minutes at 50 torr reactor pressure. We also reduced the metal flow rate by 20% while increasing growth time. For WS_2 we grew for 12 and 15 minutes at 200 torr without varying the metal flow rate. Samples were characterized via Raman Spectroscopy and Atomic Force Microscopy to analyze the quality of the growth and bilayer coverages. Using imaging processing techniques in MatLab, we found that the percent of bilayer coverage of MoS_2 varied between 57% and 24%. For WS_2, the 15 minute growth yielded a fully coalesced monolayer with approximately 16% bilayer coverage while the 12 minute growth did not fully coalesce. Raman spectroscopy of the MoS_2 samples also revealed an average 21.4 cm^{-1} difference between the A1g and E2g phonon modes, confirming monolayer growth with varying percentages of bilayer coverage. These same layers were further characterized through tip-enhanced Raman spectroscopy (TERS) and kelvin probe force microscopy (KPFM). These techniques provided insight on chemical composition at the nanometer scale and the variation of the TMD material's work function across the layer surface respectively. Our results provide fundamental insights into the conditions for nucleation and growth kinetics of wafer scale 2-dimensional TMDs and explore the chemical and electrical consistency across samples grown via the MOCVD technique.

10:30 AM NM04.03.05

Autonomous Atomic Manipulation and Characterization in the STEM Kevin Roccapriore[1], Maxim Ziatdinov[1], Matthew G. Boebinger[1], Ondrej Dyck[1], Ayana Ghosh[1], Raymond R. Unocic[1] and Sergei Kalinin[2]; [1]Oak Ridge National Laboratory, United States; [2]The University of Tennessee, Knoxville, United States

Control over matter has allowed physics, condensed matter, and materials science communities to realize a wide range of properties useful in many fields and applications. Accessing control of nanometer and smaller scales allows to shape materials properties in fundamentally new and exciting ways. The scanning transmission electron microscope (STEM), like scanning probe microscopy (SPM), routinely enables direct visualization of matter at the atomic scale. The atom-sized electron probe in the STEM, however, also contains enough energy and momentum to structurally and chemically alter matter at the same atomic scale, where this electron-matter interaction is typically considered "beam damage." It is argued that understanding and harnessing this interaction to manipulate matter at atomic scales will allow a more complete design and control of materials.

While manipulation of matter at the level of single atoms has been demonstrated in both STEM and SPM, this has primarily been performed manually without reproducibility or useful precision. Beam-induced effects in the STEM have been notoriously difficult to control, and the ordinarily stochastic changes have also been challenging to characterize analytically via electron energy loss spectroscopy (EELS) or 4D-STEM methods.

Artificial intelligence is leveraged to guide the microscope towards both atomic fabrication and autonomous characterization. The first step towards accurate atomic manipulation is to obtain knowledge of the atomic landscape in as close to real time as possible, while the second step is instructing the electron beam where to go relative to these positions. The atomic coordinate extraction – from image data - must be performed both quickly and reliably. Several methods exist that can detect atoms, but here we use deep convolutional neural networks. However even though a trained neural network is fast, it, like other methods, usually requires fine tuning of several parameters to ensure a reliable extraction. The extra time this incurs cannot be exhausted during a live experiment; further, each new image might require different parameter tuning. To overcome this and ensure robust predictability, deep ensembles are used, which handle the issues - also encountered in self-driving vehicles - of so-called "out of distribution" shifts.

Given atomic coordinates, one can classify different atomic or defect classes based on mixture models, intensities, or graph analysis, which allows to experiment with beam-induced effects precisely at the single-defect level. Different strategies of beam control are demonstrated in both graphene and MoS_2 and are shown to produce structures that cannot be fabricated by any other means.
Meanwhile, characterization of atomic and mesoscale features in the STEM is largely carried out by operator intuition and expertise such that a small region of interest is selected for detailed analyses, e.g., EELS or 4D-STEM, by inspection of the structural image, i.e., the annular dark field (ADF) signal. For several reasons, including handling beam sensitive materials, autonomous exploration of a larger sample space via EELS or 4D-STEM is useful. Deep kernel learning is utilized here to develop and learn a relationship between image data (structure) and a physical response by either EELS or 4D-STEM (property). These structure-property relationships are constructed from scratch and on-the-fly, with no prior information being supplied to the model. In this way, a material system can be explored in a completely autonomous fashion, without operator bias and without imparting too much unnecessary dose to the specimen.

Therefore, in leveraging AI and deep learning routines, atomic fabrication and autonomous characterization are made possible in the STEM. In the former, beam-matter interaction is exploited, while in the latter, it is minimized to only what is necessary. Both schemes are explored, and the challenges and practical limitations are discussed.

10:45 AM NM04.03.06

Atomic-Scale Observation of Few-Layers MoSSe Devices for Biasing *via In Situ* Transmission Electron Microscope Hsin-Ya Sung[1], Yu-Lun Chueh[2] and Wen Wei Wu[1]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]National Tsing Hua University, Taiwan

Recently, two dimensional transition metal dichalcogenides (TMDs) have been widely applied in electronic devices because of their excellent electronic, optical and mechanical properties. Nowadays, due to the scaling demand of electronic devices, it is necessary to better investigate the performance of materials in electronic and optoelectronic devices. In this regard, electrical breakdown associated with material damage is a critical issue in device failure. In this research, the device behaviors of MoSSe samples prepared under different selenization temperatures are revealed *via* in-situ biasing experiments and recorded by transmission electron microscope (TEM) at the atomic scale. The crystalline atomic-layer MoSSe was synthesized through chemical vapor deposition (CVD) system and plasma-assisted chemical vapor reaction (PACVR) process, followed by transferring the as-grown samples onto specialized TEM electrical chips. The TEM characterization of initial sample was conducted for the basic understanding of as-grown MoSSe. The advanced *in situ* technique was employed to record the structural evolution during biasing. Furthermore, we utilized atomic resolution scanning transmission electron microscope (STEM) images to identify the propagation of cracks and voids. It is noted that the selenization temperature is the key factor of defect concentration on the surface, which further affect the mechanical property of MoSSe.

11:00 AM NM04.03.07
High-performance Ambipolar Dual-gate Transistors Based on Transition Metal Dichalcogenides for Logic Applications Xintong Li[1], Peng Zhou[2], Joseph Friedman[2], Deji Akinwande[1] and Jean A. Incorvia[1]; [1]The University of Texas at Austin, United States; [2]The University of Texas at Dallas, United States

Two-dimensional materials possess distinctive electrical and physical properties, providing great opportunities towards the next-generation semiconductor devices. Compared with unipolar transistors, ambipolar devices that allows both the electron and hole transport provide more flexibility in circuit applications. The potential of the ambipolar device can be maximized in a dual-gate structure, where one of the gates can tune the ambipolar transistor from p-type to n-type, or vise versa. The major benefit of these transistors is that due to the two independent gate inputs, the number of transistors needed in a circuit can be reduced. Previously, ambipolar dual-gate transistors based on low-dimensional materials such as graphene, carbon nanotube and transition metal dichalcogenides (TMD), and their application in logic gates, are demonstrated [1][2]. But the problem exists, for example, in the unsymmetric n- and p-branch transport, lack of ability to form logic gates that can be cascaded, inequivalent gate control and so on. Till now, a well-designed ambipolar transistor that can be used in cascadable, standard, non-pass-transistor logic circuits is never developed.
In this work we designed and fabricated high-performance ambipolar dual-gate transistors based on TMDs and demonstrated their applications in logic circuits. Through the hBN sandwiched structure, the well-engineered contacts for both electron and hole injection, and the control of threshold voltages, for the first time, the transistors have achieved simultaneously the correct logic input and output, low contact resistance, high on-off ratio, well-balanced p- and n-branch transport, and low hysteresis. We then connected the devices and formed logic gates such as XOR, NAND, etc. All gate stages are connected between a Vdd and Vss, to prevent the problems brought by other pass transistor logics. We found that the logic input and output of these gates are stable, and they can work in the same operation voltages ranges, which means these logic gates can be cascaded. The total number of transistors are reduced, comparing with the traditional CMOS technology. Then the ability of forming more complicated logic circuits is demonstrated through a full adder. This work shows the potential of 2D material based transistors, and paves the way of using 2D based ambipolar transistors in practical application of logic circuits.
References:
[1] Pan, Chen, et al. Nature Electronics 3.7 (2020): 383-390.
[2] Resta, Giovanni V, et al. *ACS nano* 12.7 (2018): 7039-7047.

11:15 AM NM04.03.08
Using Suspended Graphene to Limit Beam Induced Damage in Nanometer-Sized Samples Antoine Lainé[1], Matteo Amati[2], Luca Gregoratti[2] and Miquel B. Salmeron[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]Elettra Synchrotron, Italy

Thin films and nanoparticles are ubiquitous components of many devices such as membranes for filtration or electrodes in electrochemical energy storage and reaction centers for catalysis. As the use of techniques based on high energy electron or x-ray probes for microscopy and spectroscopy is particularly relevant to study such materials operando, issues arise from material degradation by the probe radiation. Here, by using an x-ray and electron transparent graphene film as the sample support, we observe a remarkable reduction of the radiation damage in thin films. In such geometry, the amount of secondary electrons originating from the substrate vanishes, and thus the main source of damage disappears. Demonstration using highly focused x-ray beams evidences the capabilities of the technique, paving the way for the development of experimental setups with crucial damage control/reduction.

11:30 AM NM04.03.09
Self-Crosslinking of Graphene Oxide Sheets by Dehydration Haiyue Huang[1], Hun Park[2] and Jiaxing Huang[2]; [1]University of California, Los Angeles, United States; [2]Westlake University, China

Graphene oxide (GO) sheets have attracted increasingly high interest due to their relative ease of synthesis and water processability for a wide range of applications. Understanding how the sheets interact with each other is a crucial and foundational piece of knowledge guiding the production, processing, and use of GO in many applications. Here, we report that dehydration, such as by vacuum drying, triggers irreversible self-crosslinking of GO sheets and drastically alters their solution processability. Dehydrated GO films maintain structural integrity in water, and they can no longer redisperse as single layers even after agitation. At the bilayer level, dehydration fixes the stacked GO sheets together and prevents them from dissociation after sonication. Spectroscopical studies support the formation of new ester bonds, suggesting a condensation-esterification reaction between GO sheets. This new insight about a fundamental property of GO sheets should have broad implications in how the material should be processed and used.

SESSION NM04.04: Advanced Manufacturing of 2D Materials at the Atomic Scale IV
Session Chairs: Fatemeh Ahmadpoor and Mohammad Naraghi
Wednesday Afternoon, April 12, 2023
InterContinental, Fifth Floor, Ballroom B

1:30 PM *NM04.04.01
Laser Shock Nano-Straining in 2D Materials Gary J. Cheng; Purdue University, United States

Straining nanomaterials to break their lattice symmetry is perhaps the most efficient approach toward realizing bandgap tunability. Graphene has a great potential to replace silicon in prospective semiconductor industries due to its outstanding electronic and transport properties; nonetheless, its lack of energy bandgap is a substantial limitation for practical applications. In this talk, a large-scale strain engineering technique to control the local strains in 2D materials and their heterostructures will be discussed. First, laser shock nanostraining will be introduced to generate three-dimensional (3D) nanostructures and thus induce local strains in the graphene sheet. The size dependent straining limit of the graphene and the critical breaking pressure will be discussed. Moreover, laser shock nanostraining induces modulated inhomogeneous local asymmetric elastic–plastic strains as results of 1-100 GPa-level shock loading at a high strain rate of 10^6–10^8 s^{-1}. Currently, due to the weak lattice deformation induced by uniaxial or in-plane shear strain, most strained graphene studies have yielded bandgaps <0.5 eV, laser shock nanostraining can induce tunable bandgaps in graphene of up to 2.1 eV. Finally, laser shock nanostraining will be discussed to controllably tune the interlayer distance between VdW heterostructures and generate strain coupling between layers. The strains in the 2D heterolayers, providing a simple and effective way to modify their optic and electronic properties.

2:00 PM NM04.04.02
Proton Beam Modifications on 2D TMDs—Optically Active Chalcogen Vacancies and Robust N-type Doping Haidong Liang, Yuan Chen and Andrew A. Bettiol; National University of Singapore, Singapore

Defect engineering of atomically thin semiconducting crystals is an attractive route to developing single photon sources and valleytronic devices. For these applications, defects with well-defined optical characteristics need to be generated in a precisely controlled manner. However, defect-induced optical features are often complicated by the presence of multiple defect species, hindering identification of their structural origin. Here, we report systematic generation of optically active atomic defects in monolayer MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$ *via* proton beam irradiation. Defect-induced emissions are found to occur 100~200 meV below the neutral exciton peak, showing typical characteristics of localized excitons such as saturation at high excitation rate and long lifetime. Using scanning transmission electron microscopy, we show that freshly created chalcogen vacancies are responsible for the localized exciton emission. Density functional theory and GW-BSE calculations reveal that the observed emission can be attributed to transitions involving defect levels of chalcogen vacancy and the valence band edge state.
Besides the optically active property, the defects generated by proton irradiation also induce a robust n-type doping effect in 2D TMDs. For example, we demonstrated a reliable and long-time air stable n-type doping scheme with WSe$_2$ by proton irradiation. The irradiated WSe$_2$ remains an n-type semiconductor even after it is exposed to ambient conditions for a year. Localized ion irradiation with a focused beam can directly pattern on the sample to make high performance homogenous p-n junction diodes.
Controllable proton irradiation provides both optically active and N-type doping effects, which is also compatible with current CMOS processes, thus would be an ideal platform for future complementary high-performance electronics and optoelectronics applications.

2:15 PM NM04.04.03
Enhanced Robustness of Atomic Precision Devices under Accelerated Lifetime Testing Jeffrey A. Ivie[1], Connor Halsey[1], Jessica Depoy[1], DeAnna M. Campbell[1], Evan M. Anderson[1], Scott W. Schmucker[1], Daniel R. Ward[2,1], David Scrymgeour[1], Xujiao Gao[1] and Shashank Misra[1]; [1]Sandia National Laboratories, United States; [2]HRL Laboratories, LLC, United States

As transistor features move towards the atomic scale, the ability to study and design for atomic scale effects become critical for next-generation microelectronics. Atomic precision advanced manufacturing (APAM) of electrical devices, fabricated using hydrogen depassivation lithography in a scanning tunneling microscope (STM), offers a way to explore atomic scale physics with the ultimate degree of control. While almost all previous APAM work has focused on exploring applications in quantum physics, particularly with a focus on qubits, we have recently demonstrated successful integration of microelectronic-focused APAM devices within Sandia's 0.35-micron CMOS node [1]. However, demonstration of the compatibility of APAM material with CMOS at relevant operational temperatures and device drive current conditions is lacking.

To establish APAM + CMOS operational compatibility, we performed accelerated lifetime testing of both standard photolithographically patterned APAM delta layer devices (>5 µm width) as well as STM patterned APAM devices (<1 µm width). Variable width devices allow for testing at higher current densities along with connecting robustness results to a wide range of different application spaces (transistor channel, interconnect material, etc.). Analysis of the APAM devices shows that all but one device survived for several weeks at 300 °C at high current densities (minimum of 2.5 MA/cm^2) while all three implanted phosphorus samples failed under the same conditions [2]. Further characterization demonstrated that the failure mechanism was a result of the metal bond-wire interconnects used to package the devices, and not the APAM devices themselves. Modeling using Sandia's open-source TCAD code Charon validates that the current flow is tightly confined around the delta layer, resulting in an estimate of current density of >8 MA/cm^2, almost 10x higher than copper (~1 MA/cm^2 at 300 °C). Demonstration of the robustness of APAM devices relative to wire-bonds used to make device contacts coupled with the previous demonstration of APAM's integrability [1] with a CMOS process opens the door for utilizing APAM to enhance CMOS transistors along with providing wider manufacturing interest.

This work was supported by the Laboratory Directed Research and Development Program at Sandia National Laboratories and was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. DOE, Office of Basic Energy Sciences user facility. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government.

[1] Leenheer, A.; Halsey, C.; Ward, D.; Campbell, D.; Mincey, J. S.; Anderson, E. M.; Schmucker, S. W.; Ivie, J. A.; Scrymgeour, D.; Gao, X.; Lepkowski, W.; Misra, S. *ECS Meeting Abstracts* **2021,** MA2021-02, (30), 918-918.

[2] Halsey, C.; Depoy, J.; Campbell, D. M.; Ward, D. R.; Anderson, E. M.; Schmucker, S. W.; Ivie, J. A.; Gao, X.; Scrymgeour, D. A.; Misra, S. *IEEE Transactions on Device and Materials Reliability* **2022,** 22, (2), 169-174

2:30 PM NM04.04.04
Wafer-Scale 2D Molecular Crystals with Highly Anisotropic Optical Response Tomojit Chowdhury[1], Fauzia S. Mujid[1], Ce Liang[1], Ariana Ray[2], Aurelie Champagne[3], Jeffrey B. Neaton[3], David A. Muller[2], Nathan Guisinger[4] and Jiwoong Park[1]; [1]Univeristy of Chicago, United States; [2]Cornell University, United States; [3]University of California Berkeley, United States; [4]Argonne National Laboratory, United States

Two-dimensional (2D) materials are poised for the atom-precise engineering of materials morphology, composition, and phase that has established them as platforms to investigate new physical, chemical, and quantum phenomena. Given the range of exciting physics and chemistries that these materials offer, realizing diverse 2D platforms is critical to push the frontiers of next generation materials and devices. Here, we introduce 2D molecular crystal (2DMC) composed of single organic molecules in an atomically flat geometry. We develop a gas phase synthetic technique to generate high quality, high fidelity molecular crystals with wafer-scale homogeneity. Room temperature scanning tunneling microscopy (STM) together with cross-polarized microscopy reveal "superatomic" unit cells within single crystalline domains as large as a few hundred microns. Optical imaging and spectroscopic characterization reveal significant optical anisotropy in terms of polarization and birefringence in the 2DMCs, which is attributed to the diverse superatomic unit cell geometries and compositions. Further optoelectronic and time-resolved photoemission studies will be discussed to substantiate the unique excitonic properties of the 2DMCs and their heterostructures. This work expands the state-of-the-art in 2D materials through the realization of atomically thin, wafer-scale molecular films for new molecule-based nanostructures and device fabrication.

2:45 PM BREAK

3:15 PM NM04.04.05

Large-Scale Spontaneous Wrinkling of Polycrystalline Atomically Thin Films Jaehyung Yu, Colin Scheibner, Ce Liang, Vincenzo Vitelli and Jiwoong Park; The University of Chicago, United States

Wafer-scale atomically thin films are inherently polycrystalline, and therefore criss-crossed by defect laden grain boundaries. It is well understood that a single, isolated crystalline defect creates long range deformations in a thin film, much like an electron that sources an electric field. Yet, unlike Maxwell's equations, the elasticity governing a buckled sheet is nonlinear. Thus, when multiple defects are present, superimposing their undulations will not give the sheet's final shape. This poses a challenge for understanding the shape of atomically thin films when they are not confined to a substrate. Here we perform spatially resolved measurements of the wrinkling of monolayer MoS_2 in a relatively force free environement. In doing so, we directly investigate the relationship between grain size and emergent corrugations of single layer polycrystalline MoS_2. We show that polycrystallinity, even with free boundaries, gives rise to micron scale wrinkles. Using universal scaling properties of thin sheets, we rationalize the large-scale features of the topography, including wrinkle wavelength and amplitude. Though the wrinkles we observe originate from a network of topological defects, our continuum arguments depend only on average strain and grain size, and not on atomistic details. The scaling relations we obtain suggest guidelines for tailoring grain size for specific application requirements.

3:30 PM NM04.04.06
Defect Networks and Site Selective Deposition of 2D/3D Heterostructures Kate Reidy[1], Joachim Dahl Thomsen[1,2], Andrzej Zak[3], Vera Zarubin[1], Aubrey Penn[1] and Frances Ross[1]; [1]Massachusetts Institute of Technology, United States; [2]University of California, Los Angeles, United States; [3]Wroclaw University, Poland

Site selective deposition (SSD), in which substrate and deposition parameters are adjusted to allow growth in one region of a surface while avoiding growth in adjacent regions, is a promising strategy for circumventing the limitations of top-down fabrication processes and enabling etch free pattering of nanoscale features. Layered two-dimensional (2D) materials provide an excellent platform for SSD integration: their van der Waals surfaces are generally unreactive but exhibit strongly tuneable properties if heterogeneities are present. In particular, deliberate introduction of defects or other heterogeneous nucleation sites can control the diffusion and nucleation of materials grown on the surface. SSD of metals on 2D materials has been demonstrated at micrometer scales, but not at the length scales required in future devices. *Nano- and atomic- scale* guided deposition on 2D materials would meet three needs: etch-free selective deposition to form 2D/metal, 2D/dielectric, and 2D/semiconductor interfaces at specific locations; pushing the resolution limits of conventional lithography; and fabrication of structures that that require ultra-precise (<1 nm) alignment between structures, such as nanoscale interconnects, on-chip optical systems, and emerging quantum information sources.

Here, we explore the local structural properties and routes towards SSD for device-relevant 2D/3D Au/Ti interfaces using a combination of atomic resolution scanning transmission electron microscopy (STEM), *in situ* ultra-high vacuum (UHV) TEM, and monochromated high-energy resolution electron energy-loss spectroscopy (EELS). First, we demonstrate ultra-low nucleation density, single crystal, epitaxial Ti nanoislands using slow metal evaporation rates onto clean suspended 2D materials in UHV. We characterize the nucleation, epitaxy, island morphology and formation mechanism. We find that the island morphologies depend on the substrate compliance, such that thinner 2D substrates result in Ti islands that curve to accommodate strain, while thicker 2D substrates are less compliant and result in Ti islands with ordered arrays of dislocation networks. We then utilize these Ti islands as selective nucleation sites for Au metal deposition. We find 100% selectivity for Au nucleation under conditions where the substrate remains free of heterogeneous nucleation sites. We discuss the alignment and defect structures in Au grown on Ti and the stability of Au on the Ti surface on *in situ* heating. The importance of UHV conditions in the fabrication of these heterostructures is discussed. Lastly, we explore further routes towards SSD of tailored metallic nanostructures on 2D materials, such as ion beam patterning and utilizing printed nanoparticle seeds for UHV growth.

3:45 PM NM04.04.07
Isotropic Atomic Layer Etching of TiN by Oxidation to TiO_2 and Selective Etching of TiO_2 by SF_6 and H_2 Plasma Azmain A. Hossain[1], Haozhe Wang[1], David Catherall[1], Russ Renzas[2], Harm Knoops[2,3] and Austin J. Minnich[1]; [1]California Institute of Technology, United States; [2]Oxford Instruments, United Kingdom; [3]Technische Universiteit Eindhoven, Netherlands

We report isotropic plasma atomic layer etching (ALE) of titanium nitride (TiN) using sequential and self-limiting oxidation and etching steps. TiN is oxidized to TiO_2 via exposure to O_2 gas which is subsequently spontaneously etched by exposure to a H_2 and SF_6 plasma. The process exploits the selectivity of spontaneous etching of TiO_2 over TiN with the plasma. A 4:1 ratio of H_2:SF_6 is shown to be highly selective, etching TiO_2 but exhibiting negligible etching of TiN over 50 cycles. TiN ALE was observed at temperatures between 200°C and 300°C, with a maximum etch rate of 0.8 Å/cycle observed at 300°C, measured using ex-situ ellipsometry. After ALE, the etched surface was characterized using X-ray photoelectron spectroscopy and atomic force microscopy. These findings have relevance for applications of TiN in microwave kinetic inductance detectors and superconducting qubits.

4:00 PM NM04.04.08
Atomic Reconstruction in Trilayer Graphene Moiré Superlatices Isaac Craig[1,2], Madeline Van Winkle[1], Catherine Groschner[1], Kaidi Zhang[1], Nikita Dowlatshahi[1], Sinead Griffin[2] and Kwabena Bediako[1,2]; [1]Universiy of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Moiré superlattices formed from independently twisting trilayers of graphene have been proposed as an ideal model for studying electronic correlation. Multilayered moiré systems offer several advantages over their twisted bilayer analogs, including more robust and tunable superconductivity, a wide range of twist angles associated with flat band formation, and larger scale moiré patterns. Atomic reconstruction, which strongly impacts the electronic structure of twisted graphene structures, has been suggested to play a major role in the relative versatility of super-conductivity in trilayers. Despite this, reconstruction in graphene trilayers has been only probed using indirect measurements or those only applicable to exposed samples. Herein, we exploit an inteferometric 4D-STEM approach to obtain displacement and strain maps in a representative range of twisted trilayer graphene structures. This methodology correlates local intensity modulations to stacking order and allows us to selectively probe bilayer interfaces within the material. The resulting mechanism we present informs a more complete understanding of how atomic reconstruction scales with layer number in graphene moirés and modulates symmetries crucial for establishing superconductivity.

SESSION NM04.05: Poster Session: Advanced Manufacturing of 2D Materials at the Atomic Scale V
Session Chairs: Congjie Wei and Chenglin Wu
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM NM04.05.01
Nanofluidics: Transport In Chirality-Controlled Carbon Nanotube Porins (CNTPs) Sidi Zhao[1,2]; [1]University of California, Merced, United States; [2]Lawrence Livermore National Laboratory, United States

Carbon nanotubes (CNTs) with different chirality are great models to study electronic properties that influence ion transport through single-channel nanotubes. Based on band gap theory, CNTs in different chirality with different curvatures of tube surface may have different conductivity. Herein we report ion transport through chirality-separated pure (6,5), (7,4), and (7,5)/(8,4) CNT porins (CNTPs). Single channel conductance from chirality-pure, yet almost identical in diameter CNTPs indicates that electronic properties have a weak effect on ion transport. Furthermore, we measured ion transport through fluorescence ultrashort nanotubes (FUNs) – functionalized channels with defective walls. These channels have significantly lower conductance compared to the pure (6, 5) CNTPs. Besides, ions can successfully transport through CNTP dispersed by surfactants such as CHAPS and SDOC, the ion conductance of CNTPs is independent of the surfactant used to cut the CNTs.

5:00 PM NM04.05.02
Proximity Growth of Monolayer MoS$_2$ Films via Concurrent O$_2$ Etching and Sulfurization Benjamin Tan, Martha Serna, Sivasakthya Mohan, Yuqian Gu, Kenneth M. Liechti and Deji Akinwande; The University of Texas at Austin, United States

The synthesis of homogeneous monolayer molybdenum disulfide (MoS$_2$) thin films has been an important benchmark for enabling its usage in industrial scale electronic and optoelectronic devices. Recently, molecular O$_2$ has emerged as a reagent for scalable production of MoS$_2$ films through either gradual etching of an Mo source or evolution from MoO$_3$ preceding sulfurization. However, oxidation of MoS$_2$ and its precursors is not well understood and is a frequent subject of study. Here, we invert the order of traditional MoS$_2$ sulfurization to demonstrate that balancing the etch rate of partially formed MoS$_2$ films as opposed to an unreacted Mo source is an alternative pathway towards producing homogeneous monolayer MoS$_2$ films. Further, this growth enables adjacent regions of either multilayer or monolayer MoS$_2$ to be patterned dependent on whether the respective region was deposited with a Mo metal film or was left as exposed substrate. We study growth effects at 550 °C and 650 °C as well as different O$_2$ flow rates of 1 sccm and 5 sccm. This study suggests that MoS$_2$ formation through O$_2$ etching traverses two separate mechanisms based on the pristine quality of the partially formed MoS$_2$ source film. As suggested in theoretical studies, defect-filled MoS$_2$ lowers the activation energy of O$_2$ adsorption to 0.8 eV and leads to growth of monolayer-bilayer MoS$_2$ flakes. Alternatively, O$_2$ adsorption onto pristine MoS$_2$ raises the activation energy to 1.59 eV and generates monolayer MoS$_2$ films that spread homogeneously across a 1x5 cm area. The films were characterized as MoS$_2$ using Raman spectroscopy. XPS analysis also confirms peaks for MoS$_2$ that are shifted to higher energies due to the presence of trace MoO$_3$. This demonstrates that the joint adsorption of oxygen and sulfur species onto Mo is advantageous to the creation of the observed homogeneous monolayer MoS$_2$. Beyond this, Mo-O bonds present in the film could be a significant factor in increasing its photoluminescence compared to traditional MoS$_2$ syntheses.

5:00 PM NM04.05.04
Quasi-van der Waals Epitaxial Recrystallization of Gold Thin Film into Crystallographically Aligned Single Crystals Yunah Lee[1], Yunyeong Chang[1], Huije Ryu[1], Jong Hun Kim[1], Kenji Watanabe[2], Takashi Taniguchi[2], Miyoung Kim[1] and Gwan-Hyoung Lee[1]; [1]Seoul National University, Korea (the Republic of); [2]National Institute for Materials Science, Japan

Heterointerfaces between two-dimensional (2D) materials and bulk metals determine the electrical and optical properties of their heterostructures. Although deposition of various metals on 2D materials were studied, there is still lack of studies on the interaction at the van der Waals (vdW) heterointerface between 2D materials and metals. Here, we quasi-van der Waals (qvdW) epitaxial recrystallization of a gold thin film into crystallographically aligned single crystals by encapsulation annealing of gold thin film with hexagonal boron nitride (hBN). When a polycrystalline gold thin film passivated with hBN was annealed, it was recrystallized into single gold crystals with planar shape and crystallographic alignment with hBN due to a strong interaction between the gold film and hBN at the heterointerface. This reflects that a weak vdW force at the heterointerface is sufficiently strong to induce epitaxial recrystallization. Using this method, we fabricated a gold nanocrystal array with the same crystalline orientation and smooth top surface. Our work demonstrates a new method for epitaxial recrystallization of bulk crystals and provides a deep understanding of the interaction at the vdW heterointerface of 2D materials and metals.

5:00 PM NM04.05.05
Multi-Printed MoS$_2$ Semiconductor and Source and Drain Electrodes Using Jet-Printing for TFT Application Thi Thu Thuy Can and Woon-Seop Choi; Hoseo University, Korea (the Republic of)

Recently, transition-metal dichalcogenides (TMDs) have attracted much attention as new materials for electronics devices, electrocatalysts, photocatalysts, sensors, batteries, and bio-applications. Most TMDs are two-dimensional (2D) materials with a single layer. Bonds between each layer are made up of Van der Waals bonds, while intra-layer atoms bind together as covalent bonds.

Chemical vapor deposition (CVD) with sulfur gas is the most popular method for synthesizing large- scale 2D materials with high quality. Various MoS$_2$ can be obtained from this method using various precursors with different properties, process temperatures, and substrate materials. Solution process methods show advantages for preparing films with large size, high throughput, low cost, thickness control, and an environmentally friendly process. Even though there is sulfur in the precursors of the solution-process synthesis methods, supplementing the sulfur that is lost in the high-temperature CVD process is unavoidable.

Electrohydrodynamic (EHD) jet printing is a technique that uses electric fields to yield fluid flows for delivering solution/paste materials to a target substrate. EHD printing can create smooth areas or patterns with a large range of material viscosity, even with low-viscosity solutions or high-viscosity pastes, which are better by far than inkjet printing for this concern. Moreover, the merit of EHD jet printing is that MoS$_2$ TFTs can be patterned simply without using any shadow masks compared to other methods such as E-beam or thermal evaporation.

Directly printed transistors have been in the limelight due to low cost and an environmentally friendly technique. An electrohydrodynamic (EHD) jet printing technique was employed to pattern both MoS$_2$ active layer and Ag source/drain electrodes. Printed MoS$_2$ lines were patterned on a silicon wafer using a precursor solution and simple annealing, and the patterns were transferred on other SiO$_2$ substrates for TFT fabrication. On top of the patterned MoS$_2$, Ag paste was also patterned for source and drain electrodes using EHD jet printing. The printed TFTs had a high on-off current ratio exceeding 10^5, low subthreshold slope, and better hysteresis behavior after transferring MoS$_2$ patterns. This result could be important for practical TFT applications and could be extended to other 2D materials.

5:00 PM NM04.05.07
Realization of the Ideal vdW Contact Between Metals and Two-Dimensional Semiconductors Through Schottky Diode Gihyeon Kwon[1], Hyeon-Sik Kim[1], Kwangsik Jeong[2,1] and Mann-Ho Cho[1]; [1]Yonsei University, Korea (the Republic of); [2]Dong-Guk University, Korea (the Republic of)

Ideal van der Waals (vdW) metal contact with weak interaction can achieve high performance of the two-dimensional (2D) electrical and optical devices and stable interface states since it is possible to prevent Fermi level pinning (FLP) and interface defects occurring between 2D semiconductors and metals. Recently, there have been many reports to demonstrate ideal vdW metal contact by avoiding damage from metal deposition such as representative method of transferred metal contact. However, the transferred contact method through handwork technology is vulnerable from forming uniform and stable vdW interface. To overcome this limitation, we choose the vdW contact method using a selenium (Se) buffer layer that consisting of conventional fabrication processes. In this study, in order to explore the ideal vdW metal contact, we compare vdW metal contact, transferred metal contact and conventional metal contact (direct metal contact) in Schottky diode structure with graphite as 2D vdW bottom contact that can analyze difference of Schottky barrier height through rectification and photovoltaic effect. As a result, we derived that Se buffer layer method is the most suitable way to form stable and ideal vdW contact between 2D semiconductors and metal, which can prevent FLP. Using vdW Au and graphite contact, we fabricate tungsten diselenide (WSe_2) Schottky diode that exhibit excellent operation with ideality factor about 1, on/off ratio over 10^7 and coherent properties.

5:00 PM NM04.05.08
Measuring Seebeck Coefficient of High Resistance 2D $PtSe_2$ Thin Film by Annealing Process Minjeong Kim, No-Won Park, Gil-Sung Kim, Min-Sung Kang, Chanho Park and Sang Kwon Lee; Chung-Ang University, Korea (the Republic of)

Seebeck coefficient serves as an important indicator for understanding the thermoelectric (TE) properties. In order to derive thermoelectric properties, it is inevitable to measure the exact Seebeck coefficient. However, in certain cases, it is very difficult to evaluate Seebeck coefficient of a 2D film with a large area when the electrical resistance is extremely large. Here, we report a simple way to measure the in-plane Seebeck coefficient of the 2D transition metal dichalcogenide (TMDC) film, whose electrical resistance is over 2 MW, through two-step thermal annealing process. By the two-step annealing at 573 K in $PtSe_2$ film on sapphire substrate, it is possible to obtain the effect in two ways, first, between the 2D TMDC layers, and second, interface of metal and film. As a result, we observe the electrical resistance is lowered to ~400 kW and the Seebeck coefficient is also measurable, and its value is exceeding ~160 mV/K, which is a 400% improvement compared to the single-crystalline bulk of $PtSe_2$. In addition, it is confirmed that the Seebeck coefficient of the annealed samples are independent of the top electrode materials. We discuss the necessity of annealing process in measuring Seebeck coefficient of having high resistance 2D $PtSe_2$ films by atomic crystallographic characteristics and contact resistance between metal and $PtSe_2$ film. Our finding is an important accomplishment in measuring and understanding the Seebeck effect and provide a promising guideline with a high TE property in 2D TMDC material.

5:00 PM NM04.05.10
Thermoelectric Properties of the Thickness-Modulated $PtTe_2$ Thin Films Hyeok-Jun Kwon, Si-Hoo Kim, Min-Sung Kang, Jae Won Choi, Yun-Ho Kim, Jung-Min Cho, Minjeong Kim, Chanho Park, No-Won Park, Gil-Sung Kim and Sang Kwon Lee; Chung-Ang University, Korea (the Republic of)

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) -based homo- and hetero-structures result in unusual route to drastically increase the Seebeck coefficient through the interface-induced Seebeck effect. Such intriguing properties have led to us to study the in-plane Seebeck coefficient and electrical conductivity of thickness-controlled a relatively new class of metallic 2D TMDCs, 2D platinum ditelluride ($PtTe_2$) thin films. We followed a series of processes, including a simple tellurization of the Pt thin films with ~5, ~10, ~20, and ~30 nm-thick and a wet chemical transfer on sapphire substrates, to measure in-plane thermoelectric properties of the 2D $PtTe_2$ thin films. We observe the higher in-plane Seebeck coefficient and power factor of ≥ 3.0 μV/K and ≥ 16.0 μW/mK^2 in the thicker 2D $PtTe_2$ (≥ 20 nm) films, which is related to the more semimetallic transition as increasing $PtTe_2$ film thickness. These in-plane TE properties of the thickness-modulated 2D $PtTe_2$ thin films that are anticipated to offer an alternative approach for fabricating high-efficiency TE devices comprising vertically stacked 2D/2D hetero-structures (i.e., $PtTe_2/MoS_2$ and $PtTe_2/PtSe_2$)

5:00 PM NM04.05.11
Crystal Structure Identification and Application of Type-II Red Phosphorus Donggyu Kim[1], Jun-Yeong Yoon[1,2], Yangjin Lee[1], Dong Gun Oh[3], JinKyun Kim[4], Chae Un Kim[4,2], Young Jai Choi[1], Yanhang Ma[5] and Kwanpyo Kim[1,2]; [1]Yonsei University, Korea (the Republic of); [2]Institute for Basic Science, Korea (the Republic of); [3]Samsung Electronics, Korea (the Republic of); [4]UNIST, Korea (the Republic of); [5]ShanghaiTech UniversityiTech University, China

Red phosphorus (RP) is one of the allotropes of phosphorus and has many structural phases. Type-I RP is amorphous, and other types (type II, III, IV, and V) are known to be crystalline phases. The structures of Type-IV (fibrous RP) and Type-V (Hittorf's phosphorus) have been identified through previous experiments, but the structures of Type-II and Type-III have yet to be reported. Here we unravel the crystal structure of type-II RP by complementary structure characterization techniques via powder X-ray diffraction, 3D electron diffraction, and atomic-resolution scanning transmission electron microscopy (STEM) imaging. The type-II RP crystals were synthesized by the chemical vapor transport method and identified through powder XRD and Raman spectroscopy in comparison with previous literature. From our study, we successfully identify that type-II RP has approximately 250 phosphorus atoms in a triclinic unit cell. Moreover, STEM imaging clearly confirms the helical tubular structure is the building block of type-II RP. The electrical properties of type II RP toward optoelectric device applications are also experimentally verified.

5:00 PM NM04.05.12
Surface Modification of Molten Salt Etched Ti3C2Tz MXene by Annealing and their Tribological Evaluation Kailash Arole, Stefano Micci-Barreca, Swarnima Athavale, Jodie Lutkenhaus, Miladin Radovic, Hong Liang and Micah Green; Texas A&M University, United States

The new class of two-dimensional (2D) material, "MXene," has displayed state of the art of performance in energy storage, membranes, electromagnetic shielding, and chemical sensors. To further improve the performance of MXenes for diverse applications, there is a need to develop a method for the alteration of surface properties of MXene. Theoretical studies suggested that manipulation of the MXene surface termination (such as =O, -Cl, -F, -OH) strongly alter their functional properties; however, experimental control of the MXene surface termination is still in the developmental stage. Here, we demonstrated that the terminal groups of salt-etched $Ti_3C_2T_z$ MXene surface can be removed by annealing under an inert atmosphere. The removal of terminal groups of MXene was confirmed by XRD, EDS, and XPS measurements. The free active sites available after the annealing can be re-functionalized by a varied species. In this work, the annealed $Ti_3C_2T_z$ were re-functionalized by -OH groups and (3-Aminopropyl) triethoxysilane (APTES), which FTIR confirmed. The surface-modified $Ti_3C_2T_z$ were utilized as a solid lubricant showing about a 50 % reduction in friction. This paper discusses an effective approach to alter the surface functionalization of MXene, thus providing a way to utilize surface-dependent properties.

5:00 PM NM04.05.14
High Quality 2D α-MoO3 Microcrystals Produced by Laser Processing María Eva Nieto Piñero[1], Christian Lanza[2], Javier Martín Sánchez[2], Fernando Chacón[1], Beatriz Galiana[3], Isabel Muñoz Ochando[4], María del Sol López de Andrés[5] and Rosalia Serna[1]; [1]Instituto de Óptica Daza de Valdés, Spain; [2]Universidad de Oviedo, Spain; [3]Universidad Carlos III, Spain; [4]Instituto de Ciencia y Tecnología de Polímeros, Spain; [5]Universidad Complutense de Madrid, Spain

2D-Transition Metal oxides (TMOs), although less studied than the well-known 2D transition metal dichalcogenides(2D-TMCs) are appealing due to some specific advantages. Like the TMCs they are semiconductors, however they are less contaminant and offer a large potential for tuning their electro-optical properties by varying their stoichiometry. In particular, MoO_3 is transparent and shows a wide bandgap (>3 eV) and a high dielectric constant k ~ 500. Additionally, orthorhombic α-MoO_3 possesses the well-known layered crystal structure of MoO_3 which offers the possibility to create two dimensional (2D) morphologies.[1] In this context, 2D MoO_3 has shown extraordinary properties such as anisotropic polariton propagation,[2] and is an ideal material for electronic applications for high power electronics and short wavelength optoelectronics.

Currently most of the work in 2D-semiconductors is still made using small flakes obtained from mechanically exfoliated single crystals, however there is no doubt that it will be advantageous to deposit large 2D-strucutres as this will have tremendous impact both for the manipulation an integration of these materials.[3] In context we show the successful preparation of nanometer thick thin films formed by 2D MoO_3 crystals by a pulsed laser deposition-based process that starts with the deposition in vacuum from a MoO_3 target of dense, amorphous and continuous substoichimetric MoO_{3-X} layers. Subsequently, the films are annealed in air up to 300 C while following the evolution of their optical properties in-situ in the UV-VIS wavelength region by spectroscopic ellipsometry. When the temperature reaches 250 C a clear change in the optical properties starts that is related to the films crystallization. Analysis of the optical properties shows how the initially absorbing films with a metallic-like behavior after the annealing become transparent in the NIR and VIS regions, and shows a band gap >3 eV. This optical change is related to the formation of large rectangular micron size α-MoO_3 single crystals with a thickness of the order 10 nm easily observable by optical microscopy. A full characterization of the morphology, structure and stoichiometry has been confirmed by X-ray diffraction analysis, Raman spectroscopy, AFM and transmission electron microscopy. We will show the distinct fetures of the measured dielectric constant of the 2D MoO_3 microcrystals and compare them to that of the bulk in terms of defects and lattice stress. Finally, we analyze the implications for different optoelectronic applications.

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5:00 PM NM04.05.15
Improved In-plane Seebeck Coefficient in $PtTe_2/MoS_2$ Hetero-junction Structure Jung-Min Cho, Si-Hoo Kim, Minjeong Kim, Hyeok-Jun Kwon, Chanho Park, Jae Won Choi, Yun-Ho Kim and Sang Kwon Lee; Chung-Ang University, Korea (the Republic of)

Two-dimensional (2D) transition metal dichalcogenides (TMDc) is rapidly emerging as a material for thermoelectric (TE) devices. The energy conversion efficiency of the thermoelectric materials is figure of merit, $ZT=PF\times T/\kappa$ (where $PF=S^2\times\sigma$, PF is power factor, T is absolute temperature, κ is thermal conductivity, S is Seebeck coefficient, σ is electrical conductivity). In order to achieve a high ZT, it is important to obtain a high PF, and a low κ. Except for T and κ, it is important to improve $PF=S^2\times\sigma$. Unfortunately, Seebeck coefficient and electrical conductivity are through trade-off relations. In this report, we develop a $PtTe_2/MoS_2$ hetero-junction structure to break this trade-off relationship. The 2D $PtTe_2$ and MoS_2 films are synthesized by using low-pressure chemical vapor deposition (LP-CVD) method. The 2D $PtTe_2$ film exhibits a semi-metallic property with low resistance (≤ 2 kΩ), whereas the MoS_2 is considered as an insulator with high resistance (≥ 10 MΩ). We prepared five sets of samples, including $PtTe_2$ (5-nm), $PtTe_2$ (5-nm)/MoS_2 (7-nm), $PtTe_2$ (5-nm)/MoS_2 (7-nm)/MoS_2 (7-nm), $PtTe_2$ (5-nm)/MoS_2 (21-nm), and $PtTe_2$ (5-nm)/MoS_2 (21-nm)/MoS_2 (21-nm). As a result, we observe that the in-plane Seebeck coefficient for $PtTe_2$ (5-nm)/MoS_2 (7-nm)/MoS_2 (7-nm) hetero-junction structure is -19 μV/K at 300K. It indicates an increase of ~200% compared to that of the $PtTe_2$ (5-nm) thin film. Also, the electrical conductivity (5.3 kS×cm) is improved by ~170%. Consequently, the power factor (190 $\mu W/K^2m$) is improved by ~720%. These findings represent that the 2D TMDc hetero-junction structures have good advantages in improving the power factor in future TE applications.

5:00 PM NM04.05.16
Two-Dimensional Titanium Nitride ($Ti_4N_3T_x$) MXene—Synthesis, Characterization and EMI Shielding Effectiveness Tufail Hassan, Aamir Iqbal and Chong Min Koo; Sungkyunkwan University, Korea (the Republic of)

Two-dimensional transition metal carbides/carbonitrides/nitrides also known as MXenes are promising candidates for many applications due to their high electrical conductivity, mechanical flexibility, surface tunability, and easy processability. Carbide and carbonitride MXenes have been explored for multiple applications, however, a few reports are available on nitride MXenes due to higher formation energy and poor stability against etchant, typically HF. In this work, we optimize synthesis conditions of $Ti_4N_3T_x$ MXene by using molten salt etching method in air environment. Successful synthesis of $Ti_4N_3T_x$ MXene was verified by XRD, XPS, SEM, TEM, and AFM techniques. Moreover, freestanding $Ti_4N_3T_x$ films were obtained by vacuum-assisted filtration which exhibit 99.99% shielding efficiency at 150 μm thickness. Electrical and electronic properties of $Ti_4N_3T_x$ can be tailored to expand areas of applications of nitride MXenes.

5:00 PM NM04.05.17
Study of a Facile Cerium Oxide Nanoparticles Hydrothermal Synthesis by Ceric Ammonium Nitrate Yifei Fu, Craig J. Neal, Elayaraja Kolanthai, Udit Kumar and Sudipta Seal; University of Central Florida, United States

Cerium oxide nanoparticles (CNPs) are a well-known functional material with broad applications in catalysis, gas sensor, and nanomedicine due to their unique shape-dependent properties. In recent years, solutions-based, sol-gel, and template-assisted synthesis routes have been explored for CNPs synthesis. Among these methods, hydrothermal synthesis has been considered one of the most effective and scalable routes thanks to its merit of single-step, one-pot synthesis. Regarding hydrothermal synthesis, cerium (III) nitrate/chloride/sulfate, sodium hydroxide, and ammonium hydroxide are the most commonly used precursor and oxidizers in CeO_2 hydrothermal synthesis. However, the application of the nanoparticles synthesized from a harsh high-pH alkaline synthetic environment usually suffers from vigorous nanoparticle aggregation, which could severely affect their performance.
In this study, we report a facile hydrothermal synthesis method to fabricate cerium oxide nanoparticles with different shapes. The ceric ammonium nitrate (CAN) was used as a cerium precursor to synthesize a highly dispersed CNPs in a low-pH acidic environment to obtain a cubic fluorite structure with narrow size distribution. The octahedron shape of CNP was synthesized by introducing only CAN into the aqueous precursor. The strong shape transformation of CNPs from octahedron to truncated octahedron to cubical is achieved by controlling the introduction of acetic ion which is done by varying the concentration between sodium acetate and acetate acid in precursor. CNP synthesized in pH >10 environments was considered a control in this study to compare the physiochemical properties difference between CNPs synthesized in acidic or alkaline precursor environments. One of the key properties of CNPs is its cyclic change of redox potential Ce^{3+}/ Ce^{4+} on its surface. Hence the variation in the morphology of CNPs changed its redox potential, which was measured and analyzed using X-Ray photoelectron spectroscopy. CNP's change in size and shape affects its superoxide dismutase activity (SOD). The result, which showed better SOD activity, will be studied for their application in biomedical therapy.

5:00 PM NM04.05.18
Patterned Growth of Vertical van der Waals Heterostructure by Strain Modulation Jaewoong Joo, Yeonjoon Jung, Seong Chul Hong, Jin Woo Kim and Gwan-Hyong Lee; Seoul National University, Korea (the Republic of)

Van der Waals (vdW) heterostructures of transition metal dichalcogenides (TMDs) have attracted great interests because a variety of combinations in vdW heterostructures provide a platform to explore novel physics and fabricate electronic devices with superior performance. In this regard, effective methods for large-scale growth and patterning of vdW heterostructure are required. Here, we report a patterned growth method of vertical MoS_2/WS_2 heterostructure by controlling nucleation sites by strain. We generated a large strain in the local region of growth substrate, WS_2, by transferring it on a patterned SiO_2 substrate with etched steps. When MoS_2 was grown by chemical vapor deposition (CVD) on the WS_2, the strain-concentrated regions of WS_2 serve as favorable nucleation sites for MoS_2. Therefore, the vertical vdW heterostructure of MoS_2/WS_2 was successfully grown at desired positions. Our work shows a novel way to control nucleation of 2D materials by strain and to selectively produce the vertical vdW heterostructure at the patterned areas.

5:00 PM NM04.05.19
Oxygen Species Role in the Nitrogen Doping of N-rGO from GO José M. Ruiz-Marizcal[1,2], David Dominguez[2], Uriel Caudillo-Flores[2], Gabriel Alonso-Nuñez[2] and Jose M. Romo-Herrera[2]; [1]Centro de Investigación Científica y de Educación Superior de Ensenada, Mexico; [2]Universidad Autónoma de Baja California - Centro de Nanociencias y Nanotecnología, Mexico

Graphene is a nanostructure of great interest due to its extraordinary properties such as high surface area, high thermal conductivity, high mobility of charge carriers and excellent mechanical properties. However, the chemical stability of Graphene causes it to be a very inert material in chemical interactions with its environment and therefore of little catalytic activity. However, Nitrogen-doped Graphene has emerged as a great alternative to metal catalysts due to its catalytic properties. The charge distribution of the Carbon atoms is influenced by the neighboring-Nitrogen atoms doping the material, which induces active regions on the Nitrogen-doped Graphene (N-rGO) surface. These regions or active sites, together with its property as a good electrical conductor, allow it to participate in electrocatalytic reactions of great interest such as: the oxygen reduction reaction (ORR) **[1]**, the iodide reduction reaction (IRR) **[2]** or charge storage; which are essential for fuel cells, dye-sensitized solar cells (DSSC), supercapacitors or Metal-Air batteries.
These types of applications require considerable amounts of material, so it is vital to implement and understand the mechanisms involved in scalable treatments to achieve N-doping. In this sense, thermal treatments as a post-synthesis method correspond to a simple and easily scalable technique. Furthermore, it is well known that Nitrogen atoms can be incorporated into the sp^2 Carbon lattice in different configurations: pyridine nitrogen, graphitic nitrogen, pyrrolic nitrogen or even as oxidized nitrogen species **[1-2]**. However, each of these configurations or Nitrogen species may have different roles in the reactions of interest **[1]**; therefore, being able to modify or modulate the proportion between the Nitrogen species present in the N-rGO would be very useful.
The present work analyzes in detail the doping of Graphene with Nitrogen through post-synthesis thermal treatments in an inert atmosphere, using Graphene Oxide (GO) as a precursor, seeking to understand at atomic level and propose a reaction mechanism. Special emphasis has been placed on the role of oxygen species present in GO as precursor and its importance in the incorporation of Nitrogen atoms into the N-rGO network. This analysis has been carried out using different sets of samples with a systematic monitoring of their physico-chemical and structural properties using X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), Raman spectroscopy, X-ray diffraction (XRD), optical microscopy and atomic force microscopy (AFM). Even more, it is shown how the temperature in a second thermal treatment on the N-rGO obtained, plays a key role to modify or modulate the proportion of the different Nitrogen species present in the final N-rGO.

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5:00 PM NM04.05.20
Ultra-High Vacuum Molecular Beam Synthesis of 2D Molybdenum Telluride ($MoTe_x$) Grown on Epitaxial and Non-Epitaxial Substrates Ossie Douglas, Quang Ho, Elis Daniela Zamora Alviarez, Md Rubayat-E Tanjil, Zhewen Yin, Daiyue Wei, Muhammad Shahbaz Rafique and Mike C. Wang; University of South Florida, United States

Two-dimensional (2D) transition metal dichalcogenides (TMDCs), such as molybdenum tellurides ($MoTe_x$), exhibit optoelectronic and physicochemical properties strongly dependent on the material crystalline structure and polymorphic phase. Although the phase-dependent properties of 2D $MoTe_x$ are conducive for additional degrees of freedom of control at the device level, synthesis of large-area, phase-pure crystals is challenging due to the small ground-state energy differences between the different polymorphs. While established methods in synthesizing and/or isolating 2D $MoTe_x$ have enabled fundamental studies of their unique properties, they are limited in their control over crystallinity, stoichiometry, and manufacturing scalability. This work focuses on the deterministic synthesis of 2D $MoTe_x$ on epitaxial, van der Waals epitaxial, and non-epitaxial substrates via ultra-high vacuum (UHV) molecular beam "epitaxy" (MBE) and combines *in situ/in operando* and *ex situ* characterization techniques.

5:00 PM NM04.05.21
Developing High-Pressure Techniques for Controlling Twisted Trilayer Graphene Alexander Sanchez[1], Manish Kumar[1], Kenji Watanabe[2], Takashi Taniguchi[2] and Matthew Yankowitz[1,1]; [1]University of Washington, United States; [2]National Institute for Materials Science, Japan

Research into two-dimensional van der Waals (vdW) materials continues to flourish due to the large selection of crystals available. In stacks of vdW materials, the interlayer interactions prove to be a crucial variable in determining the electronic properties of a given structure. It has been shown that using hydrostatic pressure, the interlayer coupling can be finely tuned in magic angle twisted bilayer graphene (MATBG) to induce superconductivity, which is strong evidence of an induced electronic flat band, effectively simulating changing the twist angle in the heterostructure after it has been fabricated. Magic angle twisted trilayer graphene (MATTG) could prove to be an interesting platform to further study the effects of tuning interlayer coupling via hydrostatic pressure, owing to the fact that it has been shown to have a similar flat band to MATBG. Using MATTG devices inside a pressure cell loaded with hydrostatic pressure on the order of a few GPa, superconductivity could potentially be induced in an MATTG device which otherwise did not exhibit correlated phases owing to a relative twist angle that deviates too far from MATTG's magic angle of ~1.6°. Such a result could further confirm both the utility of hydrostatic pressure as a method of changing interlayer coupling, and TTG as a tunable heterostructure.

5:00 PM NM04.05.22
Oxycarbide MAX and MXenes Identification Using Ultra-Low Energy Secondary Ion Mass Spectrometry Mark Anayee[1], Pawel P. Michilowski[2] and Yury Gogotsi[1]; [1]Drexel University, United States; [2]Institute of Microelectronics and Photonics, Poland

The MXene family of two-dimensional transition metal carbides and nitrides already includes ~50 members with distinct numbers of atomic layers, stoichiometric compositions and solid solutions, in-plane or out-of-plane ordering of atoms, and a variety of surface terminations. MXenes have shown properties that make them attractive for applications ranging from energy storage to electronics and medicine. Although this compositional variability allows fine-tuning of the MXene properties, it also creates challenges during the analysis of MXenes because of the presence of multiple light elements (for example, H, C, N, O, and F) in close proximity. Here, we show depth profiling of single particles of MXenes and their parent MAX phases with atomic resolution using ultralow-energy secondary-ion mass spectrometry. We directly detect oxygen in the carbon sublattice, thereby demonstrating the existence of oxycarbide MXenes. We also determine the composition of adjacent surface termination layers and show their interaction with each other. Analysis of the metal sublattice shows that Mo_2TiAlC_2 MAX exhibits perfect out-of-plane ordering, whereas Cr_2TiAlC_2 MAX exhibits some intermixing between Cr and Ti in the inner transition metal layer. Our results showcase the capabilities of the developed secondary-ion mass spectrometry technique to probe the composition of layered and two-dimensional materials with monoatomic-layer precision.

SESSION NM04.06: Advanced Manufacturing of 2D Materials at the Atomic Scale VI
Session Chairs: Fatemeh Ahmadpoor and Wenpei Gao
Thursday Morning, April 13, 2023
InterContinental, Fifth Floor, Ballroom B

8:30 AM *NM04.06.01
***In Situ* High Resolution Liquid Cell Transmission Electron Microscopy Study of 2D Nanomaterials Formation** Haimei Zheng[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

Two-dimensional (2D) materials have attracted significant interests due to the large surface-to-volume ratio, electron confinement, and various surface-enhanced applications. Although significant advances have been made in the synthesis of 2D nanomaterials, an understanding of the formation mechanisms is crucial for the future success in design, synthesis, and applications of novel 2D materials. We use liquid cell Transmission Electron Microscopy (TEM) to study model 2D systems at the atomic resolution. Our direct observations allow to uncover the nucleation, formation of intermediates, and dynamic structural evolution leading to 2D nanostructures. Assisted with theoretical calculation, the underlying mechanisms have been revealed. In this talk, progress made in our recent in situ studies of 2D nanomaterials formation at the atomic level will be presented, including the growth of 2D nanosheet with nanoclusters as the building blocks, and the dynamic formation of 2D molecular crystals.

9:00 AM DISCUSSION TIME

9:15 AM BREAK

9:45 AM NM04.06.04
Epitaxial Growth of Single Crystalline Hexagonal Boron Nitride on Vicinal Germanium (110) for Atomically Clean Assembly of Twisted Multilayers Ju-Hyun Jung[1,2], Seong-Jun Yang[1,2] and Cheoljoo Kim[1,2]; [1]Institute for Basic Science (IBS), Korea (the Republic of); [2]Pohang University of Science and Technology, Korea (the Republic of)

Atomically-thin hexagonal boron nitride (hBN) has gained attentions as a material platform for broad applications in nano-photonics and electronics, including near-infrared waveguide, deep-ultraviolet emitter and dielectric film. Recent studies show that the dielectric and electronic properties of multilayers (ML) can be tuned with control of the interlayer rotational angle, θ. While layer by-layer assembly of singly crystalline hBN can enable fabrications of uniform, polytypical structures, large-scale films for atomically clean assembly is still missing. Here, we report the epitaxial growth of single-layer (SL) hBN fims on wafer-scale, which can be exfoliated and assembled by van der Waals interactions. Chemical vapor deposition on a vicinal (110) surface of germanium with miscut toward the <001> direction results in SL films with a single crystallographic orientation. Density functional theory calculations show that it is energetically favorable for the nitrogen-terminated zig-zag edges of hBN to be aligned to the step edges along the <110>, guiding the unidirectional growth. The SL hBN can be repeatedly grown on a same substrate after mechanical exfoliations, and assembled into twisted MLs with controlled θ. Optical absorption spectra show a clear θ-dependency, suggesting effective modulations of the band structures of hBN. Furthermore, the ML films can be integrated with a semiconducting MoS2 channel with tunable dielectric properties by θ.

10:00 AM NM04.06.05
Scalable, One-Pot, Facile Synthesis of Carbon-Doped TiO_2-Based 1D Nanofilaments and 2D Flakes, Their Properties and Potential Applications Hussein Badr and Michel Barsoum; Drexel University, United States

Two-dimensional (2D) materials, which possess atomic or nanometer thickness and infinite planner dimensions, thrive on the rich variety of features and properties that are vastly distinctive from their bulk counterparts. Conventionally, bulk synthesis of 2D materials has predominantly been through selective etching of layered solids. Herein and for the first time, we convert – near ambient conditions – a dozen of cheap, earth-abundant, water-insoulble precursors into one-dimensional (1D) nanofilaments than self-assemble into 2D flakes. In that, the precursor is simply heated in tetramethylammonium hydroxide aqueous solution at 50 -80 ° C for tens of hours. The structure, composition, oxidation state, and morphology of the resulting sheets are resolved by density functional theory, X-ray diffraction, X-ray photoelectron, electron energy loss, Raman, X-ray absorption near edge structure spectroscopies, atomic force microscope, scanning, transmission and high-resolution transmission electron microscopies and selected area diffraction. The resulting flakes showed enhanced electrochemical performance as cathodes in both Li-ion battery and Li-S battery. They also found to be biocompatible to human cells but fatal to come types of cancer cells, thus showing potential in biomedical applications. The developed synthesis protocol of 1D and 2D materials in bulk-scale at near ambient conditions is paradigm shifting and will undoubtedly open new and exciting avenues of research and applications.

10:15 AM NM04.06.06
Synthesis and Chemistry of Two-Dimensional Transition Metal Carbides (MXenes) Mark Anayee, Christopher E. Shuck, Mikhail Shekhirev, Ruocun (John) Wang and Yury Gogotsi; Drexel University, United States

The family of two-dimensional (2D) transition metal carbides and nitrides (MXenes) has grown to encompass numerous structures and compositions. MXenes have shown properties that make them attractive for applications ranging from energy storage to electronics and medicine, including high electrical conductivity, redox-active surfaces, and plasmonic behavior. MXenes are typically produced through topochemical etching of atomically thick layers from precursor layered MAX phases using corrosive aqueous etchants. However, the harsh synthesis conditions lead to various defects in the MXene lattice that make them susceptible to degradation and limit their practical storage, distribution, and application. Herein, we investigate the chemistry of the precursor MAX phases and demonstrate the existence of oxycarbides; and explore the influence of MAX stoichiometry on the chemical and thermal stability of the resulting MXenes. We also probe the mechanism and kinetics of the MAX etching reaction for MXene synthesis using in situ analytical and microscopic techniques and demonstrate the influence of critical etching parameters on the structure, chemistry, and properties of the resulting MXenes. We further develop kinetic models that allow prediction of the optimal synthesis conditions, and which make the synthesis more scalable, environmentally friendly, and efficient.

SESSION NM04.07: Advanced Manufacturing of 2D Materials at the Atomic Scale VII
Session Chairs: Fatemeh Ahmadpoor and Wenpei Gao
Thursday Afternoon, April 13, 2023
InterContinental, Fifth Floor, Ballroom B

1:30 PM *NM04.07.01
Probing Aluminum-Oxo 2D Cluster Assembly Pathways to Gibbsite Nanoplates Xin Zhang, Ying Chen, Sebastian T. Mergelsberg, James J. De Yoreo, Carolyn Pearce and Kevin Rosso; Pacific Northwest National Laboratory, United States

Aluminum is the third-most abundant element in Earth's crust. As a result, aluminum hydroxide polymorphs such as gibbsite and bayerite are abundant minerals in soils and dominate aluminum ores. They have also been widely used as adsorbents, fire retardants, coatings, catalysts, and luminescence powders, as well as comprising important precursors to various alumina products. Understanding the crystallization pathways of the aluminum hydroxide polymorphs is thus important to geochemistry, environmental science, energy storage, catalysis, biomedicine, industrial processing, and even nuclear waste treatment. Here we use *in situ* magic angle spinning nuclear magnetic resonance (MAS-NMR), scanning electron microscopy (SEM), scanning/transmission electron microscopy (S/TEM), atomic force microscopy (AFM), small angle X-ray scattering (SAXS), X-ray absorption spectroscopy (XAS), electrospray ionization (ESI)-mass spectrometry, X-ray diffraction (XRD), and X-ray pair distribution function (PDF) techniques to probe the nucleation and crystal growth mechanisms of gibbsite nanoplates in detail. By focusing on understanding the role of aluminum coordination change dynamics from tetrahedral in solution to octahedral in solids and vice versa, and by quantifying intermediate polyoxoaluminate cluster formation, some unifying principles governing these transformations emerge. Furthermore, various advanced techniques reveal the transformation and assembly of aluminum-oxo 2D clusters during the hydrothermal process, which indicate cluster assembly pathways to gibbsite nucleation and crystal growth. These findings are important for developing new methods for morphology and size-controlled synthesis of 2D aluminum hydroxide materials and may aid in the design of novel metal oxide 2D materials.

2:00 PM NM04.07.02
Spin Defects and Blue Quantum Emitters Generated by High Energy Ion Irradiations in hBN Haidong Liang, Yuan Chen, Chengyuan Yang, Goki Eda and Andrew A. Bettiol; National University of Singapore, Singapore

Recently the negatively charged boron vacancies (V_B^-) in hexagonal boron nitride (hBN) have been shown as spin defects that have great potential in quantum sensing. However, so far the sensitivity is limited by either photoluminescence (PL) brightness or the optically detected magnetic resonance (ODMR) contrast, and linewidth. In this work, we demonstrate the generation of these spin defects using high energy helium ion beams and perform ODMR measurements with different laser and microwave powers. The spin defects generated by high energy helium ions exhibit a high PL brightness and ODMR contrast while keeping a small linewidth, hence a good sensitivity. By comparing different fluences of helium irradiations, we determine an optimal fluence which is sufficient in creating spin defects without damaging the overall crystal lattice structure. With this optimal fluence, we can obtain a high signal-to-noise ratio ODMR spectrum with an accurate measurement of zero field splitting frequency, and a best sensitivity as ~2.55μT/sqrt (Hz). Moreover, with a focused beam, we can deterministically create such spin defects with nanometer precision.
Hexagonal boron nitride (hBN) has been a centre of interest due to its ability to host several bright quantum emitters at room temperature. However, the identification of the observed emitters remains challenging due to spectral variability as well as the lack of atomic defect structure information. In this work, we report two new blue quantum emitters with zero phonon line (ZPL) centred around 460 nm and 490 nm in hBN powders. We further demonstrate that the new emissions can be created by high temperature annealing or high energy ion irradiation in exfoliated hBN flakes. Scanning transmission electron microscopy (STEM) reveals that the dominant defect structures present in ion irradiated sample are vacancy type and adatom (intercalant) type. Through first principle GW-BSE (Bethe-Salpeter equation) calculation, we attribute the observed emissions at 460nm and 490nm to originate from boron intercalant and nitrogen intercalant respectively. Our results not only discover a new group of blue quantum emissions in hBN, but also provide an insight on the physical origin of the emissions by correlating the emission wavelength with local atomic structures in hBN.

2:15 PM NM04.07.03
Molybdenum Blues with Tunable Light Absorption Synthesized by Femtosecond Laser Irradiation of Molybdenum Trioxide in Water/Ethanol Mixtures Fan Ye[1,1,2], Ahsan Ayub[1], Darren Chang[1,2], Roman Chernikov[3], Qiaoyun Chen[1], Reza Karimi[1], Shawn Wettig[1], Joseph Sanderson[1] and Kevin Musselman[1,2]; [1]University of Waterloo, Canada; [2]Waterloo Institute for Nanotechnology, Canada; [3]Canadian Light Source, Canada

A novel strategy to synthesize molybdenum blue (MB) nanorings by irradiating MoO_3 suspended in water/ethanol mixtures with intense femtosecond laser pulses is demonstrated. It is found that the MoO_3 can be dissolved in the water during laser irradiation to form molybdic acid, which provides an acidic environment for the formation of MB. Concentrations of ethanol as low as 1% result in the formation of MB and by adjusting the concentration of ethanol in the solvent, the absorption band can be tuned due to the modification of Mo^{V}-O-Mo^{VI} entities. The MB synthesized in 30% ethanol appears the darkest blue and assembly of vesicles 115 nm in size is observed. At high concentrations of ethanol (>70%), H_XMoO_3 and MoO_{3-X} are preferentially formed instead of MB. The photothermal conversion efficiency of the MBs synthesized in 1% and 30% ethanol is above 40%.

2:30 PM BREAK

3:30 PM NM04.07.04
One-Dimensional Bose Gase within Mirror Twin Boundary Formations in WS_2 John C. Thomas[1], Antonio Rossi[1], Johannes T. Küchle[1,2], Elyse Barré[1], Zhouhang Yu[3], Shalini Kumari[3], Hsin-Zon Tsai[4], Joshua Robinson[3], Mauricio Terrones[3], Archana Raja[1], Ed Wong[1], Chris Jozwiak[1], Aaron Bostwick[1], David F. Ogletree[1], Jeffrey B. Neaton[1,4], Michael F. Crommie[4], Francesco Allegretti[2], Willi Auwärter[2], Eli Rotenberg[1] and Alexander Weber-Bargioni[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]Technical University of Munich, Germany; [3]The Pennsylvania State University, United States; [4]University of California, Berkeley, United States

Cross-correlation studies using nano angle-resolved photoelectron spectroscopy (nARPES) coupled with scanning tunneling microscopy and scanning tunneling spectroscopy (STM/STS) measure a band gap renormalization on purposefully induced defects in monolayer tungsten disulfide (WS$_2$). Mirror twin boundary (MTB) defects are identified with non-contact atomic force microscopy, which enables structural comparison to local studies performed with nARPES and STM. Both nARPES and STS studies a formation of Tomonaga–Luttinger Liquids within mirror twin boundary (MTB) defects, which are created through the growth of one-dimensional (1D) MTBs from point defects tht are induced into WS$_2$ with Ar$^+$ bombardment. Chalcogen defect creation also provides a path to study novel substitutional defects. 1D MTBs are substantially charged at the nanoscale.

3:45 PM NM04.07.05
Wafer-Scale Layer-by-layer Assembly of One-atom-thick Crystals with Atomically Clean Interfaces Seong-Jun Yang[1,2], Ju-Hyun Jung[1,2], Eunsook Lee[3], Edmund Han[4], Min-Yeong Choi[1,2], Daesung Jung[5], Shinyoung Choi[1,2], Jun-Ho Park[1,2], Dongseok Oh[3], Siwoo Noh[3], Ki-Jeong Kim[3], Pinshane Y. Huang[4], Chan-Cuk Hwang[3] and Cheoljoo Kim[1,2]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Institute for Basic Science (IBS), Korea (the Republic of); [3]ohang Accelerator Laboratory, Korea (the Republic of); [4]University of Illinois at Urbana-Champaign, United States; [5]Sungkyunkwan University, Korea (the Republic of)

Modulation of thicknesses and atomic structures can broadly program the physical properties of crystalline films. The layer-by-layer assembly of atomically thin crystals provides a powerful means to arbitrarily design films at the atomic level, which are unattainable with existing growth technologies. However, atomically clean assembly of the materials with high scalability and reproducibility remains challenging. Here, we report programmed crystal assembly of graphene and monolayer hexagonal boron nitride, assisted by van der Waals interactions, to form wafer-scale films of pristine interfaces with near-unity yield. The atomic configurations of the films are tailored with layer-resolved compositions and in-plane crystalline orientations. We demonstrate batch-fabricated tunnel device arrays with modulation of the resistance over orders of magnitude by thickness control of the hexagonal boron nitride barrier with single-atom thick precision and large-scale, twisted multilayer graphene with programmable electronic band structures and crystal symmetries. Our results constitute an important development in the artificial design of large-scale films.

4:00 PM NM04.07.06
Growth of Embedded Transition Metal Dichalcogenides for Ultraclean Interface with Metal Minseok Yoo, Minsu Seol, Kyung_Eun Byun, Junyoung Kwon and Sang Won Kim; Samsung Advanced Institute of Technology, Korea (the Republic of)

Transition metal dichalcogenides (TMD) is a promising candidates as a channel material for next-generation electrical and optoelectrical applications. The atomic thin body and outstanding properties of it, however, are highly affected by integration processes such as transfer, photolithography and metallization. Here, we proposed novel synthesis method for utilizing TMD having ultraclean heterojunctions by employing confined interfacial chalcogenization (CIC). We synthesized TMD at the junction of two metal, Au and transition metal (TM) and the embedded TMD exhibit high crystallinity and atomically clean interfaces with adjacent metals. Chalcogenization at confined space suppressed defect generation and guided lateral growth of TMD. In addition, top Au acts as an epitaxial template for growing underling TMD and enables the chalcogenization at low temperature. We proved that CIC is a general synthesis method for TMD including vertical heterostructure. We elucidated that TM dissolved in Au accelerated the diffusion of chalcogen inside of Au and enables the fast and controlled CIC. Moreover, we achieved the site-selective CIC and demonstrated vertical memristor with excellent device uniformity. This method, therefore, offers preparation platform for the electrical devices utilizing TMD as a vertical channel with ensuring ideal contact of metal and TMD.

4:15 PM NM04.07.07
Formation of Chiral Helices by Self-Assembling Molecules on Semiconductor Nanosubstrates Jiunn Hong Po and Sandrine Ithurria; ESPCI Paris, France

Among semiconductor colloidal nanocrystals, 2D nanoplatelets (NPLs) are geometrically seen as well-defined flexible substrates for the self-assembly of molecules. In the presence of mechanical stress brought by surface stabilizers, helical structures are formed according to the parameters of the initial material after internal energy relaxation.
Here, we demonstrate the tuning of the NPLs helices radii through the organic ligands, described as an anchoring group and an aliphatic chain of a given length. A perfect control in surface chemistry allows the switch between different morphological features of these nanohelices. Nonetheless, their optical properties in the visible region are well-preserved upon such modifications. Numerical simulations and as well as structural X-ray diffraction studies done on these anisotropic nanoparticles, unveil a strong preferential orientation effect on their resulting scattered patterns.
A mechanical model accounting for the misfit strain between the inorganic core and the organic ligands, enables to predict the nanohelices radii. The model treats these different layers of substrate, anchoring group and aliphatic chain contributions individually and demonstrates good agreement for all studied homo- and hetero-structure cadmium-based NPLs. It reveals ultimately that the self-assembly of surface molecules is equivalent to a layer, whose Young modulus in lateral compression can be estimated close to 0.9 GPa.
Furthermore, the chirality of the semiconductor nanohelices shown in this work is dictated by the ligands anchoring group and can be inverted from one population to another. Chiroptical properties exhibited in circular dichroism measurements show a special interest in investigating this type of mirror-symmetry-breaking particles and could undoubtedly, lead to the emission of circularly polarized light in the visible spectrum.

4:30 PM NM04.07.08
Thermodynamically Driven Tilt Grain Boundaries of Monolayer Crystals Using Catalytic Liquid Alloys Min-Yeong Choi[1,2], Chang-Won Choi[1,2], Dong-Yeong Kim[1,2], Si-Young Choi[1,2] and Cheoljoo Kim[1,2]; [1]Institute for Basic Science, Korea (the Republic of); [2]Pohang University of Science and Technology, Korea (the Republic of)

Grain boundaries (GBs) of two-dimensional (2D) materials host unique atomic defects that reveal novel properties, but deterministic control of the defect structures has not been achieved. Here, we report selective formations of dislocation cores at GBs of monolayer (ML) MoS$_2$ by vapor-liquid-solid (VLS) growth with Na-Mo-O eutectic alloys. The alloys function as a growth catalyst and provide Mo-rich chemical environments during the growth, which guide the formation of pentagon-heptagon defects with Mo-Mo homo-elemental bond (Mo 5|7) by yield > 95 %. In particular, we found that GBs with high tilt angle ($\theta_t > 34°$) relieve strains by deformation-twining, instead of forming a dense arrays of defects including derivatives of S 5|7 defects. Polycrystalline MoS$_2$ films grown by VLS mode present about 8 times higher photoluminescence (PL) intensity than the films grown by vapor-solid-solid (VSS) mode. Density-functional theory (DFT) calculations suggest that the enhancement of PL intensity is associated with suppression of S 5|7 donor-type derivatives and electron doping. Using eutectic alloys will be useful to precisely determine atomic defects of various polycrystalline 2D films for engineering the material properties.

4:45 PM NM04.07.09
Two-dimensional Stacked Composites of Self-Assembled Alkane Layers and Graphene for Transparent Gas Barrier Films with Low Permeability Yoonjeong Kim and Seokhoon Ahn; Korea Institute of Science and Technology, Korea (the Republic of)

Recently, demanding for OLEDs (organic light-emitting diode) has increased rapidly, many researchers are researching to develop better OLED products. Currently, it is possible to manufacture a device that can fold and bend the display, but it is still very difficult to realize flexible and stretchable displays. One of these difficulties is absence of gas barrier films. Graphene has been considered as one of the best candidates for gas barrier films, because it is theoretically ideal for flexible and transparent gas barriers. However, large-scale graphene synthesized using chemical vapor deposition (CVD) contains numerous defects, and therefore has poor gas barrier properties (water vapor transmission rate WVTR = 1.57 g/(m^2-d) for 3-layer graphene). In order to solve this problem, we introduced two-dimensional (2D) self-assembled alkane layers on graphene. The scanning tunneling microscopy (STM) study revealed that a self-assembled hexatriacontane (HTC) monolayer on graphene covers nanometer-size defects due to the flexible nature and strong intermolecular van der Waals interactions of alkane. In addition, HTC multilayers between graphene layers greatly improve their adhesion, indicating that HTC multilayers between graphene layers can effectively block the lateral pathway between graphene layers by filling open space with close-packed self-assembled alkanes. By these mechanisms, alternately-stacked composites of graphene and self-assembled alkane layers greatly increase gas-barrier property to WVTR as low as 1.2 x 10^{-3} g/(m^2-d), whereas stacked graphene layers generally show WVTR > 0.5 g/(m^2-d). Furthermore, the self-assembled alkane layers have superior crystallinity and wide band gap, so they have little effect on the transmittance. However, the limitation of this method is that defects in graphene which are larger than the length of the alkane molecule might not be covered, because absent molecule-graphene interaction impedes alkane self-assembly.

SESSION NM04.08: Advanced Manufacturing of 2D Materials at the Atomic Scale VIII
Session Chairs: Mohammad Naraghi and Chenglin Wu
Friday Morning, April 14, 2023
InterContinental, Fifth Floor, Ballroom B

8:30 AM *NM04.08.01
Operando Experiments and Modeling on the Dynamics and Heterogeneity of Composite Electrodes in Batteries Kejie Zhao; Purdue University, United States

The composition dynamics regulate the accessible capacity and rate performance of rechargeable batteries. Heterogeneous Li reactions can lead to non-uniform electrochemical activity and amplify mechanical damage in the cell. We develop operando optical microscopy as a laboratory tool to map the spatial composition heterogeneity in a solid-solution cathode for Li-ion batteries. We observe that the active particles charge asynchronously with reaction fronts propagating on the particle surfaces during the 1st charging, while the subsequent (dis)charge cycles transition to a synchronous behavior for the same group of particles. Such transition is understood by computational modeling which incorporates the dependence of Li diffusivity and interfacial reaction on the state of charge. Furthermore, we use synchrotron experiments to visualize the morphological defects at multi-scales ranging from the macroscopic composite, particle ensembles, to individual single particles. We find that the interfacial failure reconstructs the conductive network and redistribute the electrochemical activities that render a dynamic nature of electrochemistry and mechanics evolving over time in the composite electrodes.

9:00 AM NM04.08.02
Deterministic Monolayer Manipulation of Single-Crystalline Ruddlesden-Popper Halide Perovskite for Opto-Electronic Device Array Fabrication Ki-Tae Park; Seoul National University, Korea (the Republic of)

Ruddlesden-Popper perovskite (RPP), a quasi two-dimensional phase of organic-inorganic hybrid halide perovskites have been considered as promising candidates for next generation opto-electronic applications. In addition to their broad controllability of bandgap between 2 and 3 eV, their inert surface nature can realize high-performance optoelectronic devices even at nanometer scale. Moreover, phase-pure monocrystalline RPPs can be synthesized by using solution processes, which exhibit significantly enhanced optoelectronic characteristics. However, the multi-layer structure of fabricated RPP crystals and the high solubility in typical solvents have been major challenges to obtain monolayer RPP for device fabrication. Conventional layer splitting and photolithography-based patterning processes which involves solvents are incompatible with RPPs. Therefore, a dry process for monolayer manipulation of RPP must to be established to realize nanoscale device array.
In this contribution, we develop a novel all-dry layer manipulation process through adhesion control of RPP. We first synthesize inch-scale phase-pure monocrystalline RPP crystals. Using the RPP crystals, we characterize the adhesion between RPP and various inorganic materials for adhesion layer by using atomic force microscopy. We find out that adhesion between RPP and inorganic materials surface can be tailored depending on the surface roughness as well as the material of adhesion layer. We investigate the fracture mechanics of RPP monolayers by measuring the out-of-plane adhesion to in-plane toughness ratio. Simultaneous processes of deterministic monolayer spitting and lateral patterning with micrometer-scale resolution are demonstrated. Furthermore, we demonstrate RPP monolayer photodetector array fabricated by the developed monolayer manipulation process.

9:15 AM NM04.08.03
Studying the Behavior of Potential Electronic Nanodevices on Individual CNTs Hugo Borbon-Nunez[1,2], David Dominguez[2], Eduardo Murillo[2], José M. Ruiz-Marizcal[3,2], Luis A. Rios[4] and Jose M. Romo-Herrera[2]; [1]CONACyT - Centro de Nanociencias y Nanotecnología de la UNAM, Mexico; [2]Centro de Nanociencias y Nanotecnología de la UNAM (CNyN-UNAM), Mexico; [3]Programa de Posgrado en Nanociencias CICESE / CNyN-UNAM, Centro de Investigación Científica y de Educación Superior de Ensenada (CICESE), Mexico; [4]División de Física Aplicada, Centro de Investigación Científica y de Educación Superior de Ensenada (CICESE), Mexico

Electronics miniaturization has been a driving force for the development of new electronic devices. Nanotechnology can be able to contribute not only to the synthesis of new nanostructures but to the analysis of their physical properties, including the appearance and understanding of new phenomena due to the dimensions in the nano regime.
Since several decades ago, carbon nanotubes (CNTs) have shown excellent electrical conduction properties, which has allowed them to be used as efficient interconnects decreasing the required space. Following the pioneering proposes of assembling 1D nanostructures into ordered arrays as a potential alternative for developing electronic nanocircuits, Ordered Networks based on Carbon Nanotubes (ON-CNTs) were designed **[1]** and their electronic transport properties studied **[1-2]** theoretically by computational calculations. This type of CNTs arrays can be seen as electronic nanocircuits, where the CNTs junctions (network nodes) could behave as the electronic nanodevices with different functions, which are interconnected by the CNTs with good electrical conduction properties behaving as the conducting wires.
In such type of nanocircuits, the electronic nanodevices functions would be directly dictated by the physical properties of the junctions between the pair of individual CNTs. In this sense, as the first stages towards developing this type of nanocircuits based on CNTs experimentally, it is of great importance to start studying the electrical conduction properties of a single cross-junction between a pair of individual CNTs and even the electrical conduction properties of an individual CNT under the presence of spots of different materials (*e.g.* Platinum, amorphous Carbon or even holes), whose disturbance should be

different on the electronic transport properties along the CNT, therefore dictating different functions for the potential nanodevices.
Here, we will show some of our recent results on the analysis of the electrical conduction properties of individual CNTs influenced by the presence of spots of different sizes of holes, amorphous Carbon or Platinum. These spots are generated on individual CNTs either by ion milling (holes) or by controlled deposition (amorphous Carbon or Platinum) with a gas injection system (of an organometallic molecule as precursor) and a focused ion beam (FIB) in a dual-beam scanning electron microscope (FIB-SEM).

[1] Romo-Herrera J.M. *et al.* **NanoLetters** **7** (3): 570 ***(2007)***.
[2] Romo-Herrera J.M. *et al.* **ACS Nano** **2** (12): 2585 ***(2008)***.

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9:30 AM BREAK

10:00 AM NM04.08.04
Defect Engineering of 2D Hexagonal Boron Nitride Using Electron and Ion Beam Methods Dana O. Byrne[1,2], Archana Raja[2], Aleksandr Noy[3,4], Jim Ciston[2], Alex Smolyanitsky[5] and Frances I. Allen[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Lawrence Livermore National Laboratory, United States; [4]University of California, Merced, United States; [5]National Institute of Standards and Technology, United States

Vacancy defect engineering of 2D membranes is essential for advancing fundamental understanding of ion and molecule transport through subnanometer pores for applications in filtration and molecular sensing. Nanopores in 2D materials are thermally and mechanically stable, and are tunable in terms of their shape, chemistry, distribution, and size. Therefore, nanopores in solid state 2D membranes can have fine control over ion selectivity and molecule permeability and have become primary candidates for selective transport membranes. For example, recent theory and simulation has shown that ion transport behavior in graphene-embedded crown ethers and in sub-nanometer pores in MoS2 can be strain-modulated [1,2]. This behavior mimics that of mechanosensitive ion channels in biological membranes. In pursuit of a solid-state analog for biological mechanosensitivity, heteroatomic 2D materials such as MoS2 and hexagonal boron nitride (hBN) present the advantage of pre-"functionalized" nanopores by default, eliminating the need for additional chemical functionalization of the pore edges, as would be the case for graphene.

In our work we use electron beam and ion beam methods to fabricate nanopores in 2D hBN. We use hBN exfoliated from bulk and monolayer CVD-grown hBN, mechanically transferring the samples to holey substrates to produce suspended hBN. Following the electron beam method in a transmission electron microscope (TEM), we modulate the electron dose to nucleate vacancy defects and grow nanopores of desired size and shape [3]. This method enables in-situ nanopore fabrication and imaging at atomic resolution but lacks the high throughput necessary for large scale fabrication. In contrast, the ion beam method uses ion bombardment in a focused ion beam (FIB) microscope to nucleate defects and produce a large distribution of nanopores [4], offering higher throughput albeit with less control over the exact nature and size of the resulting pores. We investigate nanopores generated by irradiation with gallium, neon, and helium ions using a multibeam FIB microscope and also explore a combined ion and electron beam approach in which we seed vacancy defects using the the light helium ions and controllably grow those defects with the electron beam of the TEM. Nanopores are imaged at atomic resolution using a double-aberration-corrected (scanning)TEM (STEM).

Nanopore structure is also sensitive to environmental effects, which can alter the nanopore's functional properties. We survey the local chemistry of the electron beam and ion beam fabricated nanopores using electron energy loss spectroscopy (EELS) in the TEM, probing the local bonding and chemical composition of the nanoporous regions based on variations in the core loss signals. We find that local chemistry of the nanopores is susceptible to change both inside the vacuum environment of the various microscopes as well as upon exposure to air. Hence, we argue that the investigation of the effect of the environment on the pore edge chemistry is essential for designing nanoporous 2D membranes for real life applications.

[1] Fang, A., K. Kroenlein, D. Riccardi, and A. Smolyanitsky. 2019. "Highly Mechanosensitive Ion Channels from Graphene-Embedded Crown Ethers." Nature Materials 18 (1): 76–81.
[2] Fang, A., K. Kroenlein, and A. Smolyanitsky. 2019. "Mechanosensitive Ion Permeation across Subnanoporous MoS2 Monolayers." The Journal of Physical Chemistry C.
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[4] Allen, Frances I. 2021. "A Review of Defect Engineering, Ion Implantation, and Nanofabrication Using the Helium Ion Microscope." Beilstein Journal of Nanotechnology 12: 633–64.

10:15 AM NM04.08.05
Vertical $Ti_3C_2T_x$ MXene Nanosheets under an Alternating Current Electric Field Changjae Lee[1], Soon Mo Park[1], Dong Ki Yoon[1] and Seon Joon Kim[2]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)

Aligning atomically thin two-dimensional materials vertically to the bottom has received much attention to utilize its structural anisotropy. In particular, various strategies have been reported to achieve vertical MXene, early transition metal carbide and nitride, for high capacitive performance. However, controlling the azimuthal orientation of the vertical MXene nanosheets cannot be achived with the previous methods, so its application was limited predominantly to capacitors. Here, vertical alignment induced by applying an alternating electric field to MXene colloid is presented. The reversible alignment switching of the colloid depending on the ON and OFF states of the electric field is observed through a polarized optical microscope. The immobilized nanosheets maintaining the colloidal orientation under the electric field can be obtained through in-situ freeze-drying. The oriented vertical MXene nanosheets exhibit an anisotropic electrical conductivity with a difference of nearly 9 times depending on the direction. In addition, various patterns composed of vertical MXenes are devoloped using diversified electrode designs. Based on these results, a new paradigm is suggested for various applications of vertical MXene such as sensors, optical polarizers, and heat-dissipating films, not limited to high-performance storage batteries.

10:30 AM NM04.08.06
TMDs Functionalized-SWCNTs Based Nanosensors for the Detection and Early Warning of Gas Leakage in Li-Ion Batteries Haifa Taoum, Ileana Florea, Mariam Ezzedine, Fatima Jardali and Costel-sorin Cojocaru; Ecole Polytechnique de Paris, France

Lithium-ion battery technology has seen immense success in consumer electronics and is becoming a leading technology for the mobility electrification with increasingly more attention being paid to battery safety problems[1]. Detecting gas molecules (including hydrogen, carbon monoxide, carbon dioxide, ethylene, and methane) released from battery thermal runaway using gas sensors is one of the effective strategies to achieve early safety warnings for Lithium-ion batteries. Benefiting from the superiorities of small size/compactness, high sensitivity, and stable performance, resistive gas sensors are considered promising candidates in this field.

Two-dimensional (2D) materials have demonstrated great potential in the field of gas sensing due to their layered structures. Particularly, 2D Transition Metal Dichalcogenides (TMDs) possess high surface areas and exhibit semiconducting properties with tunable band gaps making them excellent candidates for sensing applications[2]. Among the different TMDs materials, MoS_2 has gas sensing ability comparable to graphene and WS_2 can sense both toxic and non-toxic gases. In combination with the general benefits of 2D nanomaterials, the incorporation of one-dimensional (1D) nanomaterials with 2D TMDs is a recent approach for improving the gas sensing performance of these materials by the synergistic effects of hybridization. Indeed, hybrid (2D/1D) nanostructured materials provide the opportunity to fabricate and test the synergy between two or more different materials to achieve new functions. The use of single-wall carbon nanotubes (SWCNTs) as a skeleton for the TMDs enables the tuning of the electrical properties as the d orbitals from the transition metal M may partially overlap with the Π orbitals in the SWCNTs.

The purpose of this work is to fabricate a gas nanosensor based on TMDs@SWCNTs resistive channel and to further couple it to a Lithium-ion battery with the aim of detecting toxic byproducts released due to battery thermal runaway.

In this work, high-quality WS_2@SWCNTs and MoS_2@SWCNTs are fabricated using a bottom-up approach. First, the SWCNTs are synthesized via a chemical vapor deposition (CVD) method on a quartz substrate where the characteristics of the SWCNTs, i.e., diameter, density, and length are controlled by controlling the catalyst and CNT growth conditions. Next, mono and bilayer WS_2 and MoS_2 nanoflakes with diameters ranging between 10-20 nm are directly synthesized on the walls of the CNTs using homemade molecular beam evaporation/epitaxy (MBE) system.

To test the sensing abilities of WS_2@SWCNTs and MoS_2@SWCNTs, the electrical measurements are first performed under tunable relative humidity environments. An opposite electrical response towards humidity is obtained for the two types of heterostructures. The WS2@SWCNTs have shown a positive response followed by a negative response which highlights the change in the intrinsic properties of the material depending on the injected percentage of relative humidity. Whereas, the MoS_2@SWCNTs have shown only a positive response with the change in the percentage of relative humidity. This opposite response can be explained by the fact that intrinsically WS_2 behaves as an n-type semiconductor while MoS_2 behaves as a p-type semiconductor.

Further measurements will be performed to evaluate the selectivity, sensibility, and the ability to perform monitoring functioning of TMDs@SWCNTs nanosensors in the presence of different byproduct gas molecules. Finally, the TMDs@SWCNTs nanosensors will be coupled to a homemade Li-ion pouch cell battery and will be tested under harsh environments.

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10:45 AM NM04.08.07

In Situ Self-Healing of Beam Damaged MXenes under TEM Congjie Wei[1], Yanxiao Li[2] and Chenglin Wu[1]; [1]Missouri University of Science and Technology, United States; [2]New York University, United States

With the significant improvements and developments in transmission electron microscopes (TEM) techniques, accurate observation and identification is now more commonly adopted in angstrom-level precision, which reveals as sequential images about the real-space information. However, it still has difficulties to analyze the spatial defect distribution, phase transformation and dynamic phenomena since the TEM images can only record the appearances of the surface atoms while the out-of-plane information is severely missing. In this work, the healing process, characterized by the regeneration of crystalline structures within the e-beam burned holes, has been experimentally observed using TEM images. Modeling based on density functional theory and molecular dynamics was conducted to study the energy path as well as the stabilized phases of all stages before and after the healing of MXene. Furthermore, a first principle based deep learning algorithm is proposed and adopted to reconstruct the 3D transition states of a MXene healing process experimentally observed. Starting from the TEM image. Around hole atoms are assumed to have crystalline structure and set as the input along with the in-plane information of atoms that can be observed directly within the hole. Out-of-plane information of the latter group of atoms are then treated as the output of the algorithm along with the spatial distribution of all underlying atoms. The input and output information are reformed into graphical representations and treated as a graph reference problem. The trunk of this algorithm is set as a deep convolutional neural network incorporated with attention-based and non-attention-based components. To conform to the distance prediction, smooth potentials are constructed for Ti-Ti, Ti-C and C-C interactions based on first principle calculation. The minimum potential energy accumulation of all atoms within the hole is set as one of the convergence conditions of the algorithm along with the fitting of the training data sets. Our models are trained on defected MXene structures optimized with DFT, where different sizes and number of atoms are considered. The predictions of this algorithm fit well with the TEM images and help with the understanding of the healing processes observed in MXene materials.

SESSION NM04.09: Advanced Manufacturing of 2D Materials at the Atomic Scale IX
Session Chairs: Mohammad Naraghi and Chenglin Wu
Friday Afternoon, April 14, 2023
InterContinental, Fifth Floor, Ballroom B

2:00 PM NM04.09.02

Stability of Carbon Cluster on Candidate Substrates Evaluated by Molecular Dynamics Satoru Kaneko[1,2,3], Takashi Tokumasu[4], Manabu Yasui[1], Masahito Kurouchi[1], Masahiko Mitsuhashi[1], Ruei Yu[5], Shigeo Yasuhara[6], Tamio Endo[6], Musa Can[7], Kripasindhu Sardar[3], Sumanta K. Sahoo[3], Masahiro Yoshimura[3], Akifumi Matsuda[2] and Mamoru Yoshimoto[2]; [1]KISTEC, Japan; [2]Tokyo Institute of Technology, Japan; [3]National Cheng Kung University, Taiwan; [4]Tohoku University, Japan; [5]Asian University, Taiwan; [6]Japan Advanced Chemicals, Japan; [7]Istanbul University, Turkey

Choice of substrate is one of important factors for synthesis of thin films. For oxide materials, Schlom et.al. comprehensively investigate the thermodynamic stability of more than 80 binary oxides for epitaxial growth on silicon substrates , however thermodynamics stability literary evaluates the thermal stability between oxide and silicon, and does not include any crystallographic factors such as lattice mismatch and crystal orientation. The thermal stability is literally potential use for epitaxial growth as Schlom mentioned in his report[1].

In previous report, we employed an absorption energy between oxide and silicon (Si) substrate to predict the direction of crystal growth of oxide films, and experimentally deposited oxide films on Si substrates[2]. In this study, molecular dynamics was applied on carbon clusters placed on variety of substrates with vacuum slab (supercell), and the absorption energy was estimated on the supercell. Carbon films were experimentally deposited on the target substrates by pulsed laser deposition (PLD) in carbon dioxide atmosphere[3].

For evaluation of absorption energy, supercell was consisted of carbon clusters placed on variety of substrates with vacuum slab. As carbon clusters, (1) carbon atom, (2) six-membered ring (6-ring) and (3) seven six-membered rings (nanographene) were placed on SrTiO, silicon and sapphire substrates. On the surface of SrTiO(001), for an example, carbon clusters were placed on either Sr, Ti or O atom. And the absorption energy was estimated by using the density functional theory (DFT) with a semi-core pseudopotential. The generalized gradient approximation (GGA) method was used to obtain the electron density. The energy difference for self-consistent field was set at 1.0x10-6 Ha. Crystal structure of each substrates was optimized with periodic condition, and supercell consisting of slab and vacuum layer was used to optimize the top layer of substrate. After optimal surface was prepared on each substrates, supercell with graphitic cluster and slab was optimized, and total energy was estimated on supercell combined cluster and substrate (Etot_combined). Absorption energy was evaluated to be

Etot_sub + Etot_cluster - Etot_supercell,

where Etot_sub and Etot_cluster) were total energy of subs and graphitic cluster, respectively.

Among target substrates, the absorption energy were in range from 500 to 1000 J/mol. On the surface of Si(001), nanographene was stable with the absorption energy of ~940 J/mol, however 6-ring did not flatly cover the surface. The 6-ring vertically stood up on the Si(001), which impeded flat growth of graphene. Carbon clusters flatly covered only on SrTiO(001)[4].

For demonstration deposition, PLD method was employed with carbon dioxide atmosphere and the surface morphology was observed by atomic force microscopy (AFM). As expected, the surface morphology of SrTiO(001) shows flat surface with Ra ~ 63 pm, which is comparable with superflat CVD graphene annealed in carbon dioxide atmosphere (Ra~76 pm)[5]. In general, the deposited clusters migrate on the target surface, and the clusters are captured by a kink. Interestingly, graphene showed layer by layer growth and grew not from kink but the terrace edge. We will show optimized structure of supercell with candidate substrates, and compared with experimental results.

Acknowledgments
This study was supported in part by the Amada foundation under contract no. AF-2020227-B3, Tokyo Ohka Foundation for The Promotion of Science and technology no. 22117 and the Collaborative Research Project of the Institute of Fluid Science, Tohoku University. Special acknowledgment to the National Cheng Kung University 90 and beyond (NCKU'90).

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2:15 PM NM04.09.03
Mechanics of Biosurfactant Aided Liquid Phase Exfoliation of 2D Materials Xuliang Qian[1], Matteo Andrea Lucherelli[2], Céline Corcelle[2], Alberto Bianco[2] and Huajian Gao[1,3]; [1]Nanyang Technological University, Singapore; [2]CNRS, Immunology, Immunopathology and Therapeutic Chemistry, France; [3]A*STAR, Singapore

Biosurfactant-aided liquid-phase exfoliation (LPE) is emerging as a biocompatible, green, economical, safe, and efficient approach to prepare two-dimensional (2D) materials for biomedical applications. However, relatively little is known about the molecular mechanisms of this process. Herein, we present the first study of how flavin mononucleotide (FMN) interacts with hexagonal boron nitride (hBN) nanosheets in the context of LPE. We demonstrate that FMN molecules can self-assemble on hBN via π-π interactions, as well as intermolecular hydrogen bonds (H-bonds) between the isoalloxazine moieties. Binding free energy analysis has shown FMN to be an efficient surfactant for LPE of hBN in water. According to the theoretical simulations, stable water suspension of hBN were experimentally obtained by LPE using FMN. With this work, we aim to exemplify how molecular dynamics (MD) simulation can predict and guide empirical LPE experiments, direct the surfactant screening and improve scalable production of 2D materials for biomedical applications.

2:30 PM BREAK

3:00 PM NM04.09.04
Two-Dimensional Sheets Derived from Non-Van der Waals Crystals: Mechanism of the Mechanochemical Synthesis Jing-Yang Chung, Yanwen Yuan, Tara P. Mishra, Silvija Gradečak and Slaven Garaj; National University of Singapore, Singapore

Recent studies of mechanically-synthesised two-dimensional (2D) sheets from otherwise three-dimensional non-van der Waals (vdW) crystals are harbingers of a new approach for materials engineering. Yet, the nature in which 2D sheets can be derived from a non-layered, isotropic crystal remains unknown. In the case of boron, the complex crystal structure of the bulk material and its abundance of phases, as well as the influence of crystal orientation and thickness on structure interpretation, make it challenging to determine the nature of the exfoliated 2D sheets. Here we demonstrate, using aberration-corrected scanning transmission electron microscopy (STEM) and extensive structural modelling, that liquid phase exfoliated boron sheets consist of a planar arrangement of icosahedral subunits, formed from the cleaving of the {001} planes of β-rhombohedral boron. Our experimental results supported by density functional theory (DFT) calculations show that planar defects in the form of stacking faults — which form parallel layers of faulted planes in the same orientation — play a significant role in the exfoliation of 2D sheets from bulk boron, reducing the energy required to cleave the bulk {001} surface by ~ 36%. We demonstrate that planar defects are key to an engineerable pathway for the exfoliation of 2D sheets from boron, and more broadly of other covalently-bonded materials. This provides opportunities for the design of new 2D materials from non-vdW crystals.

3:15 PM NM04.09.05
Domain-Dependent Surface Adhesion in Twisted Few-Layer Graphene Valerie Hsieh[1], Dorri Halbertal[1], Nathan R. Finney[1], Ziyan Zhu[2,3], Eli Gerber[4], Michele Pizzochero[2], Emine Kucukbenli[5,2], Gabriel R. Schleder[2], Mattia Angeli[2], Kenji Watanabe[6], Takashi Taniguchi[6], Eun-Ah Kim[4], Efthimios Kaxiras[2], James Hone[1], Cory Dean[1] and Dmitri N. Basov[1]; [1]Columbia University, United States; [2]Harvard University, United States; [3]Stanford University, United States; [4]Cornell University, United States; [5]Boston University, United States; [6]National Institute for Materials Science, Japan

Twisted van der Waals heterostructures are a highly tunable platform due to the many degrees of freedom available for controlling their electronic and chemical properties. Here, we focus on the local stacking order of low-degree twisted graphene heterostructures as a platform for manipulating the surface chemistry of this class of materials. We report the emergence and engineering of stacking domain-dependent surface adhesion in twisted few-layer graphene. Minimally twisted double bi- and tri-layer graphene heterostructures were fabricated and imaged using mid-infrared near-field optical microscopy and atomic force microscopy to identify rhombohedral and Bernal stacking domains. We then observed that metallic nanoparticles and liquid water exhibit a domain-selective adhesion on these heterostructures, with preference for the rhombohedral stacking configurations. Finally, we used an atomic force microscope to manipulate nanoparticles located at certain stacking domains, resulting in a local reconfiguration of the moiré superlattice near the nanoparticles at the μm-scale. Our findings establish a new approach to controlling moiré chemistry and nanoengineering.

3:30 PM NM04.09.06
Orientation Dependent Large Plasticity of Single Crystalline Gallium Selenide Song Xu[1], Heyi Wang[2] and Yang Lu[2]; [1]The Chinese University of Hong Kong, Hong Kong; [2]City University of Hong Kong, Hong Kong

Unlike metals and alloys with high ductility, inorganic semiconductors are mostly ceramics with brittle nature due to covalent/ionic bonding. Recent studies showed that some layered/van der Waals semiconductors could exhibit substantial room-temperature ductility, despite that the underlying mechanisms remain to be understood. Here we report that van der Waals semiconductor GaSe can have crystal orientation-dependent large plasticity at room temperature. Through in situ tensile and compressive experiments inside electron microscopes, we demonstrate that microfabricated GaSe can have substantial ductility loaded along and slanted with the intralayer direction, while showing predominantly elastic deformation perpendicular to the intralayer direction until brittle fracture. We further reveal that, despite the interlayer gliding as the main mechanism, cross-layer slips induced by buckling associated with stacking faults also contribute to the plasticity. This study offers insights to understand the ductility and plasticity of van der Waals semiconductors and shows promising flexible/deformable electronics and energy device applications.

3:45 PM NM04.09.07
Computational Perspectives on Chalcogen-Terminated MXene Pernilla Helmer, Jonas Bjork and Johanna Rosen; Linköping University, Sweden

The MXenes are a family of 2D materials which have since their discovery in 2011 received ever increasing attention. MXenes consists of alternating monoatomic layers of carbon or nitrogen and transition metals, with the metal always as the outermost layers. These structural and compositional degrees of freedom of the MXenes let them display a wealth of properties and characteristics. Many different MXenes are investigated for a variety of applications, ranging from energy storage to catalysis and water desalination. The outermost transition metal layers of MXenes are in general decorated with additional atoms and molecules, so called terminations. These also influence the MXene properties, and thus increase even further the potential for materials design and property tailoring of MXenes.

At the beginning of 2022, a new way of synthesizing S-terminated MXene through delamination of van der Waals multilayer parent phases was reported, along with two novel 2D structures synthesized in this way. These 2D structures can be viewed either as MXenes with chalcogen terminations, or – as suggested by the authors – as transition metal carbo-chalcogenides (TMCCs), to emphasize their similarity to another large family of 2D materials: the transition metal dichalcogenides (TMDCs). This structural duality of the new sub-family of chalcogen-terminated MXenes further emphasizes their relevance and calls for more in-depth investigations. Thus, we consider the possibility to expand this sub-family, by computationally evaluating the stability of the corresponding van der Waals parent phases, as well as other related potential parent phases. We confirm the results reported in the original publication, discuss computational results for prediction of further members of the chalcogen-terminated MXenes, and present materials properties of identified stable phases.

SESSION NM04.10: Virtual Session
Session Chairs: Fatemeh Ahmadpoor, Wenpei Gao, Mohammad Naraghi and Congjie Wei
Wednesday Morning, April 26, 2023
NM04-virtual

8:00 AM NM04.10.01
Large Area Synthesis of Transition Metal Chalcogenides as Semiconducting Channels in Transistors and Photodetectors Jinbo Pang[1], Chongyang Hou[1] and Hong Liu[1,2]; [1]University of Jinan, China; [2]Shandong University, China

The electronic and optoelectronic properties[1-3] of 2D materials and their stacking heterostructures[4-6] have inspired enormous interests. WSe_2, as a p-type semiconductor,[7,8] represents a foremost building block in the p-n junctions. WSe_2 shall possesses the features of large area, homogeneity, and precise layer control. To date, there is yet an ideal synthesis method ever reported. First, we present a facile approach to prepare high-quality wafer-scale homogenous WSe_2 full films. In brief, we first deposit a thin layer of metal and then do the selenization. We can control the film thickness of WSe_2 in a chemical equilibrium environment. Second, we present a facile approach to prepare high-quality large-area homogenous WSe_2 full films. In brief, we developed a pre-seeding strategy for depositing W-containing precursors over dielectric substrates, which form well-distributed particles as seeding center. Upon the salt-assisted sublimation of tungsten oxides, the WSe_2 forms over the seeded substrates (at high temperature) in the Se-rich atmosphere. Eventually the high quality of the synthetic film has been reflected on the high performances of photodetectors and field-effect transistors. Our finding may pave the way of wafer scale integration of transition metal dichalcogenides in the integrated flexible electronics.
Keywords: WSe_2; optoelectronics; photodetectors; transistors; transition metal dichalcogenides; $PdSe_2$; layered noble metal dichalcogenides
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8:15 AM NM04.10.02

Gas-Phase "Prehistory "of CVD Grown MoS_2 —Atomistic Reaction Mechanism of MoO_3 and S_2 Precursors Zhengzheng Dang and Yanming Wang; Shanghai Jiaotong University, China

Two-dimensional MoS_2 is one of the most promising materials for next-generation electric and optoelectronic devices due to its semi-conducting nature and plenty of other suitable properties. The primary approach to synthesizing large-scale and high-quality MoS_2 monolayers is chemical vapor deposition (CVD), where the gas phase process is a crucial step in CVD. However, few experiments have given a detailed explanation of the gas-phase reaction mechanism, which is essential for researching the reactive pathways to precursors and controllable growth of MoS_2. This motivates the development of atomic and molecular dynamic simulation to give micro-scale insights. Here we used reactive molecular dynamics (RMD) simulations to investigate the reaction mechanism of MoO_3 and S_2 precursors in the gas phase. Firstly, the bond-order-based algorithm was developed to automatically analyze products' real-time distribution and we used cluster analysis to screen the main intermediate product ($Mo_xO_yS_z$) statistically. Then we developed path-tracking tools based on target atoms to obtain the trajectory distribution of all Mo clusters in the entire reaction stage, and determine the most critical reaction pathway in statistics. Finally, we mapped the energy barrier pathways and did ReaxFF-NEB calculations to verify the feasibility of distributed reaction pathways, also explored their sensitivity to temperature and Mo/S ratio in the gas phase. These results provide valuable insight into guiding rational synthesis of MoS_2 and other transition metal dichalcogenides by the CVD process.

8:30 AM NM04.10.03

Bendable Xenes-Based Membranes Chiara Massetti[1,2], Christian Martella[1], Daya Dhungana[1], Carlo Grazianetti[1] and Alessandro Molle[1]; [1]CNR-IMM Agrate Brianza, Italy; [2]University of Milano-Bicocca, Italy

Xenes, the monoelemental family of two-dimensional (2D) materials, exhibit a variety of interesting physical properties with potential exploitation in nanotechnology [1]. In the framework of flexible electronics, photonics and related applications including wearable and strain-responsive devices, 2D bendable membranes are highly desired. We report here on the realization of Xenes-based membranes by taking benefit from the recently developed scheme of the Xene heterostructure, namely silicene-stanene grown by molecular beam epitaxy [2], where silicene is sandwiched in between an alumina encapsulation layer on the top surface and stanene on thin Ag(111) crystal at the bottom face. When the so-grown Xenes-base membrane is transferred onto a flexible substrate [3], the application of macroscopic mechanical deformations induces a strain-responsive behavior in the Raman spectrum of silicene. Under tensile strain, the bendable membrane shows Raman frequency shift comparable to other promising flexible systems, like those based on transition metal dichalcogenides, and high stability up to one thousand bending cycles. We also show that the membranes under elastic tension relaxation are prone to form microscale wrinkles displaying a local generation of strain in the silicene layer consistent with that observed under macroscopic mechanical deformation. Moreover, similarly to the unstrained case [4], optothermal Raman spectroscopy measurements reveal a curvature-dependent heat dispersion in silicene. Finally, as compelling evidence of the technological potential of the membranes, we demonstrate that they can be readily introduced into a lithographic process flow resulting in the definition of flexible device-ready architectures. Bendable Xenes-based memebranes may thus hold high potential for flexible and silicon-compatible applications [5]. The work is within the ERC-COG 2017 Grant N0. 772261 "XFab" and ERC-PoC 2022 Grant N. 101069262 “XMem”.

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8:45 AM NM04.10.04

Controlling Few-Donor Quantum Dots Coupled to SETs Using Surface Gates Pradeep Namboodiri[1], Fan Fei[1], Jonathan Wyrick[1], Xiqiao Wang[2], Joseph Fox[1], Utsav Utsav[1] and Richard Silver[1]; [1]National Institute of Standards and Technology, United States; [2]Rigetti Computing, United States

Monolayer phosphorous dopant devices with high dopant confinement are an emerging methodology that allows the measurement and manipulation of single or few-dopant atom quantum dots for quantum computation and arrayed devices for analogue quantum simulation. STM fabrication of these devices provides a unique ability to create near perfect atomic structures on clean atomically ordered silicon in ultrahigh vacuum conditions. The devices are encapsulated in situ with a UHV grown ~30 nm epitaxial silicon layer followed by metallization for contact to the buried device components and top gates. In this talk we will present a single electron transistor (charge sensor) coupled to a few donor cluster where the chemical potential of the central island and the charge occupation on the few atom cluster are controlled via two capacitively coupled in-plane gates while current through the source/drain-leads and the SET island are used to determine the charge state. An external aligned metal gate on the surface is integrated ex situ using HfO2 as a dielectric. We confirm the functionality of the surface gates and measure a near zero-leakage current over a large gate range. Based on charge stability measurements, the surface gates have a similar lever arm as compared to the in-plane gates and therefore greatly expand the effective device gating range. We demonstrate the tuning of a few-donor cluster coupled to an SET charge sensor using surface gates while we use in-plane gates to load/unload individual electrons from the donor-cluster as well as demonstrate spin sensitive readout in a magnetic field. We will discuss the design, fabrication, and use of surface top gates to individually or globally address individual components in few-donor/quantum dot devices as well as a 2x2 arrayed device.

April 11 - April 25, 2023

Symposium Organizers
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SESSION QM01.01: Engineering/Controlling the Properties I
Session Chairs: Santosh KC and Elton Santos
Tuesday Morning, April 11, 2023
Marriott Marquis, Fourth Level, Pacific A

10:30 AM *QM01.01.01
Broken Symmetry in van der Waals Layers Stuart S. Parkin; Max Planck Institute of Microstructure Physics, Germany

Van der waal's structures provide for many opportunities for breaking symmetry. We show that the presence of topological chiral spin textures in both Fe_3GeTe_2[1] and and $Cr_{1+\delta}Te_2$ ($\delta \approx 0.3$)[2], namely Néel skyrmions, is the result of a lowering of their nominally centrosymmetric structures. High resolution x-ray diffraction from thin lamellae of these compounds shows an asymmetric distribution of Fe vacancies in the former and in the latter a superstructure formed by Te atoms within the vdw gaps. On the other hand we show non-reciprocal superconducting properties in Josephson junctions formed by proximitizing the van der Waals compound $NiTe_2$ using superconducting electrodes formed from niobium electrodes[3]. We discuss proximity induced superconductivity in several other van der Waals materials that show evidence for intrinsic time reversal symmetry breaking.

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11:00 AM QM01.01.02
Asymmetric Magnetic Proximity Interactions in Ferromagnet/Semiconductor van der Waals Heterostructures Scott Crooker[1], Junho Choi[1], Christopher Lane[2] and Jian-Xin Zhu[2]; [1]National High Magnetic Field Lab, United States; [2]Los Alamos National Laboratory, United States

The ability of short-range proximity interactions to imbue magnetic functionality into otherwise nonmagnetic materials has exciting prospects for devices that combine the optical and electrical properties of monolayer semiconductors with additional magnetic tuning parameters that couple directly to spin and valley pseudospin. The atomically-smooth surfaces that are nowadays routinely achieved with van der Waals (vdW) materials allow for nearly ideal interfaces between monolayer transition-metal dichalcogenide semiconductors (such as WSe_2 or MoS_2) and magnetic substrates (such as EuO or CrI_3). Magnetic proximity interactions (MPIs) between atomically-thin semiconductors and two-dimensional magnets therefore provide a means to manipulate spin and valley degrees of freedom in nonmagnetic monolayers, without the use of applied magnetic fields.

In such vdW heterostructures, MPIs originate in the nanometer-scale coupling between the spin-dependent electronic wavefunctions in the two materials, and historically their overall effect is regarded as an effective magnetic field acting on the semiconductor monolayer. Here we demonstrate that this picture, while appealing, is incomplete: The effects of MPIs in vdW heterostructures can be markedly *asymmetric*, in contrast to that from an applied magnetic field [1]. Valley-resolved optical reflection spectroscopy of $MoSe_2/CrBr_3$ vdW structures reveals strikingly different energy shifts in the K and K' valleys of the $MoSe_2$, due to ferromagnetism in the $CrBr_3$ layer. Strong asymmetry is observed at both the A- and B-exciton resonances. Density-functional calculations indicate that valley-asymmetric MPIs depend sensitively on the spin-dependent hybridization of overlapping bands, and as such are likely a general feature of such hybrid vdW structures. These studies suggest routes to selectively control *specific* spin and valley states in monolayer semiconductors. [1] J. Choi, C. Lane, J.-X. Zhu, S. A. Crooker, Asymmetric magnetic proximity interactions in $MoSe_2/CrBr_3$ van der Waals heterostructures, *in press (Nature Materials); arXiv:2206.09958*

11:15 AM *QM01.01.03
Floquet Engineering of Quantum Materials on Demand Junyi Shan[1], Mengxing Ye[2], Hao Chu[1], Sungmin Lee[3], Je-Geun Park[3], Leon Balents[2] and David Hsieh[1]; [1]California Institute of Technology, United States; [2]University of California, Santa Barbara, United States; [3]Seoul National University, Korea (the Republic of)

Tuning properties of quantum materials with light has a long history - from simple heating to driving selective excitations inside the materials. While many novel optical engineering mechanisms have been proposed, there has been a gap regarding the experimental realizations of light modulating material properties without being absorbed, i.e., the Floquet engineering strategy. In this talk, I will discuss our recent experiments on using light to Floquet engineer van der Waals materials in a heating-free manner. We achieved reversible control of the nonlinear optical properties and the bandgap size of the antiferromagnetic insulator MnPS$_3$ on a timescale of 100 femtoseconds. I will also discuss how we can combine this Floquet principle and the versatile material platforms in order to create new phases of matter out of equilibrium.

11:45 AM *QM01.01.04
Spin Dynamics in Electron-Doped Cr2Ge2Te6 and Other van der Waals Magnets Hidekazu Kurebayashi; University College London, United Kingdom

Charge carrier injection into materials are a powerful way to enhance targeted material properties as well as to discover novel, hidden quantum phases. For van der Waals (vdW) materials, it is possible to inject charge carriers into nano-meter thick exfoliated flakes by solid-state and electrolyte gating, and into bulk flakes by chemical doping within vdW gaps, so-called intercalation. This approach is very effective in controlling magnetism, e.g. a dramatic change of Curie temperature of vdW magnet such as Fe3GeTe2 and Cr2Ge2Te6 been observed by electrostatic carrier injection [1, 2] and intercalation [3]. Here, we present our work on spin dynamics characterisation of Na-intercalated, electron-doped Cr2Ge2Te6. We have successfully intercalated Na atoms into the vdW gap of pristine Cr2Ge2Te6 and observed clear enhancement of its conductivity due to electron doping and an increase of Curie temperature from 65 K (undoped case) to 240 K (doped-system).
We characterised the spin dynamics properties by ferromagnetic resonance techniques and extrapolate the Gilbert damping to be in the order of 10^{-4} at higher temperatures, which is at least an order of magnitude smaller compared to spin dynamics response in other vdWs magnetic systems [4]. We also find the doped system to host exotic magnetic state at low temperature, where we pick up signatures of canonical spin glassiness in the DC magnetometry and AC magnetic susceptibility measurements. Hence, a bulk Na-Cr2Ge2Te6 system seems to have intriguing magnetic properties which are not realised by the on-chip electrostatic doping in 2D-flakes [1,2].
If time permits, we will show relevant spin dynamics properties for other materials to compare their results with those of Na-CGT.

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SESSION QM01.02: Engineering/Controlling the Properties II
Session Chairs: Srinivasa Rao Singamaneni and Michael Susner
Tuesday Afternoon, April 11, 2023
Marriott Marquis, Fourth Level, Pacific A

1:30 PM *QM01.02.01
Skyrmionics and Meronics Based on Inversion Symmetric Layered Ferromagnets Luis Balicas[1,2]; [1]Florida State Univ, United States; [2]National High Magnetic Field Lab, United States

Here, we will discuss the role of topological spin textures on the electrical and thermal transport properties of layered ferromagnets like Fe$_{3-x}$GeTe$_2$ and Fe$_{5-x}$GeTe$_2$. In Fe$_{3-x}$GeTe$_2$, a layered ferromagnetic displaying a Curie temperature $T_c \approx 220$ K, we observe[1] anomalous transport variables for magnetic fields m_0H applied along the gradient of the chemical potential generated by thermal gradients or electrical currents, a configuration that should not lead to their observation due to the absence of Lorentz force. These anomalous planar quantities are found to not scale with the component of the planar magnetization ($M_{\|}$), showing instead a sharp decrease beyond $m_0H_{\|} = 4$ T which is the field required to align the magnetic moments along $m_0H\|$. We argue that locally chiral spin structures, such as skyrmions, and probably hybrid domain walls, lead to a field dependent spin-chirality. This in turn generates a novel type of topological transport in the absence of interaction between the magnetic field and electrical or thermal currents. For Fe$_{5-x}$GeTe$_2$ ($T_c \approx 310$-330 K) this unconventional topological transport is observed at, and beyond room temperature, correlating with the observation of merons through Lorentz transmission electron microscopy (LTEM)[2]. LTEM in Fe$_{5-x}$GeTe$_2$ also reveals the coexistence of merons with skyrmions upon approaching its magnetostructural transition at $T_s \approx 110$ K, due to a progressive rotation of the magneto-crystalline axial anisotropy towards the c-axis. The presence of these spin textures and their coexistence is exposed by thermal transport measurements as a function of the temperature, which unveils, for example, an anomalously large Nernst effect. Therefore, in Fe$_{5-x}$GeTe$_2$ the formation and stabilization of distinct thermally driven topological spin textures can be chosen on demand by just adjusting the temperature. Given that Fe$_{5-x}$GeTe$_2$ can be grown in large area substrates and its Ni and Co doped crystals display T_cs well above room temperature, we suggest that this compound along with its doped variants, can, not only open a new era in skyrmionics, but also open a new field of research, that of meronics.

[1] J. Macy *et al*., Appl. Phys. Rev. **8**, 041401 (2021).
[2] B. Casas *et al*., (under review).

2:00 PM *QM01.02.02
Tailored Heterointerfaces in 2D Atomic Crystals and 2D Molecular Frameworks Thomas Kempa; Johns Hopkins University, United States

The tuning of lateral and vertical interfaces between 2D materials offers a powerful means of eliciting new phenomena. Vertical stacking of 2D atomic crystals or synthesis of 2D crystals with embedded lateral junctions furnishes materials with heterointerfaces that support unique excitonic, electronic, and magnetic properties. Here we present our progress towards the investigation of two new interfaces in and between 2D materials. First, we perform directed growth of heterostructured transition metal dichalcogenide nanoribbons with the goal of achieving precise control over the type, location, and extent of lateral heterointerfaces in these crystals. Precise spatial control over the placement of these heterointerfaces provides new avenues for tuning the optoelectronic properties of these crystals and permits realization of candidate single-photon emitters. Second, we explore the design of heterointerfaces between 2D atomic crystals and 2D molecular assemblies. The intersection of these atomic lattices with synthetic molecular lattices adds new degrees of freedom for tuning and instantiating electronic states through control of spin-orbit coupling gap, charge transfer, and dielectric environment. We demonstrate how such architectures offer fertile ground to explore new photonic devices.

2:30 PM BREAK

SESSION QM01.03: Engineering/Controlling the Properties III
Session Chairs: Angela Hight Walker and Elton Santos
Tuesday Afternoon, April 11, 2023
Marriott Marquis, Fourth Level, Pacific A

3:00 PM *QM01.03.01
Spin-Charge-Lattice Coupling in 2D Magnetic Semiconductor CrSBr John W. Cenker[1], Kaichen Xie[1], Shivesh Sivakumar[1], Geoff Diederich[1], Harvey Yang[1], Zhaoyu Liu[1], Avalon Dismukes[2], Daniel Chica[2], Xiaoyang Zhu[2], Xavier Roy[2], Jiun-Haw Chu[1], Di Xiao[1,1], Ting Cao[1] and Xiaodong Xu[1,1]; [1]University of Washington, United States; [2]Columbia University, United States

The interplay of spin and charge in magnetic semiconductors lies at the heart of the field of spintronics and has attracted significant interest for new computing technologies. In this talk, I report our recent progress in studying and controlling spin-charge coupling in the layered antiferromagnetic semiconductor CrSBr. Such coupling enables the anisotropic Wannier-type excitons to serve as a powerful sensor of the interlayer magnetic order, and the generation of giant tunneling magnetoresistance (TMR) in magnetic tunnel junction (MTJ) heterostructures. Using these probes, we found that the magnetic order is extremely tunable by the application of tensile strain, with a reversible antiferromagnetic to ferromagnetic phase transition occurring at large but experimentally feasible strains. We utilize this phase transition to realize a straintronic MTJ, with zero-field TMR switching approaching 10,000% at 30 K and remaining above 100% until ~ 140 K. Moreover, the fine and continuous control of interlayer magnetic exchange coupling enables us to create metastable domains which switch stochastically with a strain-tunable sigmoidal response curve akin to the stochastic binary neuron or probabilistic bit. Our results establish CrSBr as an exciting platform for harnessing spin-charge-lattice coupling towards new, highly tunable 2D devices for spintronic applications, such as magnetic memory, random number generation, and probabilistic and neuromorphic computing.

3:30 PM QM01.03.02
Magnetic Order Change and Proximity Coupling of Single Photon Generation in van der Waals Heterostructures Xiangzhi Li[1], Andrew Jones[1], Junho Choi[1], Huan Zhao[1], Vignesh Chandrasekaran[1], Michael T. Pettes[1], Andrei Piryatinski[1], David Aaron Broadway[2], Maerta Tschudin[2], Patrick Reiser[2], Patrick Maletinsky[2], Nikolai Sinitsyn[1], Scott Crooker[1] and Han Htoon[1]; [1]Los Alamos National Laboratory, United States; [2]University of Basel, Switzerland

Quantum light emitters (QEs) that are stable and can be positioned deterministically are of the utmost importance for the evolution of solid-state photonic quantum technologies. Highly chiral QEs are necessary for the construction of advanced quantum networks. Local strain-induced proximity effects can be employed in concert with strain engineering to generate chiral quantum effects (QEs) in WSe2/NiPS3 heterostructures.[1] One of the numerous advantages of these on-chip QEs is that they may be easily coupled to other photonic and/or plasmonic devices. In addition, magnetic two-dimensional materials provide unparalleled opportunities for studying magnetic material responses at the two-dimensional limit. These magnetic two-dimensional materials provide the optimal platform for controlling spin and photon degrees of freedom (DOF), facilitating the regulation of spin degeneracy, and enhancing light-matter interactions of quantum effects in atomically thin semiconductor nanostructures. Nonetheless, the origin of this finding is not completely understood. Here, we present the most recent experimental research discoveries that address the underlying puzzles. Using scanning NV microscopy, we are able to offer direct evidence of a change in magnetic order following the nano-indentation of NiPS3. Our findings are consistent with temperature-dependent magneto-PL studies. In addition, we have used the nano-indentation technique with other members of the TMPX3 family, the same proximity effect is in action here as well. Our recent findings establish TMD/TMPX3 heterostructures as viable material platforms for the continuing investigation of novel emergent phenomena and the advancement of solid-state quantum transduction and sensing technologies.

[1]X. Li et. al arXiv:2203.00797

3:45 PM *QM01.03.04
Topology for Energy Efficient Spintronics and Energy Conversion Claudia Felser; Max Planck Institute, Germany

Topology, a mathematical concept, recently became a hot and truly transdisciplinary topic in condensed matter physics, solid state chemistry and materials science. All 200 000 inorganic materials were recently classified into trivial and topological materials, such as topological insulators, Dirac, Weyl and nodal-line semimetals, and topological metals [1]. More than 25% of all materials host topological bands around the Fermi energy. Beyond the single particle picture, we have identified first antiferromagnetic topological materials [2]. Experimentally, we have realized ferromagnetic materials, examples are Co_2MnGa and $Co_3Sn_2S_2$. Surprisingly all crossings in the band structure of ferromagnets are Weyl nodes or nodal lines [3]. Mn_3Sn and $YbMnBi_2$ are examples of non collinear antiferromagnetic Weyl semimetals, which show giant values for the anomalous Hall and Nernst effect [4]. It is expected that many more ferromagnetic materials with Weyl Fermions are out there, also in 2D materials. In the context of real space topology, skyrmions and antiskyrmions are a possible new direction for new data storage [5]. Our goal is to identify new quantum-materials for highly efficient spintronics, quantum computing and energy conversion.

4:15 PM QM01.03.05
A Systematic DFT+U and Quantum Monte Carlo Benchmark of Magnetic Two-dimensional (2D) CrX_3 (X = I, Br, Cl, F) Daniel Wines, Kamal Choudhary and Francesca Tavazza; National Institute of Standards and Technology, United States

The search for two-dimensional (2D) magnetic materials has attracted a great deal of attention because of the experimental synthesis of 2D CrI_3, which has a measured Curie temperature of 45 K. Often times, these monolayers have a higher degree of electron correlation and require more sophisticated methods beyond density functional theory (DFT). Diffusion Monte Carlo (DMC) is a correlated electronic structure method that has been demonstrated successful for calculating the electronic and magnetic properties of a wide variety of 2D and bulk systems, since it has a weaker dependence on the Hubbard parameter (U) and density functional. In this study we designed a workflow that combines DFT+U and DMC in order to treat 2D correlated magnetic systems. We chose monolayer CrX_3 (X = I, Br, Cl, F), with a stronger focus on CrI_3 and $CrBr_3$, as a case study due to the fact that they have been experimentally realized and have a finite critical temperature. With this DFT+U and DMC workflow and the analytical method of Torelli and Olsen, we estimated an upper bound of 43.56 K for the T_c of CrI_3 and 20.78 K for the T_c of $CrBr_3$, in addition to analyzing the spin densities and magnetic properties with DMC and DFT+U. We expect that running this workflow for a well-known material class will aid in the future discovery and characterization of lesser known and more complex correlated 2D magnetic materials.

SESSION QM01.04: Sensing/Imaging/Probing/Magneto-Optical Properties I
Session Chairs: Charudatta Phatak and Michael Susner
Wednesday Morning, April 12, 2023
Marriott Marquis, Fourth Level, Pacific A

8:30 AM *QM01.04.01
Magneto-Optical Properties of Perovskite Thin Films and Crystals Angela R. Hight Walker; National Institute of Standards and Technology, United States

Hybrid lead halide perovskites have opened a new era for photovoltaics research over the last decade due to their high energy conversion energy. These materials are promising for future electronics and optoelectronics and applications in spin-electronic devices due to their unique properties, such as high coherent emission, spin-orbit coupling, and strong light-matter interaction [1]. Recent experimental and theoretical studies have shown that the polar organic cations affect the lattice polarization, giving rise to a ferroelectric behavior and enhancing their photovoltaic performance [2]. Furthermore, magnetism in halide perovskite at room temperature has been confirmed, suggesting a route toward spintronics applications based on magneto-optical perovskites [3-4]. However, the hybrid perovskites' magnetic properties are not well understood. Our work reports magneto-photoluminescence (MPL) and magneto-Raman (MR) measurements of methylammonium lead iodide $CH_3NH_3PbI_3$ ($MAPbI_3$) ~ 280 nm thin film materials at low temperatures (<60 K), where the crystalline structure is in the orthorhombic domain. We obtained different MPL spectra from random spots on the sample surface and fitted them with gaussian curves at 55 K and 1.6 K. The MPL spectra confirm the existence of a dual emission peak at a low temperature, consistent with previous works [5]. For each spot, we applied a magnetic field up to 9T in the perpendicular direction of the surface and analyzed the MPL plots as a function of the external magnetic field. Changes in the intensity, the central position, and the FWHM of the gaussian components were observed in the MPL spectra. We also compare the response of the thin film at room temperature (tetragonal domain) under the external magnetic field to the low temperature data.
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[2] Frost, J.M.,et al, Nano Lett., (2014) 14.
[3] Kepenekian,M., et al., J. Phys. Chem. Lett., (2017) 8.
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9:00 AM QM01.04.02
Probing Collective Magnetic Excitations in Magic-Angle Twisted Bilayer Graphene Correlated Insulating States with Electron Spin Resonance Spectroscopy Rupini Kamat[1], Sandesh Kalantre[1], Aaron Sharpe[2], Takashi Taniguchi[3], Kenji Watanabe[3], Marc Kastner[1] and David Goldhaber-Gordon[1]; [1]Stanford University, United States; [2]Sandia National Laboratories, United States; [3]National Institute for Materials Science, Japan

In MATBG, correlated insulating (CI) states emerge at an integer number of electrons per moiré unit cell. These states are suspected to emerge from successive filling of the fourfold degenerate spin and valley states of the nearly-flat miniband [1][2]. This would imply that different CI states in MATBG have different associated spin/valley flavor polarizations. Indeed evidence of an anomalous hall effect in MATBG, stemming from polarized orbital magnetic moments, has been observed at CI states associated with specific integer filling factors [3][4][5], albeit in only a handful of samples. However, the order in which the spin/valley flavor states are populated remains unknown, as does the nature of how electrons in these states couple to one another and to external magnetic fields. One potential technique for learning the flavor polarization properties of these CI states is to probe their excitations using resistively-detected electron spin resonance (ESR). We implement this by measuring near-DC transport through an encapsulated MATBG device, noting the change in resistivity when we couple in microwave magnetic fields from a microfabricated superconducting coplanar waveguide.

In general, ESR is a form of microwave spectroscopy: Microwaves are shone on the material, and when the energy of the microwaves exactly matches the energy cost to generate an excitation of a magnetic state, the material will absorb the microwaves. In resistively-detected ESR, this resonant microwave absorption is observed via a corresponding change in resistance, through heating of the electron system or some other mechanism. This measurement has been performed on several CVD graphene samples [6][7][8][9] as well as on MATBG with spin-orbit coupling induced by a proximal TMDC layer [10], but has yet to be seen in more canonical MATBG with clear CI states. Given the suspected spin/valley polarization of CI states and the ability of ESR to probe collective magnetic excitations, ESR offers the prospect of unambiguously establishing the flavor polarization of the CI states. Understanding the magnetic ground state of these CI states may also offer clues to the nature of superconducting pairing that occurs upon doping these flavor-polarized states.

This work is primarily supported by the U.S.Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, under contract DE-AC02-76SF00515.

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[10] Morissette, Erin, et al. *arXiv preprint arXiv:2206.08354* (2022).

9:15 AM QM01.04.03
Magnetic Properties of CrX_3 in Excited States Prakash Mishra and Tunna Baruah; The University of Texas at El Paso, United States

The CrX_3 (X=Cl,Br,I) are a new class of 2D magnetic semiconductor that show interesting properties such as ferromagnetism in monolayers, magneto-optical Kerr and Faraday effects, large tunnel magnetoresistance etc. The magnetism in these materials can be tuned through chemical doping or external field. In this talk we present our theoretical studies on the magnetic properties of the excited states of CrX_3 monolayer. Our calculations are carried out using density functional theory for different types of excitations on a cluster model of chromium trihalides. The cluster model of the monolayer is built with six Cr centers whereas a bilayer has two six-center Cr-halide clusters. These clusters are cut-outs of the bulk but are further passivated and optimized.

We performed the three types of excited state calculations namely a) photo-induced excited state, b) excited states with different symmetry, and c) spin-flip excitons. The photo-induced single particle-hole excited states are being calculated with the perturbative delta-SCF method. The dipole and spin allowed transitions are selected to determine the possible set of excited states within the range of 1.5-3.5 eV. The calculated magnetic properties such as spin moments, exchange coupling constants, and magnetic anisotropy energies of these systems will be presented and discussed.
This work is supported by the National Science foundation through grant no. DMR-2105109.

9:30 AM *QM01.04.04
Imaging Domain Switching and Revealing Emergent Orders in 2D Antiferromagnets Liang Wu; University of Pennsylvania, United States

The family of monolayer two-dimensional (2D) materials hosts a wide range of interesting phenomena, including superconductivity, charge density waves, topological states and ferromagnetism, but direct evidence for antiferromagnetism in the monolayer has been lacking. Antiferromagnets have attracted enormous interest recently in spintronics due to the absence of stray fields and their terahertz resonant frequency. Despite the great advantages of antiferromagnetic spintronics, controlling and directly detecting Neel vectors in 2D materials have been challenging. In my talk, I will show that we have developed a sensitive second harmonic generation (SHG) microscope and detected long-range Neel antiferromagnetic (AFM) order down to the monolayer in MnPSe3[1]. In MnPSe3, we observed the switching of an Ising-type Neel vector reversed by the time-reversal operation. We rotated them by an arbitrary angle irrespective of the lattice by applying uniaxial strain. The phase transition in the presence of strain in MnPSe3 falls into the Ising universality class instead of the XY type, and the Ising Neel vector is locked to the strain. I will also talk about using the newly developed optical confocal microscopy to image other emergent orders in 2D antiferromagnets[2, 3,4].
References
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10:00 AM BREAK

SESSION QM01.05: Sensing/Imaging/Probing/Magneto-Optical Properties II
Session Chairs: John Cenker and Elton Santos
Wednesday Morning, April 12, 2023
Marriott Marquis, Fourth Level, Pacific A

10:30 AM QM01.05.01
Coherent Spin-Phonon Coupling in the Layered Ferrimagnetic Crystal $Mn_3Si_2Te_6$ Luis M. Martinez[1,2], Yu Liu[2], Cedomir Petrovic[3], Marshall Campbell[2], Michael T. Pettes[2], Rohit Prasankumar[2], Srinivasa Rao Singamaneni[1] and Prashant Padmanabhan[2]; [1]The University of Texas at El Paso, United States; [2]Los Alamos National Laboratory, United States; [3]Brookhaven National Laboratory, United States

Layered magnetic materials have enormous potential in enabling the next generation of high-speed nanoscale information storage and spintronic technologies. In order to realize their promise, it is of critical importance that we understand how lattice structure and magnetic order are coupled, particularly on their intrinsic ultrafast time scales. Here, we use ultrafast optical microscopy to study the coherent lattice dynamics of the pseudo-van der Waals ferrimagnet $Mn_3Si_2Te_6$. Our results reveal strong coherent phonon oscillations under near-infrared pumping that persist from room temperature down to below the magnetic ordering temperature of ~75 K. An analysis of the frequency of these modes as a function of temperature highlights a significant stiffening of the oscillatory frequency across the critical temperature that cannot be explained using a thermal expansion model. Instead, we suggest that this is due to an exchange-mediated contraction of the lattice, highlighting a strong magneto-structural coupling in this material. This is mirrored in the temperature dependence of incoherent dynamics, measured across the magnetic phase transition. Our findings showcase the ultrafast dynamics in this semiconducting layered ferrimagnet and suggest a new route for their optical control through their intertwined electronic, lattice, and spin degrees of freedom.

10:45 AM *QM01.05.02
Imaging of Magnetic Domain Behavior in van der Waals Ferromagnets Charudatta Phatak[1], Arthur McCray[1,2], Yue Li[1], Eric Qian[2], Jianguo Wen[1], Wei Wang[1], Xuedan Ma[1], Duck Young Chung[1], Mercouri G. Kanatzidis[2] and Amanda Petford-Long[1,2]; [1]Argonne National Laboratory, United States; [2]Northwestern University, United States

Magnetic van der Waals (vdW) materials are increasingly studied due to the discovery of ordered ferromagnetism down to monolayer thickness as well as them hosting chiral and topologically protected magnetic domains. The realization of such states in van der Waals ferromagnets opens further opportunities to explore and control their behavior using interfacial interactions such as strain or interfacing with dissimilar materials to create novel functionality in heterostructures. In this work, we will present the magnetic domain behavior of two iso-structural compounds – Cr2Si2Te6 (CST) and Cr2Ge2Te6 (CGT). They both belong to the R–3 space group, with Cr forming honeycomb network and octahedrally coordinated with Te atoms. CST shows a Curie temperature of 30 K while CGT has a Curie temperature of 70 K. We have performed an in-situ study and directly imaged the magnetic domain structure under varied temperature and external magnetic fields using cryo-Lorentz transmission electron microscopy (LTEM). They both show easy-axis of magnetization along the c-axis of the crystal. In CGT, we observe the formation of Bloch-type domains and bubble lattices with mixed chirality. Despite a lack of chiral energy terms in CGT, we have also observed topologically protected lattices containing homochiral bubbles. By contrast, in CST, we observe formation of Néel-type stripe domains and skyrmions. Both these materials also possess a strong magneto-elastic coupling. We will discuss the implications of strain and magnetostriction on the alignment of magnetic domains and skyrmion/bubble lattices in these materials.

11:15 AM QM01.05.03
Coherent Exciton-Magnon-Photon Interaction in van der Waals Magnets Florian Dirnberger[1], Rezlind Bushati[1,2], Biswajit Datta[1] and Vinod Menon[1,2]; [1]The City College of New York, United States; [2]The City University of New York, United States

Strong light-matter interaction results in the formation of half-light half-matter quasiparticles (polaritons) that take on the advantages of both. The advent of van der Waals magnets that host electronic excitations (excitons) correlated to the magnetic order presents a unique opportunity to implement strong light-matter coupling and thereby manipulate electronic and spin degrees of freedom via light. Here we report our recent works on such strongly coupled exciton

polaritons that are correlated with the underlying magnetic order. Specifically, we will discuss the formation of polaritons in antiferromagnetic insulator NiPS3 and the use of polariton nonlinear spectroscopy to shed light on the nature of excitons in this system [1]. Following this, we will discuss our work on magnetic semiconductors and the potential to modify magneto-optical response via strong exciton-photon coupling.
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11:30 AM *QM01.05.04
Scanning Probe Microscopy of Stray Magnetic Fields Produced by 2D Magnets Martino Poggio; University of Basel, Switzerland

The ability to map magnetic field sensitively and on the nanometer-scale – unlike global magnetization or transport measurements – overcomes ensemble or spatial inhomogeneity in systems ranging from arrays of nanometer-scale magnets, to superconducting thin films, to strongly correlated states in van der Waals heterostructures. Local imaging of nanometer-scale magnetization, Meissner currents, or current in edge-states is the key to unraveling the microscopic mechanisms behind a wealth of new and poorly understood condensed matter phenomena.
I will discuss efforts in our group aimed at developing and applying high-sensitivity, high-resolution, non-invasive magnetic scanning probes. In particular, we have been pushing two types of sensors to their limits: mechanical sensors, based on NW cantilevers, and superconducting sensors, based on nanometer-scale superconducting quantum interference devices. I will also discuss recent imaging experiments with these tools on 2D magnets, including EuGe$_2$ and Cr$_2$Ge$_2$Te$_6$.

SESSION QM01.06: Sensing/Imaging/Probing/Magneto-Optical Properties III
Session Chairs: Wenli Bi and Srinivasa Rao Singamaneni
Wednesday Afternoon, April 12, 2023
Marriott Marquis, Fourth Level, Pacific A

1:30 PM QM01.06.01
Sensing the Local Magnetic Environment Through Optically Active Defects in a Layered Magnetic Semiconductor Julian Klein[1], Zhigang Song[2], Benjamin Pingault[2], Florian Dirnberger[3], Hang Chi[1], Jonathan Curtis[2], Rami Dana[1], Rezlind Bushati[3], Jiamin Quan[3], Lukas Dekanovsky[4], Zdeněk Sofer[4], Andrea Alu[3], Vinod Menon[3], Jagadeesh Moodera[1], Marko Loncar[2], Prineha Narang[2] and Frances Ross[1]; [1]Massachusetts Institute of Technology, United States; [2]Harvard University, United States; [3]The City College of New York, United States; [4]Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Czechia

Van der Waals layered magnets have triggered strong interest for studying low-dimensional magnetism. [1] A particularly attractive material is the magnetic semiconductor CrSBr. [2] The combination of air stability, energy band gap of approximately 1.6eV and high Néel temperature (132 K) provide several exciting avenues for scientific exploration. [3, 4, 5] CrSBr shows strong-light matter interaction with excitonic emission embedded in a rich magnetic phase diagram. Defects have been shown to be important for the magneto-transport in this material [5] and are generally attractive candidates for engineering artificial magnetic textures. [6]

Here, we show magnetically correlated optically active defects in CrSBr. [7] Optical emission properties in multilayer samples are excellent with 1 meV linewidth. We identify these properties as originating from a quasi-1D electronic behavior due to an anisotropic band dispersion and weak interlayer hybridization, allowing us to probe low-dimensional properties in a multilayered sample with high structural quality. [8] From scanning probe microscopy we observe different types of defects, with the Br vacancy as the most abundant defect (~ 10^{13} cm^{-2}). In low-temperature (T = 4K) photoluminescence and photoluminescence excitation spectroscopy we characterize the defect emission. The emission is polarized, shows power saturation, and can be efficiently populated by resonant excitation of excitonic resonances. We also probe the exciton and defect emission in magneto-PL. Both excitonic and defect emission energies are directly affected by changes in the magnetic order, but the shifts of the defect emission are up to 100 times weaker (depending on the orientation of the external magnetic field), highlighting the layer-localized nature of the defect wave function. Most strikingly, a recently discussed defect-related magnetic phase at low temperature (30 - 40K) [5] directly correlates with a strong narrowing of the defect emission, suggesting a direct change in the spin of the involved bands of the defect transition. We will finally discuss the coupling mechanisms of the defects and their interactions in the context of the quasi-1D electronic structure. We conclude that CrSBr is an exciting platform for investigating optically active defects that are correlated with the magnetic phase diagram, properties that open new avenues for tailor-made complex magnetic phases with easy direct optical access.

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1:45 PM QM01.06.02
Inversion Symmetry Breaking Revealed in Fe$_{3-x}$GeTe$_2$ by Second Harmonic Generation Kaixuan Zhang and Je-Geun Park; Seoul National University, Korea (the Republic of)

Symmetry establishes the cornerstone of modern condensed matter physics since symmetry breaking would trigger exotic phase transitions and produce emergent quantum phenomena. Therefore, tailoring symmetry by symmetry engineering provides a promising and powerful method to control matter's quantum characteristics and functionalities. As a new-and-rare case of van-der-Waals topological ferromagnetic metal, Fe$_3$GeTe$_2$ (FGT) receives intensive attention recently and exhibits a spectrum of intriguing properties. Thanks to the large Berry curvatures of its topological Noda-line bands, FGT displays large anomalous Hall conductivity[1] and anomalous Nernst effect[2]. More importantly, gigantic intrinsic spin-orbit torque[3-6] by current has been revealed both theoretically and experimentally in single FGT without additional heavy-metal layer, rendering it to be an ideal and unique model system for the new conceptual spin-orbit torque and spintronics. Pristine FGT hosts a hexagonal structure with the centrosymmetric space group P6$_3$/mmc. If inversion symmetry is broken by reducing the space group to a non-centrosymmetric one, more novel phenomena and rich physical properties might present in such a system with both time-reversal and inversion symmetry breaking.

In this work, we investigated the symmetry of $Fe_{3-x}GeTe_2$ by second harmonic generation (SHG) and convergent beam electron diffraction (CBED) techniques. We discovered the inversion symmetry breaking of $Fe_{3-x}GeTe_2$, with space group reduced from the centrosymmetrical $P6_3/mmc$ to a noncentrosymmetrical polar space group P3m1. This new symmetry was co-evidenced by SHG and CBED. Such symmetry reduction and inversion symmetry breaking give rise to non-linear optical response, i.e., three-fold SHG pattern. It also backs up the gigantic spin-orbit torque in FGT in our previous report[3][5]. Our work enriches the scope of symmetry engineering for exotic quantum properties and spintronics.

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2:00 PM BREAK

SESSION QM01.07: Pressure/New Detection Techniques/Doping
Session Chairs: Luis Balicas and Elton Santos
Wednesday Afternoon, April 12, 2023
Marriott Marquis, Fourth Level, Pacific A

3:00 PM *QM01.07.01
Studies of Topological Magnets Under High Pressure Wenli Bi; The University of Alabama at Birmingham, United States

Eu-based magnetic materials with strong local magnetic moments have attracted much attention as intrinsic magnetic topological semimetal candidates, providing a platform to control topological states by manipulating magnetism. Here in this work, we apply pressure as an effective way to tune magnetic exchange interaction and the electronic states. Due to the small sample size in high-pressure studies using diamond anvil cells, it is technically challenging to characterize material physical properties. With the development of synchrotron X-ray techniques (diffraction, scattering, and spectroscopy) combined with extreme sample environment (pressure, temperature), information on magnetic and electronic states can be obtained under pressure on a microscopic scale. In this talk, I will discuss our recent interesting results on controlling magnetism, valence, and crystal structure in selected Eu-based topological magnetic materials using high pressure and synchrotron X-ray tools.

3:30 PM QM01.07.02
Probing the Two-Dimensional Materials with Momentum and Spin Resolved Photoelectron Microscope Der Hsin Wei[1], Tzu-Hung Chuang[1], Chuan-Che Hsu[1], Jyun-Syong Jhuan[1], I-Chun Yeh[2,1], Wei-Sheng Chiu[3,1], Wei-Ting Hsu[2], Shangjr Gwo[2,1] and Chih-Kang Shih[4,2]; [1]National Synchrotron Radiation Research Center, Taiwan; [2]National Tsing Hua University, Taiwan; [3]National Taiwan University of Science and Technology, Taiwan; [4]University of Texas at Austin, United States

Two-dimensional (2D) materials are under intensive study for their unconventional properties and potential applications. During the course of study, gaining knowledge of a material's electronic structures is often the critical step. However, this is not an easy task for the conventional photoelectron/photoemission spectroscopy (PES) setup considering there is a large mismatch between the lateral dimensions of a single flake of 2D van der Waals materials (~ µm) and the detection area defined by the spectrometer (~ mm). For 2D materials, the proper PES detection scheme needs to include additional position sensitivity. At Taiwan Photon Source beamline 27A2 (TPS 27A2), we have set up a photoelectron-based momentum microscope whose position sensitivity is given by the imaging lens sitting in front of the hemispherical analyzer (HSA) [1]. In addition, the microscope can record spin-resolved images via inserting an iridium-based spin mirror. In this presentation, I will describe our microscope's performance through selected commissioning studies conducted on the single crystal surface and monolayer/multilayer transition metal dichalcogenides (TMDs). In brief, our studies indicate that the real-space images taken with work function contrast may serve as an alternative means to identify the number of layers in a vdW thin film, and the momentum-space images offer a graphical means to measure the twisted angle between stacked 2D layers directly.

[1] Chuang, Jhuang, Hsu, Chiu, Yeh, and Wei (in preparation).

3:45 PM *QM01.07.04
Direct Visualization of Electronic Transport in a Quantum Anomalous Hall Insulator Katja C. Nowack; Cornell University, United States

A quantum anomalous Hall (QAH) insulator is characterized by quantized Hall and vanishing longitudinal resistances at zero magnetic field that are protected against local perturbations and independent of sample details. This insensitivity makes the microscopic details of the local current distribution inaccessible to global transport measurements. Accordingly, the current distributions that give rise to the transport quantization are unknown. In this talk, I will discuss how we use magnetic imaging to directly visualize the transport current in the QAH regime. As we tune through the QAH plateau by electrostatic gating, we clearly identify a regime in which the sample transports current primarily in the bulk rather than along the edges. We observe the current entering the device through a hot-spot located in the corner of the contact with its location switching, when we switch the sample's magnetization. Furthermore, we image the local response of the equilibrium magnetization to electrostatic gating. Combined, these measurements suggest that the current flows through incompressible regions whose spatial structure changes throughout the QAH regime. Identifying the appropriate microscopic picture of electronic transport in QAH insulators and other topologically non-trivial states of matter is a crucial step towards realizing their potential in next-generation quantum devices.

4:15 PM QM01.07.05
Evolution of the Magnetic Properties via Pressure in Ternary Transition Metal Chalcogenides Rubyann Olmos[1,2], Po-Hao Chang[2], Prakash Mishra[2], Tunna Baruah[2], Rajendra Zope[2] and Srinivasa Rao Singamaneni[2]; [1]Rice University, United States; [2]University of Texas at El Paso, United States

Pressure has been used as a mechanism to induce structural and magnetic phase transitions in many materials whose layers are linked via vdW forces. Such materials with weakly held layers allow relatively easy manipulation of the superexchange mechanism. Using hydrostatic pressure as a disorderless means to manipulate the interlayer coupling, we apply pressure to $Mn_3Si_2Te_6$, and $CrSiTe_3$ up to ~1 GPa. Magnetic property measurements with the application of pressure on $Mn_3Si_2Te_6$ revealed that the ferrimagnetic transition temperature increases while the opposite occurs for $CrSiTe_3$. It is also observed that pressure effects the saturation magnetization for both materials by decreasing up to pressures of 0.9 GPa. However, for $Mn_3Si_2Te_6$ the magnetization changes from below pristine magnetization to being larger than pristine magnetization once reaching 1.06 GPa of pressure. The magnetization as a function of pressure reveals no clear trend, whereas the magnetic ordering temperature steadily increases or decreases for $Mn_3Si_2Te_6$ and $CrSiTe_3$, respectively, as a function of increasing pressure. Theoretical calculations show that the overall pressure effect on layer separation, bond angle, and exchange coupling are found to strongly influence the change in subsequent magnetic characteristics in $Mn_3Si_2Te_6$. We confirm that the exchange coupling in $Mn_3Si_2Te_6$ is strongly frustrated, and we find that the first nearest neighbor interaction is the most dominant component that shows a dependence with pressure. In $CrSiTe_3$, the exchange coupling parameters exhibit very little dependence on the pressure.

SESSION QM01.08: Growth Intercalculation, Magnetic and Magneto-Optical Properties

Session Chairs: Je-Geun Park and Srinivasa Rao Singamaneni
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM QM01.08.01
Investigating Structural and Magnetic Properties of Low-Dimensional Fe_xNbSe_2 Guanming Li, Matthew Erodici and Kwabena Bediako; University of California, Berkeley, United States

Magnetically intercalated 2D transition metal dichalcogenides (TMDs) represent a promising class of low-dimensional magnetic materials for ultralow-power applications based on the manipulation of electron spin. The ability to tune the magnetic properties based on the choice of intercalant and host lattice offers a versatile platform for designing novel 2D magnets that would be difficult to access from their bulk counterparts, yet the phase space afforded by this approach remains largely unexplored. Here, we study the chemical intercalation of Fe^{2+} ions into few-layer 2*H*-$NbSe_2$ to engineer long-range antiferromagnetic order approaching the 2D limit. Utilizing Raman spectroscopy, we investigate the structural changes between $NbSe_2$ and Fe_xNbSe_2 and track the phonon modes accompanied by Fe^{2+} intercalation to gauge the extent and homogeneity of intercalant ordering. Additionally, we monitor the effects of thermal annealing at various temperatures on the intercalation amount and degree of ordering in the material to potentially find an onset temperature for leveraging the intercalation process. Furthermore, we characterize the magnetic behavior of the system via variable-temperature magnetotransport measurements. We anticipate our results to be relevant in understanding the intercalation of related transition metal intercalated TMD systems and aid in the scalability and development of 2D heterostructures for use in next generation low-power electronic and spintronic devices.

5:00 PM QM01.08.02
Phase-Controlled Growth of Two-Dimensional Magnetic Chromium Tellurides Jiefu Yang, Bijun Tang, Naizhou Wang, Yao Wu and Chao Zhu; Nanyang Technological University, Singapore

The discovery of ferromagnetic ordering in two-dimensional (2D) materials has sparked significant interest in both academic and industrial communities for its great potential in fundamental research and novel application such as spintronics. Recently, chromium tellurides (Cr_xTe_y) with various phases and compositions, are emerging as a promising class of novel 2D ferromagnets, attributed to their tunable magnetic ordering, high Curie temperature (T_C), and desirable stability. It is believed that the rich structural and magnetic variations of Cr_xTe_y should arise from the position and content of the intercalated Cr atoms between adjacent layers. However, the synthesis of ultrathin and high-quality Cr_xTe_y with controlled phases and compositions is challenging, not to mention the in-depth investigation of the effect of intercalated Cr atoms on magnetic ordering. In this work, by carefully tuning the reaction temperature and carrier gas flow rate, controllable growth of various Cr_xTe_y, including CrTe, Cr_2Te_3, Cr_5Te_8, and $CrTe_2$, is achieved with the facile one-step chemical vapor deposition (CVD) method. Atomic-resolution scanning transmission electron microscopy-annular dark field imaging is adopted to unravel the phases of as-synthesized Cr_xTe_y. Magnetic properties of prepared Cr_xTe_y are probed using both reflective magnetic circular dichroism and magnetotransport measurements. Near-rectangular hysteresis loops not only indicate ferromagnetism with strong magnetic anisotropy in all Cr_xTe_y flakes but also suggest the high quality of the CVD-grown samples. Remarkably, the strong correlation between phase and magnetic ordering of Cr_xTe_y is comprehensively studied and reported for the first time. Density functional theory calculations further reveal the difference in ferromagnetic ordering between various phases, which can be well interpreted by the magnetic anisotropy and Stoner criterion. This work sheds light on the scalable and controllable synthesis of 2D magnetic materials and highlights the great potential of Cr_xTe_y for future spintronic applications.

5:00 PM QM01.08.04
Terahertz Time-Domain Spectroscopy of the van der Waals Ferromagnet CrI_3 Jonghyeon Kim[1], Minseong Lee[2], Junghyun Kim[3], Je-Geun Park[3] and Jae Hoon Kim[1]; [1]Yonsei University, Korea (the Republic of); [2]Los Alamos National Laboratory, United States; [3]Seoul National University, Korea (the Republic of)

CrI_3 is a ferromagnetic van der Waals insulator with Ising-type long-range ordering below the Curie temperature of 61 K. We have studied the low-frequency electrodynamics of bulk CrI_3 single crystals by using terahertz time-domain spectroscopy at various magnetic fields and temperatures. We identified a zero-field magnon mode at 2.5 cm^{-1} at 1.5 K and modeled the magnetic Hamiltonian based on the behavior of the magnon under the external magnetic field along each crystal axis. Also, the evidence of coupling between the crystal structure and magnetism was discovered from the temperature and magnetic field dependence of certain E_u in-plane optical phonon modes. Our results suggest a strong the Kitaev-type interaction and present the correct structure-field phase diagram of bulk CrI_3.

5:00 PM QM01.08.06
Correlated and Almost-Flat Hund's Metallic Phase in Kagome Nodal Surface Metal $Sc_3Mn_3Al_7Si_5$ Subhasis Samanta[1], Jungseek Hwang[2], Kwang-Yong Choi[2] and Heung-Sik Kim[1]; [1]Kangwon National University, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of)

Kagome lattice has been actively studied for possible realization of frustration-induced two-dimensional flat bands and a number of correlation-induced phases. The commonality of all realistic Kagome systems proposed, however, is that flat bands are quite dispersive and a charge doping is necessary to shift flat bands close to the Fermi level. Search for Kagome systems with nearly dispersionless flat band close to the Fermi level is an ongoing study. Here, by combining theoretical and experimental tools, we present $Sc_3Mn_3Al_7Si_5$ as a novel realization of correlation-induced almost-flat bands in the Kagome lattice in the vicinity of the Fermi level. Our measurements of magnetic susceptibility, nuclear magnetic resonance, and optical conductivity hint signatures of ferromagnetic fluctuation at very low temperature below 2 K. Below 30 K, temperature dependence of resistivity alludes to development of electronic correlation. Intriguingly, our dynamical mean-field calculations reveal existence of nearly flat band in proximity of Fermi level at k_z=0 plane, induced by electron correlations. Additionally, renormalized nodal surface bands, protected by a product of two-fold screw rotation and time reversal symmetry, exist at k_z=π plane in the Brillouin zone. We observe a transition from a coherent to an incoherent metallic phase, driven by strong Hund's coupling and temperature. With spin-orbit coupling, flat band becomes almost-flat and may potentially host significant spin Hall signatures. These findings broaden a new prospect to harness correlated topological phases in 3*d*-based Kagome systems.

SESSION QM01.09: Sensing/Imaging/Probing/Magneto-Optical Properties IV
Session Chairs: Santosh KC and Elton Santos
Thursday Morning, April 13, 2023
Marriott Marquis, Fourth Level, Pacific A

8:30 AM *QM01.09.01
All-Optical Control of Spin in a 2D van der Waals Magnet Maciej Dabrowski[1], Shi Guo[1], Mara Strungaru[2], Paul Keatley[1], Withers Freddie[1], Elton J. Santos[2,2,3] and Robert J. Hicken[1]; [1]University of Exeter, United Kingdom; [2]University of Edinburgh, United Kingdom; [3]Donostia International Physics Center (DIPC), Spain

Two-dimensional (2D) van der Waals magnets provide new opportunities for control of magnetism at the nanometre scale via mechanisms such as strain, voltage and the photovoltaic effect. While ultrafast laser pulses promise the fastest and most energy efficient means of manipulating electron spin, little is known so far about how laser pulses influence the spins in 2D magnets. Stacking of 2D magnetic layers promises to deliver heterostructures with new and tuneable magnetic and magneto-optical properties. Optical control of their magnetic state would provide new opportunities in both data storage and photonics, where the non-volatility of magnetism could deliver improved energy efficiency.

The search for all optical switching (AOS) of magnetic order was ignited by the observation of ultrafast demagnetization in Ni on timescales of ~100fs [1]. AOS of the magnetization was observed in ferrimagnetic GdFeCo [2] but was found to be a thermally driven toggle switching, dependent upon the exchange coupling and different demagnetization times of Gd and FeCo [3]. Helicity dependent AOS has been observed in a number of materials including [Co/Pt] multilayers [4] but usually requires multiple fs optical pulses in a process that is believed to involve full demagnetization followed by the growth of domains driven by thermally generated spin currents. More recently, toggle switching was observed in rare-earth-free synthetic ferrimagnet structures, with switching driven by the flow of optically induced spin current between the constituent ferromagnetic layers [5].

The selective optical excitation of spin-polarised electrons by circularly polarized light in direct band gap semiconductors is well established. Optical orientation of spin within magnetic semiconductors such as GaMnAs has been found to induce coherent precessional dynamics of the Mn moments [6]. However, AOS was not observed and interest waned due to the stubbornly low Curie temperature (~200K). The electronic structure of transition metal dichalcogenides (TMDCs) also permits selective optical excitation of spin-polarised electrons. By tuning to the band gap, circularly polarized light can excite spin-polarised electrons within just one of the K(K') valleys [7]. Transfer of optically excited carriers across the interface within a WSe_2/CrI_3 bilayer leads to the presence of an interfacial exchange field that influences the photoluminescence polarization dependence and intensity [8].

Here we demonstrate laser-induced magnetic domain formation and all-optical switching in ferromagnetic CrI_3 [9]. While the magnetism of bare CrI_3 layers can be manipulated with single laser pulses through thermal demagnetization processes, all-optical switching is achieved in CrI_3/WSe_2 bilayers. The out-of-plane magnetization is switched with multiple femtosecond pulses of either circular or linear polarization, while single pulses result in less reproducible and partial switching. Our results suggest that the switching is driven by spin-dependent interfacial charge transfer between the WSe_2 and the CrI_3.

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9:00 AM QM01.09.02
Resonant X-ray Photon Correlation Spectroscopy Experiments on the van der Waals Antiferromagnet $NiPS_3$ Rajan Plumley[1,2] and Joshua J. Turner[1]; [1]SLAC National Accelerator Laboratory, United States; [2]Carnegie Mellon University, United States

In magnetic Van der Waal (vdW) materials such as the Transition Metal Chalchogenophosphates (TMCPs), magnetic interactions between the transition metal cations are confined to the planes of the vdW layers, and thus present the opportunity to study physical 2D magnetic systems in the laboratory. One such TMCP is the antiferromagnetic Mott-insulator $NiPS_3$, which has recently established itself as a "magnetic analog to graphene" due to its two-dimensionality, hexagonal arrangement of cations, and tuneable transport properties. We employ resonant X-ray diffraction to directly probe the in-plane magnetic order in $NiPS_3$, and with the combination of X-ray Photon Correlation Spectroscopy (XPCS) and X-ray Photon Fluctuation Spectroscopy (XPFS), analyze its dynamics at time-scales ranging from seconds to the ultra-fast regime. We will share and discuss our first X-ray results and future outlooks for experiments using this approach.

9:15 AM QM01.09.03
Tunable Magnetic Ordering at the Interface of all-van der Waals Layered Heterostructures via Spin-Orbit Coupling Eun-Mi Choi[1,2], Taesoo Kim[1,2], Byeong Wook Cho[1,2] and Young Hee Lee[1,2,2]; [1]Institute for Basic Science (IBS), Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of)

Spin-orbit coupling (SOC) possesses versatile functionalities including magneto-crystalline anisotropy, Dzyaloshinskii–Moriya interaction, and effective conversion from charge to spin current. Engineering the strength of SOC is a core to control the conversion efficiency, complex magnetic spin structures, and spin torque. Layered van der Waals (vdW)-transition metal dichalcogenides (TMDs) with intrinsic large SOC and associated spin textures have attracted immense interest. In this work, we use all-van der Waals-layered heterostructure, Fe_3GeTe_2 (FGT)/monolayer W1-xVxSe$_2$, (x = 0, 0.05, 0.1 and 0.15), for SOC strength effect on magnetic ordering of FGT. We found that various magnetic ordering such as spin-flop, spin-flip and inverted magnetization is induced as varying V-doping concentration (i.e. modulating SOC strength). The large SOC enhances magneto-crystalline anisotropy at the proximitized FGT and subsequently stabilizes the long-range magnetic order in FGT. It results in elevating ferromagnetic Curie temperature. We further demonstrate a sharp magnetic switching from antiferromagnetic to ferromagnetic in FGT/$W_{0.95}V_{0.05}Se_2$, which is characteristic of the synthetic antiferromagnetic structure. Our proof-of-concept result offers the possibility of interface-tailoring spintronics including two-dimensional magnetoresistive random access memory toggle switching.

9:30 AM *QM01.09.04
Topology in van der Waals Antiferromagnets Je-Geun Park; Seoul National University, Korea (the Republic of)

Two-dimensional (2d) magnetism has been at the center of many decades-long researches as it offers the cleanest test bed for new ideas and physics. The prime example is the Berezinskii–Kosterlitz–Thouless transition of the XY model, which was discovered in the early 1970s. Simply, it heralds the beginning of topological physics, a new chapter in condensed matter physics. Despite the immense interest from the theoretical side, there has been relatively slow progress on an experimental side: most of which has depended on either a quai-2d materials or thin films grown by a pulsed laser deposition technique.

However, the discovery of van der Waals magnets in 2016 has completely transformed the field of 2d magnetism by providing real 2d magnets that can be experimentally studied using many tools. Despite their short lifetime, van der have magnets have been used for excitingly interesting reports and ideas. With so many successes, the eyes now turn to new directions: one of which is the exploration of possible topological physics in 2d van der Waals magnets.

Among several candidates, noncollinear metallic van der Waals antiferromagnets can reveal particularly rich topological physics due to their diverse magnetic ground states. We are particularly interested in triangular lattice antiferromagnets. By using metallic triangular antiferromagnet $Co_{1/3}TaS_2$, we show that it exhibits a substantial anomalous Hall effect (AHE) related to its noncollinear magnetic order. We show that AHE in $Co_{1/3}TaS_2$ is characterised by the toroidal moment, a vortexlike multipole component that arises from a combination of chiral lattice and geometrical frustration. We will further examine this discovery from the viewpoint of neutron scattering data.

10:00 AM BREAK

SESSION QM01.10: Emerging Materials/Properties I
Session Chairs: Santosh KC and Je-Geun Park
Thursday Morning, April 13, 2023
Marriott Marquis, Fourth Level, Pacific A

10:30 AM QM01.10.01
SANS Study of New Nanometer-Sized Magnetic Structure of the Elemental Nd Lisa De Beer-Schmitt[1], H. Suriya Arachchiage[2], Lazar Kish[3], Binod K. Rai[1,4], Andrew May[1], David Parker[1], Ganesh Pokharel[1], Wei Tian[1], David Mandrus[2], Markus Bleuel[5], Zahir Islam[6], G Fabbris[6], Haoxiang Li[1], Shang Gao[1], Hu Miao[1], Sean M. Thomas[7], Priscila Rosa[7], Joe D. Thompson[7], Shizeng Lin[7] and Andrew Christianson[1]; [1]Oak Ridge National Lab, United States; [2]The University of Tennessee, Knoxville, United States; [3]Brookhaven National Laboratory, United States; [4]Savannah River National Labortory, United States; [5]National Institute of Standards and Technology, United States; [6]Argonne National Laboratory, United States; [7]Los Alamos National Laboratory, United States

The rare earth neodymium exhibits exceedingly complex magnetic order and series of phase transitions. In this talk, we present results from small-angle neutron scattering (SANS) measurements as a function of temperature and applied magnetic field to study magnetic correlations on nanometer length scales in Nd. The SANS measurements reveal a set of new modulation vectors that characterize the ordered spin configuration. These spin textures exhibit changes in magnitude and direction that are phase dependent. Between 5.9 and 7.6 K, the additional modulation vector has a magnitude Q = 0.12 \AA^{-1} and is primarily due to order of the Nd layers which contain a center of inversion. In this region of the phase diagram, the SANS measurements also identify a phase boundary at $\approx$1 T which was not previously seen in thinner samples. An important feature of these modulation vectors is that they indicate the presence of nanometer length scale spin textures which are likely stabilized by frustrated Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions.

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10:45 AM QM01.10.03
Proliferation of Topological Magnetic Defects in a 2D Square Lattice Erxi Feng[1], Anjana Samarakoon[1], Xianghan Xu[2], Xiaojian Bai[1], Chaowei Hu[3], Lei Ding[1], Yaohua Liu[1], Ni Ni[3], Christian Batista[4], David A. Tennant[1], Sang-wook Cheong[2] and Huibo Cao[1]; [1]Oak Ridge National Laboratory, United States; [2]Rutgers University, United States; [3]University of California, United States; [4]University of Tennessee, United States

Magnetic domain walls and their crossings as magnetic vortices are typical magnetic topological defects existing in many magnetic materials. While visualizing them and their evolution under field at the atomic level are rarely reported except for magnetic skyrmions. Here I will present the proliferation of topological magnetic defects in a 2D square lattice under field, seen by neutrons.
By introducing Ising spins in a 2-dimensional (2D) bi-layer square lattice $Tb_2SrAl_2O_7$, we realized a frustrated magnet where no long-range magnetic order was found upon cooling to 100 mK. Using the local magnetic susceptibility method with polarized neutrons, we revealed canted Ising spins. With this information, we were able to simulate the neutron diffuse scattering patterns observed under selected magnetic fields through machine learning assisted spin Hamiltonian optimization. Our studies revealed a short-range ordered 2D stripe magnetic phase wrapped by domain-wall phases. By applying

magnetic field perpendicular to the square-lattice plane, the stripe magnetic phase melts and the condensed domain wall phases form a short-range ordered vortex lattice, so-called magnetic vortex liquid state, at a critical field of 2 T. Further application of the magnetic field to 4 T, makes all of the spins canted to the field direction, i.e., a polarized paramagnetic phase. Here the evolution of stripe phase and domain wall phase can be precisely controlled by a magnetic field and tracked by neutron scattering. A Z4 vortex was found to be originated from two crossed domain walls. While the density of the domain wall and vortices increase with the field and reach their maximum before entering the fully polarized paramagnetic phase.

The research was supported by the U.S. Department of Energy (DOE), Early Career Research Program Award KC0402020 and used resources at the HFIR and SNS, DOE Office of Science User Facilities operated by ORNL.

11:00 AM QM01.10.04
Structural and Magnetic Properties of EuIr$_3$Si$_7$ Single Crystals Binod K. Rai[1], Alex Bretana[1], Boris Maiorov[2], Christopher Mizzi[2], Joseph Paddison[3], Stuart Calder[3] and Matthias Frontzek[3]; [1]Savannah River National Laboratory, United States; [2]Los Alamos National Laboratory, United States; [3]Oak Ridge National Laboratory, United States

Recently, Eu-based intermetallic compounds have been reported to exhibit complex magnetic textures. In this talk, I will present the physical properties of a new member, the EuIr$_3$Si$_7$ single crystal, of the RT_3M_7 family. This family of compounds has already shown interesting magnetic properties such as anomalous metamagnetism in YbRh$_3$Si$_7$, ferromagnetic ordering along the hard axis in YbIr$_3$Ge$_7$, and charge-neutral fermions in YbIr$_3$Si$_7$. EuIr$_3$Si$_7$ crystallizes in the ScRh$_3$Si$_7$ structure type with space group R-3c, which is confirmed by single crystal XRD data. Furthermore, it exhibits two magnetic phases below T_{N1} = 5 K and T_{N2} = 15 K, with easy-axis anisotropy. The presentation discusses two magnetic phases assessed using magnetization, specific heat, ac susceptibility, and neutron diffraction data.

11:15 AM QM01.10.05
Topological Current Divider in a Chern Insulator Junction Dmitry Ovchinnikov[1,2], Jiaqi Cai[1], Zhong Lin[1], Zaiyao Fei[1], Zhaoyu Liu[1], Yongtao Cui[3], David Cobden[1], Jiun-Haw Chu[1], Cui-Zu Chang[4], Di Xiao[1], Jiaqiang Yan[5] and Xiaodong Xu[1]; [1]University of Washington, United States; [2]University of Kansas, United States; [3]University of California, Riverside, United States; [4]The Pennsylvania State University, United States; [5]Oak Ridge National Laboratory, United States

A Chern insulator is a two-dimensional material that hosts chiral edge states produced by the combination of topology with time-reversal symmetry breaking. Such edge states are perfect one-dimensional conductors, which may exist not only on sample edges but on any boundary between two materials with distinct topological invariants (or Chern numbers). MnBi$_2$Te$_4$, a recently discovered van der Waals topological magnet, offers rich opportunities for Chern number engineering. Non-trivial band structures can be engineered by means of control of the magnetic state [1], while the Chern number itself can be tuned by combining the Chern insulator and quantum Hall physics [2]. In this talk, I will report a chiral edge-current divider based on Chern insulator junctions formed within the layered topological magnet MnBi$_2$Te$_4$. In a device containing a boundary between regions of different thicknesses, topological domains with different Chern numbers can coexist [2,3]. At the domain boundary, a Chern insulator junction forms, where we identify a chiral edge mode along the junction interface. I will further demonstrate how this mode can be used to construct topological circuits in which the chiral edge current can be split, rerouted, or switched off by controlling the Chern numbers of the individual domains. Our results demonstrate MnBi$_2$Te$_4$ as an emerging platform for topological circuit design [3].
[1] Ovchinnikov, D., Huang X., Lin, Z., Fei, Z. et al. Intertwined Topological and Magnetic Orders in Atomically Thin Chern Insulator MnBi$_2$Te$_4$. Nano Lett. 21, 6, 2544–2550 (2021)
[2] Cai, J., Ovchinnikov, D. et al. Electric control of a canted-antiferromagnetic Chern insulator. Nat. Commun. 13, 1668 (2022)
[3] Ovchinnikov, D., Cai, J. et al. Topological current divider in a Chern insulator junction. Nat. Commun. 13, 5967 (2022)

SESSION QM01.11: Emerging Materials/Properties II
Session Chairs: Elton Santos and Srinivasa Rao Singamaneni
Thursday Afternoon, April 13, 2023
Marriott Marquis, Fourth Level, Pacific A

1:30 PM QM01.11.01
Negligible Hall Resistance in Dirac Semimetal EuCu$_2$Sb$_2$ Souvik Sasmal[1], Bikash Patra[1], Kritika Vijay[2], Gourav Dwari[1], Bishal Maity[1], Soma Banik[2], Bahadur Singh[1] and Arumugam Thamizhavel[1]; [1]Tata Institute of Fundamental Research, India; [2]Raja Ramanna Centre for Advanced Technology, India

Magnetic Dirac semimetal is of great interest among researchers these days. Many of these Dirac semimetals are protected by the combination of crystal symmetries and a special antiferromagnetic time-reversal symmetry [1]. There are limited systems that show magnetic Dirac state. Recently, the EuCd$_2$As$_2$ compound has been identified as magnetic Weyl semimetal [2]. A single crystal of EuCu$_2$Sb$_2$ was synthesized by flux growth method using Cu-Sb flux. The crystal structure of EuCu$_2$Sb$_2$ contains a subsequent magnetic Eu^{2+} and non-magnetic [Cu$_2$Sb$_2$]$^{2-}$ layers perpendicular to *c*- axis, and Eu moments align in antiferromagnetically between two adjacent layers. Electrical resistivity and specific heat data show antiferromagnetic transition at 5.1 K. Interestingly, it shows negligible Hall resistance with the applied magnetic field 0 – 14 T. In Angle-resolved photoemission spectroscopy measurement, the linear band crossing near the Fermi level suggests Dirac like band dispersion which results in unconventional Hall resistance.

[1] Young, Steve M. and Wieder, Benjamin J., *Phys. Rev. Lett. 118, 186401 (2017).*
[2] Soh, J.-R. *et al.*, *Phys. Rev. B* 100, 201102 (2019).

1:45 PM QM01.11.02
Partial Disorder Phase in a Shastry-Sutherland Lattice Madalynn Marshall[1], Brianna Billingsley[2], Xiaojian Bai[1], Qianli Ma[1], Tai Kong[2] and Huibo Cao[1]; [1]Oak Ridge National Laboratory, United States; [2]The University of Arizona, United States

Geometrical frustration in two-dimensional magnetic systems can drive the stabilization of exotic phases such as spin-liquids and topological states. The Shastry-Sutherland lattice is one such geometrically frustrated lattice that consists of a two-dimensional orthogonal arrangement of spin dimers and results in rich phase diagrams when manipulated by magnetic field and temperature. In this talk I will present the discovery of the possible field-induced spin liquid state of S=1 spin dimers in the Shastry-Sutherland lattice material BaNd$_2$ZnS$_5$ from utilizing neutron diffraction techniques. A metamagnetic transition in the bulk magnetization measurement was observed under field along the *ab* plane below T$_\mathrm{N}$ = 2.9K. We established the Ising behavior in the

Nd spins by the local magnetic susceptibility method with polarized neutrons at the paramagnetic state. The zero-field 2-**Q** antiferromagnetic order of ferromagnetic dimers was determined by neutrons at 1.4 K. The constituting propagation vectors $\mathbf{q_1} = (\frac{1}{2}\ \frac{1}{2}\ 0)$ and $\mathbf{q_2} = (-\frac{1}{2}\ \frac{1}{2}\ 0)$ each exhibit a "stripe" order when viewing multiple layers and a Néel-type arrangement in a single layer. By applying field along [1 -1 0] the two sublattices respond differently. The $\mathbf{q_1}$ magnetic sublattice remains relatively intact up to 6 T while the stripe phase of the $\mathbf{q_2}$ magnetic sublattice order is suppressed at the critical field H_c = 1.7 T, indicating an emerging partial disorder, liquid state of ferromagnetic dimers, corresponding to the metamagnetic transition in the bulk measurement. With this information we constructed an *H-T* phase diagram from the bulk magnetization measurements that clearly defines the "stripe" state at lower field and a field polarized state at upper fields with a critical region emerging in between represented as a spin dimer liquid phase. To further understand the evolution of the partial disorder phase we performed ultra-low temperature specific heat measurements and discovered the emergence of novel field-induced states.
The research was supported by the U.S. Department of Energy (DOE), Early Career Research Program Award KC0402020 and used resources at the High Flux Isotope Reactor, a DOE Office of Science User Facility operated by ORNL.

2:00 PM QM01.11.03
Circuit QED Characterization for the Detection of Persistent Currents on 2D Dichalcogenide Platelets Timothy W. Carlson; Wake Forest University, United States

Qubit synthesis and measurement are lingering challenges for the quantum computing community. Traditional qubit architectures have been established in ion-trapping with lasers, nitrogen vacancies in host crystals such as crystalline silicon, and Josephson junctions in superconducting circuits, but an emerging direction is to harness the topologically-protected edge states on exotic materials such as topological insulators (TI). In ordinary metallic platelets there are counter-propagating currents through the bulk and the edges which inevitably cancel each other out. On TIs, the bulk bandgap is inverted due to strong spin-orbit coupling which allows gapless, helical edge states. These edge states follow Kramer's theorem which says that the edge currents must be separated into left and right-handed components and that these states are energetically two-fold degenerate. Additionally, these edge currents are ballistic which allow for dissipationless transport. When subjected to an external magnetic field, the edge states are shifted in momentum space which causes a net angular momentum in one direction (clockwise) versus the other (counter-clockwise.)
The topological insulator Antimony Telluride is synthesized by SLS (Solution Liquid Solid) colloidal chemistry with the addition of catalysis-hydrazine cycles. The hydrazine activates a unique spiral growth on two habit planes connected by a dislocation resulting in left and right handed chiral structures. Using optical I-line lithography we fabricate and characterize microwave circuits and then selectively place the crystals in the measurement area. The measurement area is sandwiched between two parallel plates which are coupled to a transmission line cavity (TLC.) The TLC is capacitively coupled to a sensitive input-output circuit. The phase shift of the output signal determines the perimeter direction of the persistent currents. These edge states are topologically protected and conserve charge parity allowing for room-temperature measurement which otherwise would have been strongly coupled to the environment and unmeasurable.

2:15 PM QM01.11.04
Excitons in Correlated van der Waals Antiferromagnetic Nanostructures Vignesh Chandrasekaran[1], Cong Tai Trinh[1], David G. Parobek[1], Christopher R. DeLaney[1], Christopher Lane[1], Jian-Xin Zhu[1], Xiangzhi Li[1], Huan Zhao[1], Andrew Jones[1], Michael T. Pettes[1], Matthew Schneider[1], John Watt[1], David Dunlap[2], Andrei Piryatinski[1], Sergei Ivanov[1] and Han Htoon[1]; [1]Los Alamos National Laboratory, United States; [2]The University of New Mexico, United States

Transition metal phosphorus trichalcogenides, $TMPX_3$, are emerging as an exceptional van der Waals antiferromagnet material for exploring magnetic correlations, long range order and emergence of composite quasiparticles. They are reported to have a tunable bandgap from 1 eV to 3.5 eV, correlated electron physics with classification as Mott or Charge transfer insulator and different magnetic order such as Ising, XY or Heisenberg types. Here we investigate excitons in bulk and nanoflakes of different $TMPS_3$ (TM: Ni, Mn, Fe) using photoluminescence (PL) spectroscopy. By reducing the lateral dimension of flakes to tens of nanometers, we find that we could switch-off the bulk exciton emission and activate different excitonic transitions in visible range (1.8 – 2.2 eV emission peaks vary from one nanoflake to another) with much narrower linewidth of only few hundred μeV at 4.2 K. Despite the difference in energy, the excitons in nanoflakes exhibit features such as a spin correlated PL evidenced by a near-unity linear polarization and formation of exciton-polaron states evidenced by multiple phonon replicas. In addition, we also observe an intriguing behavior where nanoflakes display spectral jumps occurring randomly in time but with a near perfect regularity in energy steps. These results establish nano-structuring as an exciting pathway for inducing & manipulating quasiparticles in van der Waals antiferromagnets.

2:30 PM BREAK

SESSION QM01.12: Emerging Materials/Properties III
Session Chairs: Robert Hicken and Santosh KC
Thursday Afternoon, April 13, 2023
Marriott Marquis, Fourth Level, Pacific A

3:30 PM *QM01.12.01
Magnetic and Electronic Topological States in the Kagome-Net Magnet YMn_6Sn_6 Nirmal J. Ghimire; George Mason University, United States

Identification, understanding, and manipulation of novel electronic and magnetic states is essential for the discovery of new quantum materials for future spin-based electronic devices. In particular, materials that manifest an interplay of magnetism and electronic topology are subject to intense investigation; kagome net magnets are prime candidates. In this talk I will presnt the magnetotransport signatures of the magnetic and electronic topological states in the kagome net magnet YMn_6Sn_6.
YMn_6Sn_6 crystallizes in the hexagonal space group P6/mmm with Mn atoms forming a kagome net in the basal plane. The material orders antiferromagnetically at 345 K and quickly transitions into an incommensurate spiral below 333 K. For a magnetic field applied in the *ab*-plane, a series of competing phases namely distorted spiral (DS), transverse conical spiral (TCS) and Fan-like (FL) phases are stabilized before polarizing to the forced ferromagnetic (FF) state. In this field orientation, this coumpoud shows an enigmatic topological Hall effect near room temperature within the TCS phase, which we attribute to a new fluctuation-driven mechanism. In addition to this THE, YMn_6Sn_6 shows two other intuging magnetotransport features at lower temperatures: an anisotropic magnetoresistance drop due to a magnetization-driven topological phase transition (Lifshitz transition), and an interlayer MR due to the charge-spin coupling associated with the magnetic texture in the FL phase in absence of a strong spin orbit coupling. These phenomena provide a unique view into the magnetic and electronic topological states and their interplay in YMn_6Sn_6.

4:00 PM QM01.12.02
Rydberg Excitons—A Novel Platform for On-Chip Rydberg-Based Quantum Technologies Kinjol Barua[1], Jacob C. DeLange[1], Stephan Steinhauer[2] and Hadiseh Alaeian[1]; [1]Purdue University, United States; [2]KTH Royal Institute of Technology, Sweden

Strong photon-photon interaction is the holy grail of quantum optics, as it is essential for the development of photonic quantum networks and information processors which could revolutionize modern information technologies. However, photons in a vacuum do not interact with each other, so a nonlinear material is needed to mediate such interactions. Excitons, semiconductor electron-hole pairs, are promising candidates for creating such nonlinearities. Similar to their atomic counterparts, excitons can be promoted to highly excited Rydberg states with high principal quantum numbers. These states have exaggerated wavefunctions and interact strongly with each other via long-range strong dipole-dipole and Van der Waals potentials. These potentials perturb the energy level structure of nearby atoms such that they can no longer be excited to the same Rydberg state. This effect, known as Rydberg blockade, facilitates the deterministic single-photon nonlinearities required in quantum computing. Rydberg excitons in solid-state platforms incorporate the exceptional nonlinearities of Rydberg states on a scalable, solid-state host. As such, a suitable material system for Rydberg excitons is indispensable for harnessing the unique properties of excitons in scalable, on-chip quantum devices.

So far, cuprous oxide (Cu_2O) is the only known semiconductor where Rydberg excitons with principal quantum numbers up to n = 25 have been observed. It has a high binding energy and symmetric lattice structure, which allow it to host many Rydberg exciton states without undergoing thermal ionization. However, natural bulk cuprous oxide cannot be made defect-free, so a more controlled fabrication process is required to grow high-purity, customizable, synthetic, cuprous oxide. Thin-film cuprous oxide samples with thicknesses below the blockade radius are of particular interest because they more easily facilitate the observation and utilization of Rydberg blockade effect.

In this talk, we will present spectroscopic absorption and photoluminescence measurements of Rydberg excitons from a synthetic thin-film of cuprous oxide deposited on a transparent substrate. Our studies demonstrate Rydberg exciton states up to n=7, and their power and temperature-dependent behavior. We will also report the formation of cavity Rydberg polaritons and lifetime enhancement of exciton states via strong coupling with cavity photons. Finally, we will report on the behavior of Rydberg excitons in a sample of Cu_2O coated with the 2D material ruthenium chloride ($RuCl_3$) and how they behave near its magnetic phase transition temperature. Our results will pave the way for CMOS compatible, on-chip, Rydberg based quantum systems with a wide range of applications in solid-state quantum information processing, non-classical light sources, quantum simulators, quantum metrology, and quantum sensing.

4:15 PM *QM01.12.03
Magnetic-Field Induced Phase Transition in Centrosymmetric Superconductor $PdBi_2$ Irina Grigorieva; The University of Manchester, United Kingdom

Centrosymmetric superconductor β-$PdBi_2$ has attracted much attention recently due to its topologically nontrivial band structure and predicted multiband superconductivity. However, most studies so far – typically conducted in zero magnetic field – only detect a single s-wave gap. I will review our recent studies where we used tunnelling spectroscopy and magnetic susceptibility measurements to demonstrate a magnetic-field driven transition from s-wave superconductivity in low magnetic fields to unconventional equal-spin pairing and nodal gap in parallel magnetic fields above ~0.2T. Our theory shows that the transition is associated with local breaking of the inversion symmetry and the associated reconstruction of the electronic bands in magnetic field.

SESSION QM01.13: Imaging and Switching/Coupling
Session Chairs: Elton Santos and Srinivasa Rao Singamaneni
Tuesday Morning, April 25, 2023
QM01-virtual

8:00 AM *QM01.13.01
Imaging 2D Magnetic Structures with a Quantum Sensor Joerg Wrachtrup; Univ of Stuttgart, Germany

Spins in wide band gap semiconductors are a leading contender in various areas of quantum technology. Most notably they have been established as a novel tool for nanoscale quantum sensing [1,2,3]. Specifically, I will discuss quantum and imaging with spins to investigate magnetism in 2D materials including the investigation domain patterns [4] and Moiré structures in twisted 2D magnetic layers [5]. Here the nitrogen vacancy center in diamond is used as a scanning probe to image electronic magnetism in mono- and multilayers of materials like $CrBr_3$ as well as twisted multilayers of CrI_3 By using dedicated measurements strategies we improve the sensitivity [6] as well as the dynamic range of the method and show its use in static as well as dynamic probing of magnetism.

[1] T. Oeckinghaus et al., Nano Lett. 20, 463 (2020)
[2] N. Morioka et al. Nature Com. 2516 (2020)
[3] N. Chejanovsky et al. Nature Mat. 20, 1079 (2021)
[4] Qi-Chao Sun et al. Nature Com. 12, 1989 (2021)
[5] T. Son et al. Science 374, 1140 (2021)
[6] V. Vorobyov et al., njp Quantum Information 7, 124 (2021)

8:30 AM QM01.13.02
Quantitative Imaging of 2D Magnets Down to the Monolayer Limit Patrick Reiser, Maerta Tschudin, David Aaron Broadway and Patrick Maletinsky; University of Basel, Switzerland

The discovery of 2D magnetic van-der-Waals systems lead to investigations of novel physical phenomena at a reduced dimensionality and enables the realization of novel heterostructures for spintronic applications [1]. Due to their intrinsic weak magnetic signal strength, advanced characterization techniques are required. Here, we use the single spin of a nitrogen-vacancy (NV) in diamond embedded into an all-diamond AFM tip to obtain images of the stray field arising from 2D magnetic systems [2]. In a scanning configuration, we obtain a spatial resolution of approximately 50 nm and a field sensitivity of 1 $\mu T/Hz^{0.5}$. Complementary to other techniques, scanning NV magnetometry is a non-invasive method that can operate in the full temperature range from mK to room-temperature and is not restricted to a specific type of material.

We investigated the properties of mechanically exfoliated chromium trihalides. We determined the out-of-plane magnetization of a single layer of CrI3 quantitatively and confirmed the unexpected antiferromagnetic interlayer coupling. We relate this behavior to its monoclinic phase at low-temperatures and could switch it to a ferromagnetic coupling by inducing a phase transition to its rhombohedral structure [3]. In preliminary work, we also studied the monolayer of CrCl3 that exhibits an easy-plane anisotropy and shows characteristics of an ideal XY magnet. We study its magnetic phase transition and show how its magnetization is stabilized below its critical temperature.

In contrast to mechanical exfoliation, molecular-beam-epitaxy can be used to grow 2D magnets on larger scales with a well-defined geometry. We studied the lanthanide metalloxene EuGe2 that is a layered 2D antiferromagnet with ferromagnetic interlayer coupling. We show that such a system can be grown on a prepatterned substrate allowing us to define its geometry to an arbitrary shape. We find that the magnetization of the monolayer is reduced compared to its bulk value consistent with previous film characterization [4] and that the monolayer behaves like an XY magnet. However, our technique reveals that the film consists of independent magnetic grains of around 100 nm size resulting in a complex stray field pattern. The field dependence of that pattern suggests that these grains possess a varying critical temperature that can explain the previous observed anomalies [5].

Overall, our technique quantitatively determines the magnetic properties of the 2D magnets down to the monolayer limit and is capable of capturing anomalies at the nanoscale. As such, our technique provides a basis for both a deeper fundamental understanding of magnetization in 2D systems and the development of future engineering of 2D magnets.

[1] Wang et al., The Magnetic Genome of Two-Dimensional van der Waals Materials, ACS Nano 16(5), 2022.
[2] Hedrich et al., Parabolic Diamond Scanning Probes for Single-Spin Magnetic Field Imaging, Phys. Rev. Applied 14(6), 2020.
[3] Thiel et al., Probing magnetism in 2D materials at the nanoscale with single-spin microscopy, Science 364(6444), 2019.
[4] Tockmachev et al., Lanthanide f7 metalloxenes – a class of intrinsic 2D ferromagnets, Mater. Horiz. 6(7), 2019.
[5] Reiser et al., in preparation.

8:45 AM QM01.13.03
Heterobilayer with Ferroelectric Switching of Topological State Junjie Zhang and Boris I. Yakobson; Rice University, United States

The realization of multifunctional nanomaterials is both fundamentally intriguing and practically appealing to be used in nanoscale devices. Here, a heterobilayer consisting of realistic 2D-material components of matching lattice symmetry, that is, one being the β-phase antimonene β-Sb known for its strong spin–orbit coupling and ferroelectric In_2Se_3 monolayer, is designed and explored with first-principles density functional theory. The ferroelectric polarization of the In_2Se_3 layer induces distinctly different electronic properties in the bilayer. With polarization directed "inward", the bilayer is a trivial insulator with spatially-indirect band gap (potentially beneficial for photovoltaics). Surprisingly, when polarized "outward", the bilayer displays nontrivial topological state, $\mathbf{Z}_2 = 1$. This suggests that the external electric field can reversibly switch between these two states, inviting potential applications in future multifunctional devices.

9:00 AM QM01.13.05
Interfacial Magnetic Coupling Effects on the Magnetic and Magnetocaloric Properties of Rare Earth Element Doped LCMO-Mn_3O_4 Nanocomposites Md Farhan Azim[1], Jeotikanta Mohapatra[2] and Sanjay R Mishra[1]; [1]University of Memphis, United States; [2]The University of Texas at Arlington, United States

Magnetic refrigeration technology, which works on the magnetocaloric effect (MCE) of magnetic materials, has attracted the interest of numerous research groups over traditional gas refrigeration. It has several advantages, including being highly energy-efficient, environmentally friendly, and cost-effective. The major effort is directed in improving the magnetic entropy change along with the relative cooling power (RCP) of oxide magnetocaloric materials. This study reports the synthesis and magnetocaloric properties of the novel rare earth element doped LCMO composites. These tetragonal crystal structure shaped compounds were synthesized with respect to AB_2O_7 type perovskite oxides with the *I4/mmm* group via the facile autocombustion technique. This rare earth europium element expanded the curie temperatures from $La_{1.4}Ca_{1.6}Mn_2O_7$ ~ 182 K to $La_{1.3}Ca_{1.6}Eu_{0.1}Mn_2O_7$ of ~ 186 K, which consequently enhanced the RCP value. Moreover, these composites were also prepared in the presence of 10 wt. % of Mn_3O_4 nanoparticles. The presence of Mn_3O_4 at the intervening grain boundaries between $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Ca_{1.6}Eu_{0.1}Mn_2O_7$ phases altered the double exchange interaction between Mn^{3+} and Mn^{4+} ions. The result do show that these interfacial disordered magnetic interactions of these nanocomposites further expanded the second order paramagnetic-to-ferromagnetic phase transition temperature up to 257 K at the temperature-dependent field-cooled magnetization curve which also led to enhance the change in magnitudes of magnetic entropy - $\triangle$s to 0.52 J/kg/k under an applied magnetic field of 5T .The fundamental key of this work is to demonstrate the potentiality of enhancing the magnetic phase transition temperature and magnetocaloric effect in the framework of interfacial coupling between Mn_3O_4 and LCMO nanocomposites.

9:05 AM QM01.13.06
Study of Magnetic and Magnetocaloric Properties of Calcium (Ca) Doped $La_{0.97-x}Ca_xHo_{0.03}MnO_3$ Nanocomposites Synthesized by Facile Auto-Combustion Method Md Farhan Azim[1], Jeotikanta Mohapatra[2] and Sanjay R Mishra[1]; [1]University of Memphis, United States; [2]The University of Texas at Arlington, United States

Magnetic refrigeration technology, which works on the magnetocaloric effect (MCE) of magnetic materials, has attracted the interest of numerous research groups over traditional gas refrigeration. It has several advantages, including being highly energy-efficient, environmentally friendly, and cost-effective. The major effort is directed in improving the magnetic entropy change along with the relative cooling power (RCP) of rare earth double perovskite oxide magnetocaloric materials. This study reports the magnetic and magnetocaloric properties of different concentration of alkaline earth metal such as Ca doped $La_{0.97-x}Ca_xHo_{0.03}MnO_3$ (x = 0.3, 0.33 and 0.37) composites which were synthesized via the facile autocombustion technique. The second-order paramagnetic-to-ferromagnetic phase transition temperature appeared at the temperature-dependent field-cooled magnetization curve. The result do show that greater amount of Calcium enhanced the curie temperature, T_c up to 76 K. Ferromagnetic ordering was observed in these composites due to the existence of double exchange mechanism from both Mn^{3+} and Mn^{4+} ions that develops the electronic holes in Mn–O bands, which is favored by the doped Ca^{2+} ion. In addition, increasing the doping concentration of Calcium further increased change in magnetic entropy, $-\triangle S_m$ up to 0.21 J/Kg/K that led to have the result in higher RCP values. The fundamental key of this work is to demonstrate the potentiality of enhancing the magnetocaloric effect in the framework via spin coupling mechanism of Calcium doped rare earth perovskite compounds.

9:10 AM QM01.13.08
Fermiology Underpinning Enhanced Magnetic Ordering in Cr2Ge2Te6 van der Waals Magnets Liam Trzaska[1], Igor Marković[2], Tommaso Antonelli[1], Edgar Abarca Morales[1,3], Matthew D. Watson[4], Cephise Cacho[4], Monica Ciomaga Hatnean[5], Geetha Balakrishnan[6] and Philip D. King[1]; [1]University of St Andrews, United Kingdom; [2]The University of British Columbia, Canada; [3]Max Planck Institute for Chemical Physics of Solids,

Germany; [4]Diamond Light Source, United Kingdom; [5]Swiss Federal Institute of Technology Zurich, Switzerland; [6]The University of Warwick, United Kingdom

The recent discovery of long-range magnetic order in van der Waals layered materials, persisting to the few-layer limit, has provided a tuneable platform for the engineering of novel magnetic structures and devices. $Cr_2Ge_2Te_6$ is such a material [1]. It is known to be a ferromagnetic semiconductor with a T_C of approximately 63 K in the bulk crystal. The T_C reduces with sample thickness but remains finite down to the bilayer limit. Electrostatic gating studies on $Cr_2Ge_2Te_6$ have demonstrated how the induced carrier doping can drive a marked increase in T_C, as well as switching the magnetic anisotropy [2]. Here we show how features of the electronic structure, extracted from angle-resolved photoemission spectroscopy (ARPES), can be used to provide a direct probe of orbital-specific energy gains underpinning the magnetic ordering. We perform measurements as a function of temperature and alkali surface deposition, an analogue to electrostatic-gating, to simultaneously investigate the effects of electron doping on the near-surface band-structure, and to extract the T_C of the surface region. We find how T_C is increased in the electron-doped surface as compared to the bulk system, and image the population of the nominally unoccupied conduction band that underpins these changes in magnetic ordering.

References

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[3] Watson, *et al*, Direct observation of the energy gain underpinning ferromagnetic superexchange in the electronic structure of $CrGeTe_3$, *Phys Rev B* 101, (2020)

9:25 AM QM01.13.09
Development of a Novel Liquid Helium Sample Holder for TEM Denys Sutter; condenZero, Switzerland

Since 2017 the team of condenZero, a spin-off company from the University of Zurich, Switzerland (founded in 2019), has been developing new design principles for liquid helium cryostats. Initially created for x-ray diffraction experiments in pulsed magnetic fields, condenZero adapts the miniaturizable cryostat design for TEM sample holder applications. The main goal of the design is to provide a stable base temperature (<10K) over long time periods, enabling new experimental possibilities for TEM research. In this talk, we outline a brief history of condenZero, current challenges, related engineering projects and future milestones for the further development of our next-generation cryo-TEM sample holders.

SYMPOSIUM

April 11 - April 25, 2023

Symposium Organizers
Naoya Kanazawa, The University of Tokyo
Dennis Meier, Norwegian University of Science and Technology
Beatriz Noheda, University of Groningen
Susan Trolier-McKinstry, The Pennsylvania State University

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* Invited Paper
\+ Distinguished Invited

SESSION QM02.01: Control of Magnetic and Ferroelectric Orders I
Session Chairs: Vincent Garcia and Dennis Meier
Tuesday Morning, April 11, 2023
Marriott Marquis, Fourth Level, Pacific B

10:30 AM *QM02.01.01
3D Topological Solitons and Their Dynamics Xiuzhen Yu[1], Yizhou Liu[1], Kostatian Iakoubovskii[1], Kiyomi Nakajima[1], Naoya Kanazawa[2], Naoto Nagaosa[1,2] and Yoshinori Tokura[1,3]; [1]RIKEN, Japan; [2]The University of Tokyo, Japan; [3]The University of Toledo, Japan

The three-dimensional (3D) topological solitons – hopfions [1]– were predicted in the chiral-lattice magnets [2] but have not been experimentally confirmed thus far. By utilizing the external magnetic field and electric current, the fractional hopfions with nonzero topological charge and their ensembles can be excited at lower temperatures ~ 100 K far from T_C (~ 278 K) [3] in a chiral-lattice magnet FeGe, in which 2D topological soliton lattice - skyrmion lattice - are thermodynamically stable near T_C [3]. Microsecond current pulses and in-plane magnetic field were employed to control dynamics of the expansion and contraction of the bundle of skyrmion and fractional hopfion, as well as its current-driven Hall motion [4]. The present work demonstrates how to manipulate and control 3D topological objects such as hopfion and its bound state in magnets.
In this talk, I will also present other topological solitons like merons, bimerons, and their current-driven dynamics in the FeGe with the Co-dopant.
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(JSPS) and the Japan Science and Technology Agency (JST) CREST program (Grant No. JPMJCR1874, JPMJCR20T1), Japan.

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11:00 AM *QM02.01.02
Triangular-Lattice Magnetic Semiconductor Producing Giant Anomalous Hall Signals Masaki Uchida; Tokyo Institute of Technology, Japan

Magnetic semiconductors have both semiconducting and magnetic properties that support the modern information society respectively. These materials are broadly classified into two categories. One is rare-earth chalcogenides such as EuO, from which research on magnetic semiconductors started. The other is dilute magnetic semiconductors such as (Ga,Mn)As, in which a small amount of transition metal elements are doped into conventional semiconductors.
In order to develop new magnetic semiconductors, here we focus on the combination of rare-earth magnetic elements and arsenic. We then find out a new magnetic semiconductor EuAs, where Eu^{2+} ions with large magnetic moments form distorted triangular lattice. EuAs epitaxial thin films grown by molecular beam epitaxy exhibit giant anomalous Hall signals with an anomalous Hall angle exceeding of 0.13 [1]. The giant signals can be theoretically explained by spin cluster scattering [2,3] in a hopping conduction regime. Our findings shed light on magnetic semiconductors hosting topological spin textures, developing a field targeting diluted carriers strongly coupled to noncoplanar spin structures for future device applications.

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11:30 AM QM02.01.04
Depth Resolved Interfacial Magnetic Spin Spiral at (111)-La0.7Sr0.3MnO3/LaFeO3 Epitaxial Thin Films Yu Liu, Mari-Ann Einarsrud and Ingrid Hallsteinsen; NTNU, Norway

To probe the emerging switchable magnetic spin spiral at the antiferromagnetic LaFeO3 layer due to interfacial effect with element specificity in (111)-La0.7Sr0.3MnO3/LaFeO3 epitaxial thin films we utilise a resonant soft X-ray reflectivity (RSXR) technique providing axial sensitivity. This emerging magnetism and magnetic anisotropy control at the ferromagnet (FM) /antiferromagnet (AFM) interface in perovskite transition metal oxides is interesting for energy efficient spintronics applications. However, studies of magnetic interactions at heterostructure interfaces are often limited by direct measurements, especially of AF spin structures. Here, we present a novel method of probe the spin structure at the AF layer on oxide heterostructures.

(111) pc-La0.7Sr0.3 MnO3/LaFeO3 (LSMO/LFO) heterostructures were epitaxially grown on (101) DyScO3 substrates by pulsed laser deposition as our model system to probe the spin alignment at the antiferromagnetic LaFeO3 layer. REED revealed layer by layer growth, and fully single crystalline epitaxy was confirmed by X-ray diffraction. Vibrating sample magnetometer measurements confirmed bulk ferromagnetism. RSXR data was collected at Advanced Light Source beamline 4.0.2 at Lawrence Berkeley Lab using linear polarized X- rays at soft x-ray energy range, with applied magnetic field parallel to the sample surface within the scattering plane using permanent magnet at 0.1 T. Data analysis was carried out with RemagX using the magnetic matrix formalism.

X-ray reflectometry data were recorded at the Fe L3 edge (708.32 eV) for the bilayer along LSMO easy and hard axis. From fitting the preliminary data on the bilayered samples, the model with a spin spiral reproduced the spin structure of the system with a weakly pronounced cross-over at Qz = 0.125 nm-1. Furthermore, a characteristic top/dip at Qz = 0.18 nm-1 in the asymmetry is reversed for the easy and hard axis, which can only be attained by axial switching indicating a directional transition in spin spirals. This suggests a translation of ferromagnetic momenta from the LSMO layer to LFO due to exchange coupling at the interface, which is controllable by rotating the applied field. We demonstratethat RSXR with linearly polarised light presents a unique means of resolving FM and AFM spins at buried interfaces in multistructures, providing valuable details about the spin texture that are necessary in order to exploit emerging interfacial phenomena towards applications.

SESSION QM02.02: Control of Magnetic and Ferroelectric Orders II
Session Chairs: Naoya Kanazawa and Xiuzhen Yu
Tuesday Afternoon, April 11, 2023
Marriott Marquis, Fourth Level, Pacific B

1:30 PM *QM02.02.01
Nanoscale Quantum Inductor in Helical-Spin Magnets—Latest Material Discoveries and Future Perspective Yukako Fujishiro; RIKEN Center for Emergent Matter Science, Japan

A strong coupling between spin texture and conduction electron provides a platform for various electromagnetic responses which can be exploited for future electronic devices. One recent discovery is a quantum inductor in helical-spin magnets, where the quantum-mechanical Berry phase generated by current-driven dynamics of non-collinear spin texture leads to giant inductive voltage. While it has been experimentally demonstrated in several short-period helical-spin magnets (e.g. $Gd_3Ru_4Al_{12}$ and YMn_6Sn_6), the origin of unusual properties distinct from classical inductors, especially the sign change of inductance, had remained largely elusive.
In this study, we report the latest discovery of giant emergent electromagnetic inductance (EEMI) in a new Eu-based helical-spin magnet. In particular, we have demonstrated various sign changes of EEMI within a single material, upon the commensurate-incommensurate magnetic transition as well as the domain wall formation, providing new insights into microscopic origins of EEMI. Furthermore, positive EEMI was identified without long-range magnetic order just above the magnetic transition temperature, due to thermally induced vector-spin chirality. This suggests a possibility of realizing EEMI in a wider range of magnetic compounds or systems (i.e. not limited to helical-spin magnets), paving the way for future material discoveries as well as technological applications of the quantum inductors.

2:00 PM QM02.02.02

Tuning the magnetic anisotropy, Curie temperature, and Dzyaloshinskii–Moriya interaction in the $FeCl_2$ monolayer Shubham Tyagi, Paresh C. Rout and Udo Schwingenschlögl; King Abdullah University of Science and Technology, Saudi Arabia

The emergence of magnetic ordering in two-dimensional materials offers unique opportunities for developing novel spintronics devices. However, these materials suffer from low magnetic critical temperature, in-plane anisotropy, and low magnetic anisotropy energy.
We will discuss a strategy for the ferromagnetic $FeCl_2$ monolayer (based on first-principles and Monte Carlo simulations) to enhance the **Curie temperature** to above room temperature and enhance the **magnetic anisotropy** energy by nearly three orders of magnitude, which is essential for sustaining long-range magnetic ordering. In addition, we find a **non-polar (1T)** to **polar (1H)** structural phase transition and induced **Dzyaloshinskii–Moriya** interaction, which is crucial for generating chiral magnetic structures such as skyrmions.

2:15 PM QM02.02.03
Experimental Study of Spin Orbit Torque in All Oxide Interface Mi-Jin Jin[1,2], Guang Yang[2] and Jason Robinson[2]; [1]Institute for Basic Science (IBS), Korea (the Republic of); [2]University of Cambridge, United Kingdom

Spin orbit coupling (SOC) interplays crucial role in between spin and charge currents. Also, effective spin orbit torque (SOT) can modulate magnetization in various ferromagnetic/non-magnetic bilayers. In this study, we demonstrate spin orbit torque induced magnetization switching at all oxide structure of $La_{1-x}Ca_xMnO_3$ (LCMO)/$SrTiO_3$ (STO) bilayer. Quasi 2-dimensional conducting surface of STO was prepared by Ar plasma treatment. After then, the magnetic oxide LCMO thin film was deposited by using Pulsed Laser Deposition (PLD) method. Further, possible origins of the spin orbit torque generated at the conducting interface between LCMO and STO will be discussed later. Also, we studied spin orbit torque strength by measuring ferromagnetic resonance (FMR). This all oxide magnetization switching could be one of the important approaches for future electronics/spintronics devices.

2:30 PM QM02.02.04
Interfacial Metallic Ferromagnetism Coupled to a Two-Dimensional Electron Gas Byungmin Sohn[1], Guillaume Marcaud[1], Yeongjae Shin[1], Sangjae Lee[1], Tyler Werner[1], Turgut Yilmaz[2], Jinming Yang[1], Wenzheng Wei[1], Alexei Fedorov[3], Elio Vescovo[2], Yu He[1], Sohrab Ismail-Beigi[1], Charles H. Ahn[1,1] and Frederick J. Walker[1]; [1]Yale University, United States; [2]Brookhaven National Laboratory, United States; [3]Lawrence Berkeley National Laboratory, United States

Two-dimensional electron gas (2DEG) states at oxide interfaces have been of interest for a few decades. Here, we investigate with angle-resolved photoemission spectroscopy (ARPES) a potential ferromagnetic 2DEG state on a ferroelectric, $BaTiO_3$, induced by a layer of iron atoms. As the iron layer is introduced, orbital-selective charge transfer, coupled with magnetic signatures, appears in 2DEG states, which is well resolved by ARPES measurements. First-principles calculations show that ferromagnetic atoms such as iron can introduce magnetism in 2DEG states by interfacial coupling effects. These observations lead to an understanding of how interfacial ferromagnetism in 2DEG states can be induced, shedding light on potential platforms that use ferromagnetic 2DEG states as a spin-dependent electric channel.

2:45 PM QM02.02.05
Strain-Dependent Structural and Magnetic Properties of Pb_2CoTeO_6 from First Principles Md Kamal Hossain and Elizabeth Nowadnick; University of California, Merced, United States

Pb_2CoTeO_6 is a B-site ordered double perovskite that is a multiferroic candidate due to the presence of lone pair-active Pb on the A-site and magnetic Co on the B-site. However, experimental work so far has not reported a polar phase, although a sequence of structural phase transitions with different octahedral rotation patterns has been observed as a function of temperature and pressure. Going from low to high temperature, these phases include monoclinic $P2_1/c$ ($a^-a^-c^+$ octahedral rotations in Glazer notation), monoclinic I2/m ($a^0b^-b^-$ octahedral rotations), rhombohedral in R-3 ($a^-a^-a^-$ octahedral rotations), and cubic Fm-3m. To investigate potential strategies to stabilize Pb_2CoTeO_6 in a polar structure, we combine group theoretic analysis with density functional theory calculations to explore the energetics and crystal structure of bulk Pb_2CoTeO_6. We find that a $P2_1/c$ phase with A-type antiferromagnetic order is the ground state, in agreement with the experiment, and identify a competing R-3 phase that is slightly higher in energy. A systematic study of the structural and magnetic properties of Pb_2CoTeO_6 under epitaxial biaxial strain is carried out, and we investigate whether any polar instabilities arise under strain. Our results provide new insight into strain control of the structural and magnetic properties of Pb_2CoTeO_6.

3:00 PM BREAK

3:30 PM *QM02.02.06
Current-Driven Nonvolatile Phase Change of Electronic/Magnetic/Superconducting States Fumitaka Kagawa[1,2]; [1]Tokyo Institute of Technology, Japan; [2]RIKEN CEMS, Japan

Electrons in condensed matter have internal degrees of freedom, such as charge, spin, and orbital, leading to various forms of ordered states through phase transitions. However, in individual materials, a charge/spin/orbital ordered state of the lowest temperature is normally uniquely determined in terms of the lowest-energy state, i.e., the ground state. In this presentation, I summarize our results showing that under rapid cooling based on electric pulse, this principle does not necessarily hold, and thus, the cooling rate is a control parameter of the lowest-temperature state beyond the framework of the thermal equilibrium phase diagram [1]. Although the cooling rate utilized in low-temperature experiments is typically 2×10^{-3} to 4×10^{-1} K/s, the use of optical/electronic pulses facilitates rapid cooling, such as 10^2–10^7 K/s. Such an unconventionally high cooling rate allows some systems to kinetically avoid a first-order phase transition, resulting in a quenched charge/spin/superconducting state that differs from the ground state. It is also demonstrated that quenched states can be exploited as a non-volatile state variable when designing phase-change memory function, such as charge [2] and spin [3, 4] degrees of freedom and even superconductivity [5]. In a microfabricated sample, we found that the application of DC current can trigger a nonthermal magnetic transition from the skyrmion phase to nonskyrmion phases [6], implying that a tantalizing variety of novel nonequilibrium phenomena and their applications in quantum materials should be explored with attention to the system size. On the other hand, real-space observations using scanning Raman microscopy revealed that complex behaviors in the phase evolution may be involved in a small-sized specimen [7]; therefore, it may be necessary to confront these complexities when constructing nanodevices based on first-order transitions.

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4:00 PM *QM02.02.07
Using Model Atomic Spin Systems to Learn About *in materia* Computing Alexander A. Khajetoorians; Radboud University, Netherlands

The quest to implement machine learning algorithms in hardware has focused on combining various materials, each mimicking a computational primitive, to create device functionality. These endeavors have led to the beautiful development of dedicated hardware that, working in combination with software, can perform pattern recognition tasks. Ultimately, these piecewise approaches limit functionality and efficiency, while complicating scaling and on-chip learning, necessitating new approaches linking physical phenomena to machine learning models. Likewise, this raises the question if there are new machine learning algorithms to be discovered, utilizing the particular properties of quantum properties of matter where there are no obvious links to established models. Here, I will discuss the first steps toward a new paradigm in computing, routed in fundamentals studies based on the idea of letting the physics do the work. I will introduce the concept of an atomic orbital memory and how coupling leads to tunable multi-well landscapes. I will discuss how the ensuing stochastic dynamics mimics the perennial model in machine learning, the Boltzmann machine. In this discussion, I will review the emergence of multiple and separable time scales, an adaption of long-term potentiation in biological matter, which serves the basis for self-adaption. I will also discuss more recent develops moving toward local gate control of stochastic behavior, AC response, and finally new types of orbital memory. I will conclude with an outlook on concepts that go beyond the current neuromorphic paradigm, combining concepts related to quantum coherent and quantum technologies.

4:30 PM QM02.02.08

Computational and Theoretical Underpinnings of the Coupling Between Deformation and Electrical Polarization in Ferroelectric Layered Material In_2Se_3. Tawfiqur Rakib[1], Edmund Han[1], Shahriar Muhammad Nahid[1], Gillian Nolan[1], Mohammad Hossain[1], SungWoo Nam[2], Andre Schleife[1], Arend M. van der Zande[1], Pinshane Y. Huang[1] and Elif Ertekin[1]; [1]University of Illinois Urbana-Champaign, United States; [2]University of California, Irvine, United States

Two-dimensional (2D) ferroelectric materials have attracted interest in the scientific community due to their ability to undergo nanoscale deformation and the coupling of this deformation to electrical polarization. For nanoscale electromechanical devices, 2D ferroelectric materials provide an alternative to conventional bulk ferroelectrics since they retain their polarization down to ultra-low thicknesses. Recently, using measurements from transmission electron microscopy (STEM) and piezoelectric force microscopy (PFM), our team has demonstrated coupling between deformation and polarization switching in the 2D ferroelectric layered material In_2Se_3. Upon bending, a sharp structural transformation from smooth arcs to sharp kinks above a critical bending angle of approximately 35° is observed. This bend-induced structural transformation is accompanied by a polarization switch in the kinked structure. In this work, we will highlight our first-principles and continuum mechanics analysis of the origin of the formation of kinks accompanied by polarization switching in bent In_2Se_3. Using density functional theory simulations, we calculate the bending energy of the smooth arcs and sharp kinks at different bending angle and find a critical bending angle of 36° above which kinks are more favorable. We explain the formation of the kinked structures in terms of the nucleation of monolayer 2D topological defects akin to wedge disclinations, serving as point sources of curvature that spatially localize the bending. We suggest a bending model that captures the structural transformation from smooth arc to sharp kink, as well as the critical angle at which it occurs. This analysis of the coupling of deformation and polarization offers pathways for manipulating electrical polarization in 2D materials through controlled mechanical deformations.

SESSION QM02.03: Domain Walls and Excitations for Unconventional Computing I

Session Chairs: Erika Covi and Fumitaka Kagawa
Wednesday Morning, April 12, 2023
Marriott Marquis, Fourth Level, Pacific B

8:30 AM *QM02.03.01

Topological Excitations in Ferroelectrics for Unconventional Computing Igor Lukyanchuk[1,2]; [1]University of Picardie, France; [2]Terraquantum AG, Switzerland

Modern electronics is currently facing a profound challenge. The demand for even smaller and more closely packed elements has hit a stumbling block: the power emitted in these devices releases more heat than can be efficiently removed; the scalability of the traditional devices cannot go below the atomic scale of 1nm; the clock rate of calculation is restricted by 100 GHz which is set by the restrictions of the frequency of the signal transmitted by a wire; big data processing volume and enormously growing data traffic amount and rate.

We propose several solutions based on the unique functionality of electrically polarised nanomaterials, nanoferroelectrics, to host complex polarization textures that are incredibly stable due to topological self-protection mediated by elasticity and electrical boundary conditions.

(i) Ferroelectric negative capacitance (NC) for low-dissipative nanoelectronics

The operational functional element of the proposed circuit is a nanodot-scale capacitor with a ferroelectric spacer.

We put forth a foundational mechanism of the NC demonstrating the inevitable emergence of the NC due to the formation of polarization domains. We establish a practical design of the stable and reversible NC FET based on the domain layout. The proposed device is tunable and downscales to the 2.5–5 nm technology node.

(ii) Ferroelectric THz vibrations for ultrafast nanoelectronics

The suggested technology employs a ferroelectric material with a ferroelectric-dielectric heterostructure as a resonator for electrons of an electrical circuit or for a terahertz electromagnetic wave. A peculiarity of the described structure is that the polarization of each ferroelectric layer variates periodically in space, forming a set of domains that exhibits a diverse wealth of oscillation modes in the terahertz spectral band. These vibration modes are directly coupled with the applied electromagnetic field. Because of its small size, the ferroelectric terahertz-generating device can be used as a resonator in wireless circuits, for instance, as a resonator in the terahertz antennas, a sensor of terahertz radiation, and a detector of the terahertz signals injected by an adjacent electrical device integrated into the same chip

(iii) Ferroelectric tunable chirality for optoelectronics

The topological chirality in nanostructured ferroelectrics is intimately related to topological polarization ordering. It emerges together with the polarization by spontaneous symmetry breaking from the non-chiral paraelectric state. This synergistic connection provides, possibly,

the most important operational feature of the topological chirality in ferroelectrics: it can be tuned and manipulated by changing the polarization ordering. Given that the latter is directly coupled to an electric field, the chirality switching, hence optical activity manipulation, by the electric field offers a remarkable operational platform, which looks extremely attractive, especially because such an opportunity is unique in nature

(iv) Ferroelectric multilevel logic unit for non von Neumann & neuromorphic computing

We establish that ferroelectric nanodots hold two, three, or even four polarization states that are energetically stable thus providing a platform for encoding information. We reveal stable configurations and how to manipulate the polarization to move it between stable positions using electric fields. The important problems we address are the novel data protection and encryption protocols implementing these states and the ways the multilevel systems can enhance machine learning capable of better-emulating systems like the human brain, since., they do not only allow basic states like yes/no, but also yes/maybe/no or even more refined multi-logic levels.

9:00 AM QM02.03.02

Ferroelectric Switching Paths and Domain Structure of Aurivillius-Phase $SrBi_2(Ta,Nb)_2O_9$ from First Principles Elizabeth Nowadnick and Nabaraj Pokhrel; University of California, Merced, United States

In the last decade, layered perovskite oxide materials – with crystal structures that interleave perovskite blocks with other structural units – have emerged as a family of materials the combine novel ferroelectric mechanisms with additional functionalities. Amongst layered perovskites, the Aurivillius-phase ferroelectrics have been known for decades for their fatigue resistance and robust ferroelectric properties. More recently, the ferroelectricity in two prominent members of the Aurivillius family, $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$, has been shown to arise from a novel trilinear coupling mechanism between polarization and octahedral rotation distortions. This coupling also has been shown to play a key role in the complex paraelectric-ferroelectric structural phase transition sequences of these materials. However, the implications of the trilinear coupling on the ferroelectric switching mechanism in $SrBi_2B_2O_9$ (B=Ta, Nb) remains to be understood. In this work, we use group theoretic analysis and density functional theory calculations to enumerate and explore the energetics of ferroelectric switching paths in $SrBi_2B_2O_9$ and identify low-energy two-step switching pathways facilitated by structural order parameter rotations. Moreover, we show how the relative energy barriers of these switching paths can provide insight into the domain structure of these oxides. In particular, our findings indicate that three-fold domain wall vortices are energetically favorable in $SrBi_2B_2O_9$. This work provides new insight into the origin of low-energy ferroelectric switching in $SrBi_2B_2O_9$ and provides strategies to further lower the switching barrier, which is a key parameter for ferroelectric performance.

9:15 AM QM02.03.03

***Operando* Electron Holography Experiments of Dielectric and Ferroelectric Thin Films** Leifeng Zhang[1], Bumsu Park[1], Kilian Gruel[1], Rafaël Serra[1], Lucas Chapuis[1], Dong-Jik Kim[2], Ibukun Olaniyan[2], Catherine Dubourdieu[2,3], Christophe Gatel[1,4] and Martin J. Hÿtch[1]; [1]CEMES-CNRS, France; [2]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; [3]Freie Universität Berlin, Germany; [4]Université Paul Sabatier, France

The metal-oxide-semiconductor (MOS) capacitor, employed individually or as an element of more advanced electronic components, is one of the fundamental electrical components used in integrated circuits [1, 2]. While much effort is currently being made to integrate new dielectric or ferroelectric materials, capacitors of silicon dioxide (SiO_2) on silicon remain the most prevalent. Therefore, it is perhaps surprising that the electric field within such a capacitor has never been measured or mapped out at the nanoscale.

Here, by adopting the *operando* electron holography methodology in transmission electron microscopy (TEM) with delicate focused ion beam (FIB, ThermoFisher Helios 600i) specimen preparation, we have successfully mapped the electric potential across a working MOS nanocapacitor with unprecedented sensitivity and revealed unexpected charging of the dielectric material bordering the electrodes [3]. The extended charge layer is up to 5.5±0.5 nm, much larger than the structural or chemical width of the interface. Moreover, the charge density varies monotonically with the applied bias, with an almost linear dependence, and follows the sign of the applied bias with an opposite sign to the charges on the nearby electrodes. In our device, we find a reduced capacitance of 17 nF/cm^2 compared with an ideal capacitor (without the dielectric charge layers) of 29 nF/cm^2. Our another example using this methodology is a real nanodevice extracted from 28 nm process test chip [4].

We also applied the *operando* electron holography methodology in the Ti/$BaTiO_3$ (100)/$SrTiO_3$ (100)/SiO_2 (110)/*p*-type Si (110) system, in which the $BaTiO_3$ and $SrTiO_3$ layers were fabricated by molecular beam epitaxy (MBE) technique. The charge and potential distributions were successfully mapped for various ferroelectric or dielectric layers with the applied bias, in which SiO_2, with low dielectric constant, possesses the highest electric field. Although difficult to study the ferroelectric switching dynamics in this structure, our methodology extends its ability to deal with FIB-prepared complex device structures. Furthermore, by adopting the metal-insulator-metal-ferroelectrics-metal (MIMFM) structure, we are able to, by the first time, measure the relative permittivity of ferroelectric material upon polarization switching owing to the existence of floating gate during our *operando* electron holography analyses.

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9:30 AM QM02.03.04

A Multiscale Study of Ferroelastic Domain Dynamics as a Function of Aspect Ratio John J. Scott[1], Tamsin I. O'Reilly[1], Blai Casals Montserrat[2], King-Fa Luo[1], Ekhard Salje[3] and Miryam Arredondo[1]; [1]Queen's University Belfast, United Kingdom; [2]Universitat de Barcelona, Spain; [3]University of Cambridge, United Kingdom

Akin to their sister ferroics (e.g ferroelectrics and ferromagnetics), ferroelastics are characterised by regions of differently orientated states (domains), separated by interfaces known as domain walls, that form when cooled below a critical temperature (T_C) in order to reduce its inherent free energy. Domain walls are of particular interest, exhibiting unique properties on the nanoscale from the bulk such as super-conductivity in an insulating medium[1]. When an external field is applied, domains can further nucleate, annihilate or become mobile in response to the stimuli, presenting unique possibilities for active-adaptable devices[2].

Temperature and stress are examples of such stimuli which are capable of switching the domain structure, a mechanism that mediates many of the functional properties utilised in applications such as memory devices[3], switches and sensors. The understanding of how domains behave in response to externally applied fields is critical to the development of advanced applications such as neuromorphic computing[4]; based on the jerky mobility of DWs, and by extension domains, in materials with ferroelastic components[5]. These discrete jerks emit elastic fields that can destabilise surrounding structures and trigger a cascade of switching events known as avalanches, which can be utilised in conjunction with mean-field theory to characterise the overall behaviour of these dynamics[6] which is an element of this investigation.

Within this study, we complement work achieved on manipulating bulk behaviours[6] and investigate ferroelastic domain dynamics at the microscale via *in situ* transmission electron microscopy (TEM) techniques. Varying the sample aspect ratios of free standing $LaAlO_3$ (LAO) lamella, samples were heat cycled *in situ* from room temperature, beyond T_C and back. We touch upon the effects of etched patterns within this context and explore the different domain behaviour with theoretical models. Finally, we correlate these results to the effects observed in free-standing $BaTiO_3$ lamella, to compare ferroelastic and ferroelectric systems. The results here presented highlight the inherent differences not only in domain dynamics as a function of the aspect ratio, but between different size scales, which are not comparable when mechanisms such as surface effects are considered on the microscale. Knowledge of the domain dynamics in bulk and towards micro-objects, is fundamental for the advancement of active adaptable and substrate free devices.

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9:45 AM QM02.03.05
Mechanically Generated Ferroelectric Domains in van der Waals α-In_2Se_3 Shahriar Muhammad Nahid[1], Edmund Han[1], Tawfiqur Rakib[1], Gillian Nolan[1], Mohammad Hossain[1], Andre Schleife[1], Elif Ertekin[1], Pinshane Y. Huang[1], SungWoo Nam[2] and Arend M. van der Zande[1]; [1]University of Illinois Urbana Champaign, United States; [2]University of California Irvine, United States

Mechanical deformations, such as strain or strain gradient, offer a facile way to modulate the polarization of ferroelectric materials. As the sizes of the electromechanical systems approach nanoscale, strain gradient becomes important due to its inverse scaling with sample size. So, it is imperative to understand how extreme strain gradient, such as bending to a nanoscale radius of curvature, tunes the electrical polarization of ferroelectrics. Conventional perovskite ferroelectric systems are fundamentally limited in their ability to undergo nanoscale mechanical deformations before fracture. In this regard, van der Waals ferroelectric materials, such as α-In_2Se_3, provide a unique opportunity to understand the interplay between electrical polarization and mechanical deformation at strain gradients orders of magnitude higher than previously explored, due to their ability to deform to nanoscale curvatures. The key questions here are how bending multilayer α-In_2Se_3 to an extremely high and previously unexplored strain gradient regime modulates the ferroelectric domains.
In this study, we investigate the modulation of out-of-plane polarization in highly localized bends in multilayer α-In_2Se_3. Bending of the material is achieved by buckle delamination created by the residual stress from mechanical exfoliation process. We study the atomic structure, energetics of the domains, and electrical polarization using scanning transmission electron microscopy (STEM), density functional theory (DFT), and piezoelectric force microscopy (PFM). Finally, we fabricate patterned trenches and transfer α-In_2Se_3 flakes to controllably tune the material.
We show that bending multilayer α-In_2Se_3 to a nanoscale curvature leads to two different types of deformation which depends on the bending angle. Bending angle below 35° results in smooth arcs where the polarization of the material is uniformly maintained throughout the arc. However, bending above 35° results in highly localized kink formation. This kink formation is associated with a structural transformation and creation of a domain wall that results in polarization switching. Using DFT, we show the energetic favorability of kink formation at high bending angle. We also explain the origin of threshold bending angle from the geometric favorability of one disclination formation per layer. PFM measurement shows that the newly formed domain at the kink propagates inside the material and is arrested by material defects, such as crack, edge, or another kink. Finally, we demonstrate control over this bend-induced domain wall formation by transferring α-In_2Se_3 onto patterned trenches to artificially bend the material over threshold angle and subsequently create alternating domain structures.
Altogether, these results unveil the interplay between ferroelectricity and mechanical deformation at extreme curvatures between 7×10^6 m^{-1} and 3×10^9 m^{-1}, establishing opportunities of electrical polarization manipulation and domain wall engineering. These findings lay the groundwork for flexible and reconfigurable nanoelectronics based on van der Waals ferroelectric materials.

10:00 AM BREAK

10:30 AM *QM02.03.06
Conducting Ferroelectric Domain Walls in Neuromorphic and Conventional Logic Device Demonstrators Marty Gregg, Ahmet Suna, Conor J. McCluskey, Olivia Baxter, Jesi Maguire, Amit Kumar and Ray McQuaid; Queen's Univ Belfast, United Kingdom

The electrical conductivity of lithium niobate thin film capacitor structures depends on the density of conducting 180 degree domain walls, that traverse the interelectrode gap, and on their inclination angles with respect to the polarization axis. Both microstructural characteristics can be altered by applying electric fields, but changes are time-dependent and relax, upon field removal, into a diverse range of remanent states. As a result, the measured conductance is a complex history-dependent function of electric field and time. Here, we discuss how the complexity in the kinetics of microstructural change, in this ferroelectric system, can generate transport behavior that is strongly reminiscent of that seen in key neurological building blocks, such as synapses and neurons. We show that potentiation-depression, spike-rate-dependent plasticity (SRDP) and spike-timing-dependent-plasticity (STDP) typically seen in synapses can also be seen in domain wall-based memristors. Even Ebbinghaus forgetting (a response more typical of an entire brain) can be replicated. Not only do such capacitor structures allow for neuromorphic responses, but the strong diode-like behaviours found can also be used to construct "AND" and inclusive "OR" logic gates, where "0" and "1" output states are clearly distinguishable. Realistic device modelling allows an extrapolation of results in more complex arrangements and, although non-ideal, output states can still be distinguished even in two-level cascade logic. Thus domain wall based devices allow for new kinds of processing in which both neuromorphic and conventional notions of computation sit side-by-side.

11:00 AM *QM02.03.07
Leveraging Domain Walls and Stochasticity in Ferromagnetic Materials for Unconventional Computing Jean Anne C. Incorvia and Samuel Liu; The University of Texas at Austin, United States

Future unconventional computing systems will require computers with high energy efficiency, low compute-memory bottlenecks, can be immersed in harsh conditions, are adaptive to sensory inputs, and can perform analog computations on the edge. A leading material class to tackle these extreme conditions are ferromagnetic materials and associated devices based on magnet tunnel junctions (MTJ). Devices made from magnetic materials, for example spin transfer torque magnetic random-access memory (STT MRAM), have relatively low switching energy, are nonvolatile, can be directly integrated with silicon CMOS, and are robust to radiation. They also have dynamical behaviors that can be leveraged for new computing paradigms, such as neuromorphic computing, for real-time training and inference on the edge. They also can sense electromagnetic fields, which could eventually lead to sensor-memory-processing combined analog systems.

We will present our results on leveraging domain walls (DWs) and stochasticity in ferromagnetic materials for these applications. We will show experimental results on how DWs integrated into MTJs (DW-MTJs) can act as both artificial synapses and artificial neurons [1]. We will show our results applied the devices to neural networks, as well as to a nearer-term application of analog content addressable memory (aCAM). We will show how the stochasticity of the DW motion aids in online learning without forgetting; how the stochasticity of the MTJ can be used as a random number generator with many knobs to control its randomness; and how the combination of both stochastic DWs and stochastic MTJs can be used to implement efficient Bayesian neural networks [2]. These results elucidate the wide design space for using ferromagnetic materials for unconventional computing.

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11:30 AM QM02.03.08
Ferroelastic Domain Walls in $BiFeO_3$ as Memristive Networks Jan L. Rieck[1,1], Davide Cipollini[1,1], Mart Salverda[1,1], Cynthia Quinteros[2], Lambert Schomaker[1,1] and Beatriz Noheda[1,1]; [1]University of Groningen, Netherlands; [2]Universidad Nacional de San Martín, Argentina

Within the last few years, memristors have aroused much interest in the scientific community due to the tunability of their resistive states.[1] Their hysteretic and non-volatile behaviour has made them attractive for memory applications. Recently, memristors are actively investigated due to their unique advantages as hardware in future neuromorphic computers. This emerging field comprises novel electronic circuits inspired by the human brain, motivated by its strikingly low energy consumption, high efficiency of cognitive tasks, such as image or pattern recognition, and the ability of the brain to reconfigure nervous connections, also called neuronal plasticity.[2] Prominent candidates for materials enabling neuromorphic computing on a hardware-level are ferroics,[3] in particular transition-metal oxides. A pervasive feature of ferroic material is the occurrence of domain walls (DWs) separating domains, which have different orientation of the order parameter (electric polarization in the case of ferroelectrics). Ferroelectrics have been already successfully employed for memristive devices such as ferroelectric tunnel junctions.[4] At the same time, ferroic materials paved the way for the large class of DW-based nanodevices, which can exhibit high reconfigurability as DWs can be easily written and erased.[5] Extensive works on the multiferroic oxide bismuth ferrite ($BiFeO_3$) have shown that DWs in thin films can be more conducting than the domains.[6] During thin film growth, $BiFeO_3$ self-assembles into a nanoscale network of conducting domain walls,[7] which can be tailored by varying the growth parameters. After growth, the electrical or even memristive properties[8] of the DWs can be potentially manipulated by driving electrical current through the DW network using electrodes on the film. Previous works on self-assembled $BiFeO_3$ DWs mainly focus on "vertical" (out-of-plane) DW conduction,[8,9] while the few reports on "lateral" (in-plane) conduction investigate single domain wall conduction.[10] In this work, lateral conduction (from wall to wall) through the self-assembled $BiFeO_3$ DW network is presented. The network is characterized using scanning probe techniques allowing local DW probing to investigate the memristive properties and mapping of the conductive DW network. The electrical response of the DW network is further studied by applying electrical stimuli to top electrode arrays. This project is part of the EU-funded *Innovative Training Network MANIC* ("*Materials for neuromorphic circuits*") and is embedded in the neuromorphic research initiative *Cognigron* of the University of Groningen to enable interdisciplinary cooperation from material science, mathematics and artificial intelligence.
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11:45 AM QM02.03.09
Direct Imaging of Heterogeneous Structure and Domain Switching in Nanocrystalline Ferroelectric Thin Films Daniel B. Durham[1], Khandker Akif Aabrar[2], Suman Datta[2], Nestor Zaluzec[1], Supratik Guha[3] and Charudatta Phatak[1]; [1]Argonne National Laboratory, United States; [2]Georgia Institute of Technology, United States; [3]The University of Chicago, United States

Ultrathin doped HfO_2 ferroelectric films are gaining increasing interest for next-generation computing technologies such as transistors, memories, and neuromorphic devices thanks to their high performance, reliability, and CMOS compatibility. FerroFETs using a ferroelectric/dielectric/ferroelectric gate stack are of particular interest for analog computing applications as they exhibit highly linear potentiation and depression curves. However, the underlying structural and domain switching mechanisms in these materials as compared to ferroelectric-only gates are not well understood. We will present correlative imaging of the grain and domain structure in Zr-doped HfO_2 (HZO) films and superlattices with nm-scale resolution using advanced electron microscopy approaches, including off-axis electron holography and scanning electron nanodiffraction with in-situ electrical biasing. We will discuss links observed so far between the compositional layers, the grain structure (including size, orientation, and structural phase), and polarization domain size and behavior. Finally, we will discuss opportunities for further development of imaging approaches as well as how our initial observations can inform pathways to improve device performance and scalability.

SESSION QM02.04: Control of Magnetic and Ferroelectric Orders III
Session Chairs: Dennis Meier and Jan Schultheiß
Wednesday Afternoon, April 12, 2023
Marriott Marquis, Fourth Level, Pacific B

1:30 PM *QM02.04.01
Controlling Topological Polar and Antiferromagnetic Textures in Multiferroic $BiFeO_3$ Vincent Garcia; CNRS-Thales, France

Antiferromagnetic materials are currently emerging as a new paradigm for spintronics as they offer key advantages over ferromagnets: insensitivity to external magnetic fields, much faster spin dynamics (THz range), and higher density packing because of the absence of stray fields. Moreover, tailoring topological spin textures in antiferromagnetic materials as it was done for ferromagnetic skyrmions is generating a lot of attention in the spintronics community. As antiferromagnets are insensitive to external magnetic fields, one must find alternative ways to control them. An optimal writing mechanism would demand low current densities (or ideally no current) to generate a complete reversal of antiferromagnetic domains or textures.

Here we take advantage of the room-temperature magnetoelectric coupling in epitaxial thin films of multiferroic $BiFeO_3$ to deterministically control antiferromagnetic spin textures via the ferroelectric domains. In as-grown single ferroelectric domains, while the surface of single crystals shows an unexpected continuous rotation of the antiferromagnetic cycloid propagation vector with the presence of antiferromagnetic topological defects [1], we are able to design a single antiferromagnetic domain by imposing an anisotropic strain in (111) epitaxial thin films. This model system, containing both a single ferroelectric and cycloidal domains, opens further opportunities for investigations of the interplay between non-collinear antiferromagnetic orders and spin transport. In striped ferroelectric domains of (001) BiFeO$_3$ thin films, we use epitaxial strain to finely tune the as-grown spin textures [2]. The anisotropy induced by epitaxial strain leads to a single antiferromagnetic cycloid within each ferroelectric domain [3]. The modification of the ferroelectric landscape allows us to control the propagation vector of the spin cycloid, to switch from one type of spin cycloid to another, or to convert from a collinear antiferromagnetic texture to a spin cycloid [1]. Furthermore, using resonant elastic X-ray scattering, we reveal the existence of chiral antiferromagnetic and ferroelectric objects at the domain walls of these periodic arrays [4, 5]. Finally, in BiFeO$_3$ nanostructures, we stabilize topological centre polar states using a radial electric field with antiferromagnetic objects embedded. These results open the way for electrically-reconfigurable antiferromagnetic topological objects.

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2:00 PM QM02.04.02
Control of Ordering in Polar Skyrmions Through the Ferroelectric Proximity Effect Peter Meisenheimer[1], Han Geyol Lee[1], Zhiyang Wang[2], Piush Behera[1], Vishantak Srikrishna[1], Yu-Tsun Shao[3], David A. Muller[3], Javier Junquera[4], Long-Qing Chen[2], Lane Martin[1] and Ramamoorthy Ramesh[1]; [1]University of California, Berkeley, United States; [2]The Pennsylvania State University, United States; [3]Cornell University, United States; [4]Universidad de Cantabria, Spain

Complex topological configurations are fertile ground for exploring emergent phenomena and exotic phases in condensed-matter physics. Topological solitons such as magnetic skyrmions have long drawn attention as stable quasi-particle-like objects, but the recent discovery of polar vortices and skyrmions in ferroelectric oxide superlattices has opened the door for new length scales and electric-field manipulation. Functional phenomena can be distinct from those of normal ferroelectrics, with properties such as collective dynamics, chirality, and negative capacitance. Topologically nontrivial ferroelectric textures are uniquely possible and manipulable by careful control of thin film boundary conditions, allowing for the exploration of phase space and order-disorder transitions with atomic precision. Here, we show controlled ordering of polar skyrmions enabled through electrostatic coupling, controlled by the ferroelectric proximity effect in incipient ferroelectric SrTiO$_3$.

2:15 PM QM02.04.03
Coherent Electric Field Manipulation of Single-Spins in Er^{3+} -Doped PbTiO$_3$ Thin Films Rafaela M. Brinn[1], Piush Behera[1], Peter Meisenheimer[1], Medha Dandu[2], Archana Raja[2] and Ramamoorthy Ramesh[3,1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Rice University, United States

Manipulation of spins by an electric field, rather than a magnetic field, has been an active area of research due to the potential applications in low power spintronics. Existing studies have focused on the manipulation of magnetization in materials with long range magnetic order. Recently, however, the manipulation of single spins with an electric field in doped ferroelectric systems has attracted interest. Ferroelectric oxides, such as PbTiO$_3$, offer a pathway to control the spin direction by manipulation of the ferroelectric order parameter, and thus the local crystal field of the defect site. Recent work on bulk Fe^{3+} doped PbTi^{4+}O$_3$ crystals have shown that the anisotropy of the Fe spins can be controlled by rotation of the electric dipole in PbTiO$_3$[1], however this effect only appears at low temperatures and has only been observed using microwave spectroscopy. In this work, we prepared Pb$_{1.199}$Er$_{0.001}$TiO$_3$ films with a thickness of 100 nm on top of TiO$_2$-terminated single-crystalline SrTiO$_3$ (001) substrates via pulsed-laser deposition. The Er ion substitutes the *A*-site (Pb-site) of the perovskite. Er^{3+}-doped materials are heavily studied, due to long electron and nuclear spin coherence times and telecom-wavelength spin-photon interfaces, making Er-dopants a strong potential candidate for long-distance quantum communication. Using time-resolved photoluminescence, we can measure the spin-lifetime by examining the decay of our photoluminescence signal after optically exciting an electronic transition in the Er^{3+}. Previous measurements of bulk Er^{3+} doped crystals have shown spin lifetimes on the order of 100s of microseconds[2]. Though less than that of quantum emitters in state-of-the-art systems, the potential for tunability with electric field may open the path for a new way of manipulating information without using energy intensive magnetic fields or large photonic based systems.

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2:30 PM QM02.04.04
Giant Conduction at 180° Domain Walls in Tetragonal PZT Controlled by Monolayer 2D Graphene Electrodes for Memristive Applications Felix Risch[1], Panagiotis Koutsogiannis[2], Yurii Tikhonov[3], Sadegh Kamaei Bahmaei[1], Adrian Ionescu[1], Cesar Magen[2], Igor Lukyanchuk[3] and Igor Stolichnov[1]; [1]Ecole Polytechnique Federale de Lausanne, Switzerland; [2]Universidad de Zaragoza (CSIC), Spain; [3]University of Picardie, France

Conductive domain walls (DWs) in ferroelectrics offer a promising concept for future memristive nanoelectronics in which these 2D channels function either as the nanoscale information storage units or as synaptic interconnections. The progress towards applications is impeded by relatively low DW conduction in the picoampere range as well as a lack of a precise control of the DW position.
Here we present highly conductive domain-wall-based device concept using the well-studied material Pb(ZrTi)O$_3$ (PZT) in combination with monolayer patterned graphene electrodes. The artificially created 180° domain walls in our strained 60nm PZT films (deposited on a DyScO$_3$ substrate with a SrRuO$_3$ bottom electrode) exhibit non-thermally activated currents of 200-400nA/μm for voltages $\leq$2V. They are created by electrically poling with moderate voltages of ~5V and show excellent stability enhanced by adjacent stable a- and c-domain configurations. Our recent results (Ref.1) suggest that the anomalously high conduction originates from the interplay between the interconnected a-domains and c-domains during the poling process in these thin films. This leads to the formation of nested and non-vertical 180° domain walls in the proximity of the bottom interface as well as to the distortion of a-domains, which break the domain boundary neutrality. First predicted by simulations, recent TEM studies now experimentally prove these non-trivial interdependent structures involving 180° domain walls and a-domains which lead to highly charged interfaces within the film, responsible for the extraordinary conductive response. Vertical parallel-plate capacitor devices using standard Cr/Au electrodes were tested, forming deterministically-switchable non-volatile resistive states with on/off ratios of 10^3 and tens of nanoampere read-out currents at 2V with excellent retention and stability characteristics. These functionalities were enabled by movement of a domain wall through an applied electric field. Moving towards more advanced functionalities, graphene flake electrodes were employed, allowing for a set of different resistive levels within one device by injecting and removing of more than one conductive domain wall under the electrode. More precise injection control is further offered by using patterned monolayer graphene devices as well as exploiting pressure induced conductive tuning. Thus, the multistate memristive devices are enabled by injection of the highly conductive domain walls, bridging the two electrodes of the capacitor, in combination with modified internal structure of the c-/a-domain interconnections, which

gradually alter the conductive response.
The authors gratefully acknowledge funding from the EU Horizon 2020 program under the MSCA-ITN action MANIC.

Reference:
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2:45 PM QM02.04.05
Strain Engineering of $KTaO_3$—Route to Stabilize Cooperative Polar Orders Salva Salmani-Rezaie[1], Tobias Schwaigert[1], Darrell Schlom[1], Kaveh Ahadi[2] and David A. Muller[1]; [1]Cornell University, United States; [2]North Carolina State University, United States

Potassium tantalate ($KTaO_3$) is an incipient ferroelectric perovskite in which quantum fluctuations prevent the emergence of a ferroelectric state. Because of its proximity to ferroelectricity, the structure can be tuned toward a ferroelectric state by small external perturbations, including applied stress or chemical substitution[1,2]. Despite being studied for a while, the mechanism of the emergence of ferroelectricity from the paraelectric state as a function of an external tunning parameter is not clearly understood. The lack of defect-free systems makes it difficult to distinguish between defect-induced or intrinsic off-centering of atoms and leads to an elusive picture of the ferroelectric phase transition of $KTaO_3$.
In this work, we report on using molecular-beam epitaxy to grow high-quality $KTaO_3$ films in an adsorption-controlled regime where film composition is controlled automatically via thermodynamics[3]. This growth regime for $KTaO_3$ granted us a viable means to apply epitaxial strain systematically and tune the structure toward the polar state. Here, using high-angle annual dark-field scanning transmission electron microscopy, we investigate local polar regions in a range of films with 0.5-2.1% compressive strain. We use the average deviation of the potassium column from the center of the cubic as a polar order parameter. We find that while atomic displacements are small and random in films with lower epitaxial strain, the displacements are cooperative in films with large strains forming nano-polar regions. We discuss the role of polar orders on the superconductivity of $KTaO_3$, in which a combination of large spin-orbit coupling and polar orders can give rise to intrinsic topological superconductors[4–6].

*This work was supported by the National Science Foundation (Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM)) under Cooperative Agreement No. DMR-2039380.

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3:00 PM BREAK

SESSION QM02.06: Domain Walls and Excitations for Unconventional Computing II
Session Chairs: Marty Gregg and Susan Trolier-McKinstry
Thursday Morning, April 13, 2023
Marriott Marquis, Fourth Level, Pacific B

8:30 AM *QM02.06.01
Hybrid Magnon Modes for Coherent Information Processing Axel Hoffmann; University of Illinois-Urbana Champaign, United States

Magnons are the fundamental excitations of magnetically ordered materials and span frequencies from GHz to THz at wavelengths down to the nm-regime. Because of their convenient frequencies and wavelengths, they have been considered for computational applications by encoding information into their phase and amplitude. Concurrently, magnons readily interact with a wide variety of different excitations, including microwave and optical photons, phonons, and other magnons. Such hybrid magnon dynamic excitations have recently gained increased interest due to their potential impact on coherent information processing [1]. This in turn opens new pathways for hybrid quantum information systems [2]. I will discuss two specific examples, where we developed fully integrated devices to demonstrate strong magnon-photon coupling in scalable coplanar devices [3], as well as magnon-magnon hybrid modes, which reveal new damping-like torques due to coherent spin pumping [4]. Lastly, I will show how we demonstrated strongly nonreciprocal magnon transduction using nano-scale microwave antennae. This provides a practical way for implementing high performance magnon isolation in magnetic thin-film devices for practical applications.

This work was supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division under Contract No. DE-SC0022060.

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9:00 AM *QM02.06.02
Ising Machines Based on Probabilistic Computing with P-Bits Giovanni Finocchio and Brahim Dkhil; University of Messina, Italy

Probabilistic computing with p-bits is a computing paradigm which has been proposed as a potential tool for dealing with different tasks such as inference. The identification of a strategy and the design of a hardware realization of probabilistic computers is very active nowadays.
In addition, it is very promising for the calculation of the ground state of an Ising Hamiltonian, i.e. to implement an Ising machine, and hence can have an impact in the solution of combinatorial optimization problems which can be mapped into the Ising model. Currently, the research on Ising machines is growing in the light of the fact they have a hardware-friendly implementation, it is necessary a binary state variable (Ising spin) together with a multiply and accumulate operation. It can be realized with semiconductor technology, optics, and spintronics. In particular, most of the efforts have been focused on the use of parametrically-driven oscillators to generate the binarization of the oscillator phase necessary to define the Ising spin. Those implementations have been mainly benchmarked with max-cut optimization combinatorial problems. Recently, it has been proposed the implementation of invertible logic gates, within the framework of probabilistic computing, with the aim to solve the classes of combinatorial optimization problems which can be described by logic circuits. The procedure, proposed for the first time for memcomputing, is based on the creation of the logic circuits representing the specific problem to solve, the replacement of the standard logic gates with the invertible logic gates, and the clamping of the outputs in order to let the circuit working in reverse.
In the talk, I will review our recent results on Ising machines (IMs) and their potential hardware implementation with spintronic technology focusing on oscillator-based IMs and IMs built with p-bits (probabilistic computing) [1].
This computing paradigm is very promising to solve combinatorial optimization problems (COPs), which are a class of mathematical problems that have important applications in a variety of industrial and scientific fields, which span from logistics to geoscience, from water distribution network design to job scheduling. Many of these, such as maximum cut (Max-Cut), maximum Boolean satisfiability (max-SAT) or the travelling salesman problem, are NP-complete or NP-hard, meaning in their worst-case instances they have no polynomial-time solution.
We show how the probabilistic computing can be used to solve max-sat instances (the other problems can be mapped on them) beating state-of-the art solvers having a time-to-solution to 95% at least one order of magnitude smaller [2].
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9:30 AM QM02.06.03
Tail-to-Tail and Head-to-Head Domain Walls in Ferroelectric Hafnium Zirconium Oxide—A First-Principle Analysis Tanmoy Kumar Paul, Atanu K. Saha and Sumeet Gupta; Purdue University, United States

Hafnium Zirconium Oxide (HZO) is a promising ferroelectric (FE) material for future electronic devices owing to its CMOS compatibility, strong ferroelectricity in ultrathin films and rich multidomain characteristics. Due to its unique atomic arrangement, the domain walls (DW) in different spatial directions can exhibit different properties. Most of the studies so far have focused on lateral DWs in HZO based FEs [1][2]. On the other hand, Tail-to-Tail/ Head-to-Head (T-T/H-H) DWs have not been well explored. To understand domain growth mechanism in HZO more comprehensively, there is a strong need to analyze the nature and characteristics of T-T/H-H DWs formed along the polarization direction.
In this work, we use First-Principle Density Functional Theory (DFT) calculations to predict domain formation along the polarization direction in HZO. We find that, although stable T-T DWs can form in HZO, H-H DW formation is energetically unfavorable. This phenomenon originates due to the unique segmentation of FE HZO unit cells in polar and non-polar layers with different ionic charge density as well as the energy minimization through oxygen termination at the surface/interface. We substantiate this claim further by studying the electrostatic potential profiles obtained from DFT calculations. Moreover, due to the depolarization energy, the formation of T-T DW is only possible above a critical thickness. The important consequence of the instability of H-H DW is twofold. H-H/T-T DW of periodic nature cannot form. Also, the nucleation must occur from interfacial sites to avoid H-H DW formation. Previous theoretical works [3] have shown different microscopic configurations of both upward and downward polarized domains in HZO. Considering all different combinations of the domains, we obtain the most energetically favorable T-T DW as the configuration where *pbcn* phase forms between the two neighboring FE domains. We analyze both freestanding HZO and metal-HZO-metal samples to establish the conditions for the stability of T-T DW.
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9:45 AM QM02.06.04
Decoupling Microstructure and Oxygen Vacancy Impacts to Phase Stability in Pure Hafnium Oxide Thin Films Samantha Jaszewski[1], Eric R. Hoglund[1], Anna Costine[1], Marc Weber[2], Shelby Fields[1], Alejandro Salanova[1], M. David Henry[3], Petra Reinke[1], James M. Howe[1] and Jon Ihlefeld[1]; [1]University of Virginia, United States; [2]Washington State University, United States; [3]Sandia National Laboratories, United States

The impact of oxygen content in the plasma on the crystallization and ferroelectric properties of HfO_2 films deposited by High Power Impulse Magnetron Sputtering (HiPIMS) will be shown. 20 nm HfO_2 films were sputtered from a 99.9% purity Hf metal target in Ar/O_2 atmosphere with varying O_2 content. Grazing-incidence X-ray diffraction (XRD) measurements show that films with the lowest and intermediate O_2 content are nearly 100% orthorhombic and/or tetragonal phases, while those with the highest O_2 content also contain the monoclinic phase, with a relative monoclinic phase fraction of 0.43. These differences in phase constitution produce unique polarization responses. The microstructure of these films is evaluated from scanning electron and atomic force microscopy images and grain size measurements reveal equivalent microstructures for each film, suggesting that oxygen content is responsible for the differences in phase assemblage and ferroelectric properties of these films. Several methods are used to assess the oxygen content in the films. Electron energy-loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS) show that oxygen content in the plasma correlates with oxygen content in the films, and that the films are significantly oxygen deficient. Quantification of the stoichiometry in the films after annealing by XPS and EELS results in values of x in HfO_x ranging from 1.3 to 1.7. Additionally, in spite of the large oxygen non-stoichiometries in these films, the leakage currents remain low ($<10^{-7}$ A/cm^2 at 2 MV/cm). XPS measurements reveal the presence of Hf^{3+} in the amorphous phase, which signifies the presence of positively charged oxygen vacancies, suggesting that the electrons compensating the oxygen point defects were delocalized from the vacancies. In the crystalline samples, however, no Hf^{3+} signature is observed, although the films are more oxygen deficient. These results, combined with the low leakage currents, indicate that the electrons are localized to the oxygen point defects and are not ionized in the samples after annealing. These results demonstrate that the properties of ferroelectric HfO_2 thin films are highly sensitive to oxygen content and that high oxygen vacancy concentrations do not necessarily lead to large leakage currents.

10:00 AM BREAK

10:30 AM *QM02.06.05
Bio-Inspired Time Varying Networks Hermann Kohlstedt; Kiel University, Germany

As a result of a hundred million years of evolution, living animals have adapted extremely well to their ecological niche. Such adaptation implies species-specific interactions with their immediate environment by processing sensory cues and responding with appropriate behavior. Understanding how living creatures perform pattern recognition and cognitive tasks is of particular importance for computing architectures: by studying these information pathways refined over eons of evolution, researchers may be able to streamline the process of developing more highly advanced, energy efficient autonomous systems.

With the advent of novel electronic and ionic components along with a deeper understanding of information pathways in living species, a plethora of opportunities to develop completely novel information processing avenues are within reach.

Basal biological principles are highlighted, including phylogenies, ontogenesis, and homeostasis, with particular emphasis on network topology and dynamics. While in machine learning, system training is performed on virgin networks without any a priori knowledge, the approach proposed here distinguishes itself unambiguously by employing growth mechanisms as a guideline to design novel computing architectures. Within this framework, experiments on low-frequency relaxation type oscillators coupled via complex time-varying networks will be presents. The spatio-temporal development of the network results from a mutual interaction between the oscillator ensemble and the network structure. The blooming and pruning of suddenly appearing conductive bridges and their relation to the synchrony state of the oscillator ensemble will be discussed.

11:00 AM QM02.06.06

Surface-Assisted Stabilization of Epitaxial Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Thin Films Jesse Schimpf[1], Xuezeng Lu[2], Abel Fernandez[1], James M. Rondinelli[3] and Lane Martin[1]; [1]University of California, Berkeley, United States; [2]Southeast University, China; [3]Northwestern University, United States

HfO_2-based ferroelectric thin films have drawn recent interest due to their compatibility with silicon and robust, scalable polarization, making them strong candidates for next-generation logic and memory technologies (*e.g.*, ferroelectric tunnel junctions and field-effect transistors). The metastability of the ferroelectric phase, however, poses a challenge to reliable fabrication, as phase impurities from partial decomposition increase leakage and reduce the switchable polarization. Such defects are highly dependent on film thickness, chemistry, processing conditions, and even the underlying electrode, leaving many questions as to how the ferroelectric phase is stabilized. Recent theoretical work suggests the presence of oxygen vacancies to be integral to both the formation energy and properties of the ferroelectric phase, but little has been done to experimentally verify and understand these claims.

Here, we show that the oxygen ambient during pulsed-laser deposition and subsequent annealing of epitaxial $Hf_{0.5}Zr_{0.5}O_2$ (HZO) films does not significantly affect the resulting crystal structure and ferroelectric properties. It is found, however, that the formation of the ferroelectric phase has a strong dependence on the chemistry of the underlying layer. Specifically, HZO grown on $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) exhibits the highest crystalline quality and ferroelectric polarization compared to other perovskite oxide electrodes explored so far, and this behavior can further be tuned through epitaxial strain. While the HZO itself is not strained to the electrode, its crystalline quality and remanent polarization improve as the LSMO is subjected to higher tensile strain. This implies that strain-induced changes to electrode properties have an influence on the stability of ferroelectric HZO. To glean more into which electrode properties are important, we synthesized HZO on a variety of perovskite oxide substrates and electrodes. While trends in lattice parameter, chemistry, and electronic structure appear to not influence the stability of the ferroelectric phase, differences in electrochemical properties of the underlying material do seem to affect the crystalline quality of the HZO, leading to varying levels of decomposition. It is proposed that the electrochemical activity of the substrate layer plays a role in mediating the oxygen vacancy content in the subsequent HZO film. To further explore this concept, we provide a direct comparison to films grown on $LaNiO_3$ (LNO), which is similar in lattice parameter to LSMO but less electrochemically active and find that growth thereon does not support the formation of ferroelectric HZO. In turn, to further explore the electrochemical activity of these electrodes, we employ electrochemical impedance spectroscopy and electrical conductivity relaxation measurements through a range of temperatures and background gases/pressures to quantify the ionic conductivity and surface exchange rates of the LSMO and LNO electrodes as a function of strain, mapping the results to structure and properties of the HZO grown thereafter. While bulk ionic conductivity and surface ionic exchange both increase with tensile strain, additional studies on electrode thickness reveal that bulk electrode properties do not have a significant impact on the HZO, thereby suggesting that surface ionic exchange is the principal factor in stabilizing the ferroelectric phase. To verify this, we include a comparison to other well-studied electrochemically active perovskites, $La_{0.9}Sr_{0.1}Ga_{0.95}Mg_{0.05}O_3$ (LSGM) and $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_3$ (LSCF), which have exceptional ionic conductivity and surface-ionic exchange, respectively. Again, we see that the higher surface exchange in LSCF produces higher quality HZO compared to LSGM. This insight is crucial to understanding the metastability of ferroelectric HZO, enabling the design of higher quality materials and devices for future technologies.

11:15 AM QM02.06.07

Chemically Inspired High Throughput Study for New Stable Ferroelectric Nitride Perovskites Bastien F. Grosso[1], Daniel Davies[1], Bonan Zhu[1], Aron Walsh[2] and David O. Scanlon[1]; [1]University College London, United Kingdom; [2]Imperial College London, United Kingdom

Nitride perovskites, with ABN_3 formula, have the potential to start a new paradigm in semiconductor devices. Indeed, this new class of materials is of great interest for developing oxygen-free functional materials, integrable in microelectronic devices and able to operate at low voltage. In this talk, we present a high throughput study of (AB)-N_3compositional space and show how candidate materials can be identified using simple chemical and structural considerations. We further thoroughly explore the potential energy surface of our candidate materials using symmetry elements and ab initio random structure searching (AIRSS) in order to identify a possible ground state structure. The outcome of our workflow is twofold. On the one hand, we provide new insights on the ground state structure of already identified candidate compositions and on the other hand we propose new thermodynamically stable, likely synthesizable, nitride perovskites. We conclude our study by highlighting the interesting functionalities of our most promising candidates and in particular we evaluate their potential for being ferroelectric.

11:30 AM QM02.06.08

Ferroelectric Enhancement of Superconductivity in Incipient Ferroelectrics Athby Al-Tawhid[1], Salva Salmani-Rezaie[2], Divine Kumah[1] and Kaveh Ahadi[1]; [1]North Carolina State University, United States; [2]Cornell University, United States

A combination of broken inversion symmetry and spin-orbit coupling gives rise to a wide range of exotic superconducting states, such as mixed-parity superconductivity and superconducting diode effect which can be harnessed towards unconvensional computation. Incipient ferroelectrics e.g., $SrTiO_3$, $KTaO_3$, $EuTiO_3$, and PbTe are near a polar instability. The emergence of superconductivity has been reported in some of these incipient ferroelectrics upon doping. Many unconventional superconductors, such as the cuprates, pnictides, and heavy fermion systems, occur in close proximity to magnetic fluctuations or magnetic orders, suggesting that these are important ingredients in the superconductivity in these materials. Here, ferroelectricity and superconductivity could be connected or accidental neighbors. Furthermore, the intersection of superconductivity and topologically nontrivial states is a fertile landscape for exciting quantum phenomena, including non-abelian excitations. Topologically nontrivial states have been reported in some of these polar superconductors. First, I will introduce the emergence of superconductivity and its interplay with ferroelectricity in tuned $SrTiO_3$ thin films. The ferroelectric films reveal a doubling in the critical temperature of superconductivity. Next, I will present our recent results on the emergence of 2D superconductivity in $KTaO_3$ (111) interfaces and doped SnTe. I will discuss the nature of superconductivity in the context of electronic structure, orbital character, and spin texture in thes materials systems.

SESSION QM02.07: Ferroelectrics for Unconventional Computing
Session Chairs: Dennis Meier and Jan Schultheiß
Thursday Afternoon, April 13, 2023
Marriott Marquis, Fourth Level, Pacific B

1:30 PM *QM02.07.01
Ferroelectric Devices for Neuromorphic Edge Computing Erika Covi; NaMLab, Germany

As the world is becoming more and more interconnected, systems increasingly operate on the edge – we have many wearable and implantable devices which monitor our health or our daily routine, give us suggestions on how to improve our wellbeing, or even save our lives, e.g., by preventing heart failure. To work properly, these devices need to be able to process the data generated and use them to learn, adapt, and interact with the external environment [1]. In this scenario, the assumption of fungibility, i.e., all the machines in a network have the same capabilities and can accomplish all tasks, which is the basis of the paradigm of powerful mainframes we have used so far, does not hold anymore, since the quality of data that our devices have to process is very diverse and has to be taken into consideration. Designing intelligent systems capable of local edge computing is therefore becoming a strategic goal in next generation smart systems. Event-based neuromorphic systems provide a low-power solution by using artificial neurons and synapses to process data asynchronously in the form of spikes [2]. However, the tight memory and power constraints in edge systems call for the design of novel architectures that use emerging technologies based on new concepts and materials to extend the functionality of state-of-the-art Complementary Metal Oxide Semiconductor (CMOS) technology [3].
Thanks to its CMOS-compatible fabrication process and extreme energy efficiency, Hf-based ferroelectric devices are rapidly affirming themselves as one of the most promising technologies for neuromorphic computing [4]. Here, we present fundamental building blocks, i.e., neurons and synapses, for edge computing neuromorphic networks that combine ferroelectric and CMOS technologies. We demonstrate electrically tuneable neural and synaptic dynamics achievable by tuning the switching of the Hf-based ferroelectric devices. Finally, the main challenges to achieve a neuromorphic-ferroelectric hardware are presented, particularly in the context of optimising such systems for applications on the edge.

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2:00 PM QM02.07.02
Quantifying the Electrode Capping Effect’s Role on Phase Stability in Ferroelectric Hafnium Zirconium Oxide Jon Ihlefeld[1], Shelby Fields[1], Truong Cai[2], Samantha Jaszewski[1], Kyle Kelley[3], Helge Heinrich[1], M. David Henry[4] and Brian Sheldon[2]; [1]University of Virginia, United States; [2]Brown University, United States; [3]Oak Ridge National Laboratory, United States; [4]Sandia National Laboratories, United States

Ferroelectric hafnia is poised to enable a next generation of microelectronic devices owing to its unprecedented compatibility with mainstream semiconductors and ability to maintain ferroelectricity to single unit-cell dimensions without the necessity of epitaxy. Realizing broad implementation, however, likely requires phase pure materials. It is widely known that ferroelectric hafnium oxide-based films exhibit larger orthorhombic phase fractions and polarization responses when crystallized with a top electrode in place. The top electrode is described as providing a ‘capping effect’ that imparts stress to the hafnia film upon cooling and prevents transformation into the non-ferroelectric monoclinic phase. While compelling evidence of the importance of the top electrode has been presented previously, the quantitative impacts of its role on phase stability are lacking. In this work, the biaxial stresses imparted by the electrode clamping effect are quantified using X-ray diffraction $\sin^2(\Psi)$ analyses measured on 20 nm thick $Hf_{0.5}Zr_{0.5}O_2$ (HZO) films processed on TaN bottom electrodes with and without top TaN electrodes. Both HZO films are in a state of biaxial stress after crystallization, however the film with a top electrode has a 70% larger (3.5 GPa) stress magnitude than the film without a top electrode (2.1 GPa). Furthermore, the film processed with a top electrode is nearly 100 vol.% the ferroelectric phase whereas the film processed without the top electrode contains only 60 vol.% of the ferroelectric phase. Removal of the top electrode results in a reduction in tensile stress in the hafnia layer by 0.8 GPa and is accompanied by a 10% reduction in ferroelectric phase fraction. On the basis of strain energy reduction, we calculate an energy barrier for the total orthorhombic to monoclinic phase transformation to be 12 meV/f.u. This quantitative assessment of the clamping effect is accompanied by wafer flexure-based stress measurements to quantify stress development for each processing step, as well as temperature-dependent X-ray diffraction and wafer flexure measurements that allow us quantify the temperatures that accompany phase formation and stress evolution. We will show that it is not an in-plane mechanical constraint imposed by the top ‘capping’ electrode that leads to the large biaxial tensile stress in the hafnia layer. Rather, the electrode serves to limit out-of-plane displacements and prevent formation of the monoclinic phase. This work provides a foundation by which phase-pure ferroelectric hafnia can be prepared by careful consideration of top electrode deposition and processing.

2:15 PM QM02.07.03
Phase Transformation Driven Wake-Up in Ferroelectric Hafnium-Zirconium Oxide Films Observed Using Nano-FTIR Thomas Beechem[1], Samantha Jaszewski[2], Kyle Kelley[3], Jacob Minyard[1], Fernando Vega[1], Stephanie Gilbert Corder[4], Hans Bechtel[4] and Jon Ihlefeld[2]; [1]Purdue University, United States; [2]University of Virginia, United States; [3]Oak Ridge National Laboratory, United States; [4]Lawrence Berkeley National Laboratory, United States

Ferroelectric hafnium zirconium oxide (HZO) is being pursued as a near-memory computing technology as it can be densely scaled and is compatible with silicon. The orthorhombic phase making HZO ferroelectric is metastable, however. Being metastable, the formation of this technology-enabling orthorhombic phase can be affected by several factors including dopants, stress, crystal size, and oxygen vacancies. HZO devices are typically multi-phase in their as fabricated state and require wake-up to realize a stable ferroelectric polarization. The mechanisms driving this wake-up are under debate. Maturation of ferroelectric HZO technology, therefore, requires means of observing, understanding, and ultimately controlling the wake-up process.

Here, we observe an electric-field driven transformation from the non-ferroelectric tetragonal to ferroelectric orthorhombic phase in 20 nm thick atomic layer deposited (ALD) HZO films using a combination of piezoresponse force microscopy (PFM) and tip-enhanced nanoscale Fourier transform infrared spectroscopy (nano-FTIR). HZO films were subject to varying magnitudes and polarities of electric field over 20x20 µm areas as applied by PFM within a glovebox filled with inert gas. The ferroelectric response was then measured in each of these regions with PFM, whereupon the local phase fraction was assessed with nano-FTIR. IR-spectra show that the orthorhombic phase becomes more predominant relative to its non-ferroelectric tetragonal form in areas exposed to larger electric field magnitudes. The field driven nature of the phase-transformation, in turn, suggests the central role of the charged oxygen vacancies in orthorhombic phase formation, wake-up, and ultimately device performance.

2:30 PM BREAK

3:30 PM *QM02.07.04
Exploring Architectural Innovations with Ferroelectronics Vijaykrishnan Narayanan[1], Yi Xiao[1], Yixin Xu[1] and Kai Ni[2]; [1]Penn State University, United States; [2]Rochester Institute of Technology, United States

Data generated over social media, biomedical monitoring, and the Internet-of-Things is increasing exponentially. The ability to extract useful information from this big data is critical towards advances in varied domains. The enormity of the data is outstripping the ability for electronic systems to process, communicate and store the data that is being generated. While historically transistor scaling helped address the growth in computational needs, with scaling now reaching its limits, new approaches are needed. To this end, this work envisions a new ferroelectric-based platform that can provide unprecedented opportunities to scale chip designs in the third dimension, to blur the gap between memory and logic functionality through seamless integration and novel beyond Von Neumann architectures to accelerate big data analytics.

Ferroelectric devices leverage the ability of an electric field to induce reversible polarization. This polarization provides a state representation of digital design. The discovery of ferroelectricity in doped hafnia, reported in 2011, has had a transformative Impact on ferroelectric driven semiconductor platforms. As hafnia is integral to advanced CMOS nodes, the prospect of rapid integration of ferroelectric elements in advanced CMOS process nodes is promising. The integration of a ferroelectric material in the gate stack of a CMOS device enables another desirable feature, that of a logic compatible, compact single device memory primitive. This capability allows fine-grain integration of logic and memory, enabling processing in memory and reducing overheads of data movement. These prospects have fueled ferroelectric innovations from new materials to novel architectures. This work will emphasize the need for co-design of materials, devices and circuits informed by architectural and application needs.

By utilizing distinct properties of ferroelectric devices such as Ferroelectric Tunnel Junction (FTJ) and Ferroelectric Field-Effect Transistor (FeFET), system-level benefits for different metrics such as performance, power, area or security will be discussed. An example of that is an FeFET-based active interconnect that supports hardware functional obfuscation by utilizing the threshold voltage programmability of the FeFET. Another example is a FeFET 1T NOR array. FeFET 1T NOR array has many potential applications: routing switches for field-programmable gate array (FPGA), weight cells in a crossbar array to accelerate multiplication-accumulation computations in machine learning accelerators, and interaction controllers between artificial spins in Ising machines. We will discuss challenges in efficient write mechanisms in such NOR arrays.

4:00 PM QM02.07.07
Studying the Effect of Cation Stoichiometry and Thickness Gradients on Epitaxial BaTiO3 Films Using Off-Center Pulsed Laser Deposition
Romar Angelo Avila[1], Yorick A Birkhölzer[1,2], Panagiotis Koutsogiannis[3], Menno Struik[1], Yibin Bu[1], Cesar Magen[3], Guus Rijnders[1] and Gertjan Koster[1]; [1]University of Twente, Netherlands; [2]Cornell University, United States; [3]University of Zaragoza, Spain

The growth parameters used in complex oxide thin film deposition are typically tuned to minimize heterogeneity. However, composition gradients in film thickness and stoichiometry can be created intentionally by taking advantage of the anisotropic expansion of the plasma plume in pulsed laser deposition (PLD). Here, we apply off-center PLD to study epitaxially grown $BaTiO_3$ (BTO) thin films on (001) oriented $SrTiO_3$ single crystal substrates. Instead of aligning the substrate symmetrically in front of the ablated target area, we deliberately offset the substrate by several millimeters from the central position while keeping the target and substrate surfaces parallel. The Ba:Ti ratio was measured as a function of laser fluence by microfocus X-ray photoemission spectroscopy at multiple positions along the sample length. We managed to obtain a stoichiometric film, i.e. 1:1 cation ratio, all across the 10 mm long sample once the fluence was increased above a threshold value. Microfocus X-ray diffraction shows a monotonic decrease in the out-of-plane lattice parameter when measuring further away from the central position at which the plume impinges on the substrate at the shortest distance. Furthermore, scanning transmission electron microscopy was used to elucidate the microstructural defects present in the nonstoichiometric samples and their localized effect on the lattice parameter by comparing lamella obtained from different locations along the sample length. This study highlights the potential of off-center PLD as an efficient way to study the effect of compositional gradients on the material properties of BTO and other multi-cation functional oxides.

4:15 PM QM02.07.08
Optimizing Monolayer Ferroelectric ZrO_2 on Si (001) Kidae Shin, Frederick J. Walker and Charles H. Ahn; Yale University, United States

A single atomic layer of ZrO_2 grown directly on an abrupt Si (001) surface shows ferroelectric switching behavior.[1] Being at the ultimate thickness limit of a monolayer (ML), this system has the potential to aggressively scale down device size. Motivated by density functional theory (DFT) calculations that attribute the polarization switching to displacements of Zr-O dipoles, we aim to control the magnitude of capacitance – voltage (C-V) hysteresis by controlling the density of Zr-O dipoles in the ML ZrO_2 film. We report that the Zr-O dipole density in the ML ZrO_2 can be controlled by varying film annealing conditions and characterized using x-ray photoelectron spectroscopy (XPS) measurements of Zr 3d core level energies. Results show that the Zr^{4+} XPS relative intensity can vary from about 30% to 90% depending on the film annealing conditions. Using C-V measurements, we show that the magnitude of the hysteresis is proportional to the density of Zr-O dipoles as characterized by XPS, and thus can be optimized by varying the annealing conditions.

Reference
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SESSION QM02.08: Poster Session: Functional Ferroic Materials for Unconventional Computing
Session Chairs: Naoya Kanazawa and Beatriz Noheda
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM QM02.08.01
Identifying Local Structural Features to Characterize Phase Transitions and Energy Landscape in the Thiophosphate Ferroelectric $Sn_2P_2S_6$
Albina Borisevich[1], Blair Tuttle[2], Andrew O'Hara[3], Sabine M. Neumayer[1], Rama K. Vasudevan[1], Sokrates Pantelides[3] and Petro Maksymovych[1]; [1]Oak Ridge National Laboratory, United States; [2]Pennsylvania State University Behrend, United States; [3]Vanderbilt University, United States

Recently ferroelectric materials from the thiophosphate and related families have attracted considerable attention due to their rich functional behavior and related potential for applications. For example, for the layered ferroelectric material $CuInP_2S_6$, a quadruple-well potential was discovered, with four distinct polarization states that are stable at room temperature [1]. For $Sn_2P_2S_6$, a 3D ferroelectric, a triple-well potential was predicted, where both a polar and a non-polar state coexist below the Curie temperature [2]. In this work, we explore local structural features of $Sn_2P_2S_6$ to identify the relevant descriptors that correlate with polar order and observe their evolution across the phase transition using high-resolution scanning transmission electron microscopy (STEM) and density-functional-theory (DFT) calculations.
$Sn_2P_2S_6$ has a monoclinic structure that changes in complex ways as a function of strain/pressure and polar state. Observing $Sn_2P_2S_6$ flakes below and above the phase transition temperature in the electron microscope, we can identify changes in the diffractogram (overall structure) that is consistent with the published structures of the low-[3] and high-temperature[4] forms. We then use a combination of high-resolution STEM and theoretical studies to find promising candidates for local structural correlates of ferroelectric behavior. In particular, Sn_2 dimers are easily identifiable on high-resolution images for multiple zone-axis orientations. DFT calculations conducted for both polar and non-polar states show that Sn_2 dimer rotations with respect to lattice direction correlates with changing isostatic pressure on the system and lattice polarization and that the rotation angles are measurably distinct for polar and non-polar states. STEM imaging across the phase transition yielded a complex picture of Sn_2 rotations below the Curie temperature, while above it the rotations correspond closely to those expected for the non-polar state, suggesting the coexistence of different states below the transition.
*This work was funded by MSED of the DOE BES and conducted in part at the CNMS, a DOE Office of Science User Facility. The theoretical work was funded by DOE BES grant No. DE-FG02-09ER46554.
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5:00 PM QM02.08.02
Enhancement of Optical Activity and Properties of Barium Titanium Oxides to Be Active in Sunlight through Using Hollandite Phase Instead of Perovskite Phase Adil Alshoaibi; King Faisal University, Saudi Arabia

The present study aims to enhance the optical properties of barium titanate through
narrowing its band gap energy to be effective for photocatalytic reactions in sunlight and be useful for solar cells. This target was achieved through growth of the hollandite phase instead of the perovskite phase inside the barium titanate crystals. By using solvent thermal reactions and thermal treatment at different temperatures (250 �C, 600 �C, and 900 �C), the hollandite phase of barium titanate was
successfully obtained and confirmed through X-ray diffraction (XRD), Raman spectra and scanning electron microscopy techniques. XRD patterns showed a clear hollandite phase of barium titanium oxides for the sample calcined at 900 �C (BT1-900); however, the samples at 600 �C showed the presence of mixed phases. The mean crystallite size of the BT1-900 sample was found to be 38 nm.
Morphological images revealed that the hollandite phase of barium titanate consisted of a mixed morphology of spheres and sheet-like features. The optical properties of barium titanate showed that its absorption edge shifted to the visible region and indicated band gap energy tuning ranging from 1.75 eV to 2.3 eV. Photocatalytic studies showed the complete and fast decolorization and
mineralization of green pollutants (naphthol green B; NGB) in the prepared barium titanate with hollandite phase after illumination in sunlight for ten minutes. Finally, it can be concluded that the low band gap energy of barium titanate having the hollandite phase introduces beneficial structures for optical applications in sunlight.

5:00 PM QM02.08.04
Designing High-T_c Bulk and Two-Dimensional (2D) Superconductors with BCS-Inspired Screening, Density Functional Theory, Deep-Learning and Experiments Daniel Wines, Kamal Choudhary, Adam Biacchi, Kevin Garrity and Francesca Tavazza; National Institute of Standards and Technology, United States

High-throughput density functional theory (DFT) calculations allow for a systematic search for conventional Bardeen–Cooper–Schrieffer (BCS) superconductors. With the recent interest in bulk and two-dimensional (2D) superconductors, we develop a multi-step workflow for the discovery of conventional superconductors. After screening over 55,000 bulk and 1,000 2D materials in the JARVIS-DFT database, we perform electron-phonon coupling (EPC) calculations and use the McMillan-Allen-Dynes formula to calculate the superconducting transition temperature (T_c) for 1,736 bulk and 172 2D materials. From this, we identify 112 bulk and 33 monolayer structures that are dynamically stable with superconducting transition temperatures above 5 K, including bulk materials such as VTe, KB_6, Ru_3NbC, V_3Pt, ScN, LaN_2, RuO_2, and TaC and 2D materials such as W_2N_3, NbO_2, ZrBrO, TiClO, $NaSn_2S_4$, $Mg_2B_4C_2$ and the previously undiscovered $Mg_2B_4N_2$, which has a T_c of 22.51 K. Additionally, we demonstrate that deep-learning models can predict superconductor properties, including the Eliashberg function, thousands of times faster than direct first principles computations for bulk materials. Finally, we performed experiments to determine the T_c of selected layered superconductors (2H-$NbSe_2$, 2H-NbS_2, ZrSiS, FeSe) and discuss the measured results within the context of our DFT computed results. We aim that the outcome of this workflow can guide future computational and experimental studies of new and emerging superconductors by providing a roadmap of high-throughput DFT data.

5:00 PM QM02.08.05
Piezoelectricity in Li-based Layered Perovskite Oxides from First Principles Kishwar-E Hasin, Nabaraj Pokhrel and Elizabeth Nowadnick; University of California, Merced, United States

Layered perovskite oxides such as the $A_3B_2O_7$ n=2 Ruddlesden-Popper family have generated significant recent interest because they host a variety of novel properties such as hybrid improper ferroelectricity, competing structural phases, and complex domain structures. A closely related family of materials are the Li-based layered perovskites $Li_2AB_2O_7$, with crystal structures characterized by alternating perovskite and lithium oxide layers. Recent experiments have reported a competition between ferroelectric and non-polar phases in $Li_2SrNb_2O_7$, mediated by coupled octahedral rotation distortions, polarization, and antipolar distortions. In this work, we use density functional theory to explore piezoelectricity in $Li_2SrNb_2O_7$ and the related Li-based layered perovskites $Li_2CaNb_2O_7$, $Li_2SrTa_2O_7$, and $Li_2CaTa_2O_7$. We investigate both the clamped-ion and internal strain contribution of the piezoelectric coefficients, and determine how the piezoelectric tensors depend on crystal structure and chemical composition. Our results advance fundamental understanding of piezoelectricity in this novel family of Li-based ferroelectric oxide materials.

5:00 PM QM02.08.06
In-Plane and Out-of-Plane Magnetic Behavior in Iron Borate Single Crystal Jacob Pfund, Jacob Franklin, Joshua Bedard, Ilya Sochnikov and Menka Jain; University of Connecticut, United States

Iron Borate ($FeBO_3$) is a unique material with promising applications in magnetic memory and magneto-optical devices. Single crystal of FeBO3 is transparent and green with rhombohedral calcite-type structure (space group D^6_{3d}). It is a room temperature ferromagnet with an optical band gap of 2.9 eV and plate-like growth. Neutron studies have shown that $FeBO_3$ becomes antiferromagnetic (AFM) below T_N ~348 K, with weak ferromagnetism in which the magnetic moments of the sublattice lie in the basal plane. However, there is lack of in-plane and out-of-plane magnetic data at low temperatures. In this work, we present the detailed in-plane and out-of-plane magnetic behavior in single crystal of $FeBO_3$. Temperature-dependent magnetic measurements show applied magnetic field dependent behavior at low temperatures (T< 25 K). Low temperature SQUID images are presented to identify the canting of magnetic moment and novel behavior near the ground state. Detailed magnetic properties, such as magnetic moment, exchange interaction parameters, and canting angles are calculated and presented.

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5:00 PM QM02.08.07
Storage Charge Boosting Dependence of Ferroelectric-Based Capacitors on Various Electrical Input Pulse Yoomi Kang, Minjeong Kang, Jisu Byun and Seung Eon Ahn; Tech University of Korea, Korea (the Republic of)

With the development of high-technology industries, advanced semiconductor studies to further reduce power consumption in nanoscale devices and store extremely large amounts of data are actively conducted. In DRAM technology, the efforts to overcome the reduced storage charge caused by scaling down are increasing. Recently, the negative capacitance (NC) effect of Ferroelectric is attracting attention as a solution that can provide operation with large capacitance density and low power consumption by improving energy efficiency. The NC effect based on Landau-Ginzburg-Devonshire Theory (LGD) is related to the intrinsic double-well shape of the Ferroelectric polarization-energy landscape. In addition, electrical measurements under certain conditions occur charge boosting by controlling the depolarization field. Many studies have demonstrated the possibility of direct NC effect observation and charge boosting due to the polarization switching of ferroelectricity. However, the key factor of the direct correlation between the polarization switching of ferroelectricity and charge boosting, according to input energy, is still not identified. In this study, polarization switching and charge boosting according to pulse conditions applied to Ferroelectric capacitors were analyzed from an energy perspective. A Zr-doped HfO_2-based Ferroelectric capacitor was developed, and the effect of controlling charge boosting was observed depending on the artificial electrical signals. With These results, we will present the applicability of DRAM cell CAP of Ferroelectric capacitors.

5:00 PM QM02.08.08
Understanding the Effects of Polar Topological Phases in Epitaxial Oxide Superlattices on Phonon Scattering Rate Sara Makarem[1], Eric R. Hoglund[1], Peter Meisenheimer[2], Patrick E. Hopkins[1] and Ramamoorthy Ramesh[2]; [1]University of Virginia, United States; [2]University of California, Berkeley, United States

Epitaxial oxide superlattices and heterostructures give rise to spatially complex topological configuration such as polar skyrmions and vortices. Some of the emergent properties of these stable quasi-particle objects in epitaxially grown (PbTiO3)n/(SrTiO3)n (PTO/STO) superlattices have been extensively studied[1,2]. However, a detailed study of the effects of these topological phases on the scattering mechanisms and resulting thermal properties was unexplored. Since The type of topology introduces different long to medium range order, in this study we aim to investigate phonon relaxation time as one of the key parameters involved in both thermal transport and coherent phonon phenomena. We perform Time-domain Brillouin scattering (TDBS), an ultrafast laser spectroscopy technique, on the (PTO/STO) superlattices and trilayers to interrogate the underlying changes in phonon dynamics. The displacements and the length scales associated with the existing topological phases in these superlattices change phonon lifetimes where all of these phases have collective topological modes. In other words, we reveal the effect of (anti)ferroelectric displacements near phase boundaries on phonon dampening due to different degrees of frustrated acoustic phonons.
1. Nat. Comm. **12**, 6273 (2021)
2. Nat. Mater. **20**, 194–201 (2021)

5:00 PM QM02.08.09
Charge Boosting Effect with Polarization Switching Properties of Zr Doped HfO_2 based Ferroelectric Capacitors for DRAM Cell Capacitor Application Minjeong Kang, Yoomi Kang, Jisu Byun and Seung Eon Ahn; Tech University of Korea, Korea (the Republic of)

As the 4th industry accelerates, there are continuous requirements to enhance the density and performance of DRAMs. Efforts to increase integration density and improve the performance of DRAM have continued, but the development of a new concept of cell-cap due to the limitation of scaling down of Cell-CAP EOT is necessary. In recent studies, the possibility of increasing the amount of storage charge using the negative capacitance (NC) effect of ferroelectrics has been suggested to overcome this issue. However, a direct association between charge boosting and the ferroelectric characteristics such as domain switching distribution at the coercive field (Vc), and remanent polarization (Pr) has not been proved. Therefore, in this study, we analyzed the correlation of charge boosting according to ferroelectric properties in a cap for DRAM (TiN/Hf0.5Zr0.5O2/TiN) of less than 10nm. The dependence of the switching slope at Vc and storage charge amplification on Pr was confirmed. In this study, we show the charge boosting according to the device characteristics and propose conditions to maximize them.

5:00 PM QM02.08.10
Imaging Ferroelectric Switching in Transition Metal Dichalcogenide Moiré Bilayers Using 4D-STEM Nikta Khaloo, Madeline Van Winkle and Kwabena Bediako; University of California, Berkeley, United States

Interfacial ferroelectricity is a relatively new phenomenon that has been observed in two-dimensional (2D) materials, including group VI transition metal dichalcogenide (TMD) moirsuperlattices. While H-phase TMDs are not inherently ferroelectric, artificially stacking two TMD monolayers with a near 0° (3R-like) alignment between the lattices produces a moiré bilayer with broken inversion symmetry and a spontaneous, switchable out-of-plane polarization at room temperature. Further, the size of polarized domains, and resulting coercive field, can be controlled by changing the interlayer twist angle, making this a highly tunable platform for studying ferroelectric behavior in the 2D limit. Previous scanning probe and electron microscopy experiments have provided a microscale picture of polarization switching in TMD moiré bilayers, illustrating localized motion of domain walls within the moiré superlattice upon application of an external electric field. However, a detailed understanding of this structural response on an atomic to nanoscale remains outstanding. There is also an open question of how intralayer strain evolves during the switching process, which would have significant implications for the (opto)electronic properties of the system. Here we use interferometric four-dimensional scanning transmission electron microscopy (4D-STEM) to image ferroelectric switching and map intralayer strain distributions in TMD moiré bilayers with sub-nanometer resolution. This work offers fundamental insight into how an electrical stimulus produces a modified moiré structure and opens avenues for imaging other electrically controllable phenomena in moiré architectures.

5:00 PM QM02.08.13
Exploring a New Polar Symmetry for $BiInO_3$ Deokyoung Kang[1], Megha Acharya[1,2], Piush Behera[1,2], Ching-Che Lin[1] and Lane Martin[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

While there are numerous perovskite oxides known to exhibit polar symmetry already, the search for new polar materials continues with urgency due to the range of advanced functional properties exhibited by these materials (*e.g.*, piezoelectricity, pyroelectricity, ferroelectricity, *etc*.) and the slew of applications that such materials can be used in. Modern high-throughput workflows based on density-functional theory (DFT) calculations are now identifying new candidate ferroelectrics with emerging functionalities[1]. One example is $BiInO_3$ which is an underexplored perovskite oxide that was predicted to show Rashba effects and persistent spin texture with high spin-orbit coupling when stabilized in the polar $Pna2_1$ phase[2]. Initial efforts to synthesize $BiInO_3$, however, reveal that thin films tend to adopt a non-polar orthorhombic *Pnma* structure which, of course, precludes the observation of such exotic properties[3]. Here, we explore routes to manipulate the energy landscape of $BiInO_3$ and induce polar symmetry by controlling the growth kinetics.
While the goal was still to achieve the polar $Pna2_1$ phase of $BiInO_3$, we have observed a new polar phase of $BiInO_3$ when it is epitaxially grown as a thin film on perovskite substrates at high growth temperatures using pulsed-laser deposition. Detailed X-ray diffraction studies reveal that the resulting films exhibit what appears to be $LiNbO_3$-type structure with space group $R3c$ (henceforth R-$BiInO_3$) which was neither reported in computational work nor in other thin-film studies (*Pnma*, henceforth, O-$BiInO_3$). This new phase has a smaller pseudocubic lattice parameter (~3.95 Å) than that of *Pnma* phase (4.2 Å), which allows the R-$BiInO_3$ phase to have a smaller lattice mismatch with conventional perovskite substrates with pseudocubic lattice parameters generally between 3.6-4 Å. X-ray-based reciprocal space mapping studies indicate that the R-$BiInO_3$ phase has a larger than usual rhombohedral distortion angle (~3.7°) due to it having a low tolerance factor value (~0.78) which makes the film fully relaxed on all perovskite substrates tested regardless of the lattice mismatch. The R-$BiInO_3$ phase has a monoclinic distortion along the $<110>_{pc}$, where the structural variants and the domain structure are determined by the symmetry of the substrate. The R-$BiInO_3$ phase was found to exhibit four structural variants when grown on $SrTiO_3$ (001) and only two structural variants when grown on $GdScO_3$ (110) and $DyScO_3$ (110) substrates. The polar nature of the R-$BiInO_3$ phase was further confirmed using second harmonic generation (SHG) polar mapping and is found to be consistent with rhombohedral symmetry with 109° domain structures as measured in X-ray diffraction studies. We observed from dielectric and transport studies that the R-$BiInO_3$ phase exhibits lower resistivity ($\sim 10^4$ Ω●cm) than O-$BiInO_3$ ($\sim 10^7$ Ω●cm) and higher dielectric constant (~110) than O-$BiInO_3$ (~40). We further study the optical and ferroelectric properties to fully understand this new phase. While this phase is different from the desired $Pna2_1$ phase, this work on a $LiNbO_3$-type $BiInO_3$ still motivates future research efforts on emerging functionalities including piezoelectricity, ferroelectricity, and Rashba effect. Furthermore, since it has isosymmetric phase with $BiFeO_3$, a room-temperature multiferroic material, $BiIn_xFe_{1-x}O_3$ solid solution system can potentially exhibit novel magnetic and ferroelectric properties by modifying lattice structure.

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SESSION QM02.09: Virtual Session: Functional Ferroic Materials for Unconventional Computing
Session Chair: Erika Covi
Tuesday Morning, April 25, 2023
QM02-virtual

8:00 AM *QM02.09.01
Ferroelectric Synapses in Neuromorphic Circuits—Integration of Perovskite- and Hafnia-Based Crossbars Laura Bégon-Lours[1], Mattia Halter[1,2,3], Cécile Carretero[4], Donato F. Falcone[1], Marilyne Sousa[1] and Bert Offrein[1]; [1]IBM Research - Zurich, Switzerland; [2]ETH Zürich, Switzerland; [3]Lumiphase AG, Switzerland; [4]Centre National de la Recherche Scientifique, France

Training neural networks nowadays demands a large time and energy budget, slowing the spread of so-called “neuromorphic computing”. Efforts have been put in developing bio-inspired devices supporting neuromorphic computers, targeting a nano-sized (5x50x50 nm^3), low-power (~20 W/petaflop), non-volatile (>1 year), fast (100 ns set/read pulses) and analog (>5 bits) memory. In Mbit arrays, such devices will co-locate storage and computing. Today’s options rely on ion-motion (e.g. red-ox reactions or phase change materials) with intrinsic limitations in terms of endurance and stochasticity. In contrast, the ferroelectric memristor is a purely electronic concept.
In this talk, we present integration schemes for crossbar arrays based on two ferroelectric memristors technology. The first one is based on epitaxial ($BiFeO_3$) on an oxide electrode ($Ca_{0.96}Ce_{0.04}MnO_3$), grown on 1x1cm^2 single crystal substrates ($YAlO_3$). The synaptic functionality of such heterostructure was demonstrated earlier using simple nanocapacitors (shared bottom electrode)[1]. The second technology is on based polycrystalline $HfZrO_4$, also on an oxide electrode (WO_x), but directly integrated on Silicium. It follows the Back-End-Of-Line compatible process-flow proposed by Bégon-Lours *et al*.[2]. Passive crossbar arrays are fabricated for both technologies, with different constraints on the processing conditions.
The dynamics and the synaptic behavior of the devices are presented, and the functionality of small-scale cross-bar arrays are compared for both technologies. The memristors have comparable On/Off ratio (5-10) and resistance ranges (10-100 MOhms), although their footprint differ by two orders of magnitude. They both show gradual, long-term plasticity upon the application of pulses of increasing amplitude: despite a similar film thickness (~4 nm), the voltage required to operate the hafnia devices is 2V, compared to 5 to 8V for the perovskite. The conduction mechanisms across the ferroelectric thin films are interpreted from temperature dependent measurements. The reliability is also different, with a limited effect of fatigue and retention on the $HfZrO_4$ devices[3], but a relatively strong aging effect on the $BiFeO_3$.
Remarkably, the $BiFeO_3$ thin films have a single crystalline orientation, whereas the hafnia film is polycrystalline. The texture affects the coercive field distribution, with consequences on the multi-level functionality and on the cross-talk in passive crossbars. The prospects of these technologies for

neuromorphic computing are discussed: if epitaxial perovskites are promising for unsupervised learning schemes in a passive crossbar array configuration, the back-end compatibility of hafnia synaptic weights offers the possibility of using selectors, with excellent predicted accuracy in tasks such as pattern recognition[4].

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8:30 AM *QM02.09.02
Reservoir Computing with Magnetic Skyrmions Karin Everschor-Sitte; University of Duisburg-Essen, Germany

Novel computational paradigms in combination with proper hardware solutions are required to overcome the limitations of our state-of-the-art computer technology [1-3]. In this talk, I will focus on the potential of magnetic skyrmion structures for reservoir computing. Reservoir computing is a computational paradigm that, in contrast to neural networks, requires fewer computational resources while considerably reducing computing time by several orders of magnitude. By means of simulations, we have shown that random skyrmion fabrics provide a competitive ultra-low power physical implementation of the key ingredient of reservoir computing – the reservoir [4-6]. We developed efficient task-agnostic metrics benchmarking the reservoir's key features – non-linearity, complexity, and fading memory [7]. For the benchmark test of classifying spoken digits, we demonstrated the highest performance ever reported for in-materio reservoir computers using a multi-input channel skyrmion reservoir architecture [8]. Our results are on par with state-of-the-art non-in-materio reservoir systems.
Experimental realizations of skyrmion reservoirs further highlight the potential for energy-efficient high-performance skyrmion-based reservoir computing [9,10].

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9:00 AM *QM02.09.03
Ferroelectric Tunneling Junctions for Beyond vonNeumann Computing Stefan Slesazeck; NaMLab gGmbH, Germany

The discovery of ferroelectricity in doped HfO_2 that was firstly published in 2011 by Böschke et al. strongly increased the interest in ferroelectricity. The polarization reversal in ferroelectric HfO_2 films can be adopted to store information in three distinct device classes. Depending on the material stack composition different devices can be constructed from the very same ferroelectric layer - ferroelectric capacitors (FeCAP), ferroelectric field effect transistors (FeFET) and ferroelectric tunnel junctions (FTJ). The electrical characteristics of these devices are strongly influenced by the whole material stack, rather than being dictated by the properties of the ferroelectric layer itself. In this talk I will shed some light on the design and electrical characteristics of HfO_2-based FTJ bi-layer devices. Specifically, the interplay between charge trapping and ferroelectric switching and its impact on device on- and off-currents as well as on reliability in terms of data retention, and cycling endurance will be discussed. Based on these insights I will review the constraints on the circuit design for beyond von-Neumann architectures that arise from the specific FTJs device properties. Specifically, the application of FTJs in more digital applications like ternary adders or hyper dimensional computing architectures, and in more analogue application cases like synaptic devices will be considered.

9:30 AM QM02.09.05
Role of Processing Conditions on the Chemistry of Interfaces, Crystallinity and Ferroelectric Polarization of $Hf_{0.5}Zr_{0.5}O_2$-based Tunnel Junctions
Wassim Hamouda[1], Ines Häusler[2], Florian Maudet[1], Hafiz Muhammad Hamid Raza[1], Keerthana Shajil Nair[1,3], Marco Holzer[1,3], Zora Chalkley[1,3], Christoph Schlueter[4], Adnan Hammud[5], Christoph T. Koch[2], Veeresh Deshpande[1] and Catherine Dubourdieu[1,3]; [1]Helmholtz-Zentrum Berlin für Materialien und Energie, Germany; [2]Humboldt-Universität zu Berlin, Germany; [3]Freie Universitat Berlin, Physical Chemistry, Germany; [4]Photon Science, Deutsches Elektronen-Synchrotron DESY, Germany; [5]Fritz-Haber Institute of the Max-Planck Society, Germany

Ferroelectric tunnel junctions (FTJs) have been intensively explored for future low power non-volatile data storage and information processing applications. Among various studied ferroelectric (FE) materials, polycrystalline HfO_2 and $Hf_{0.5}Zr_{0.5}O_2$ (HZO) solid solution thin films have the advantage of CMOS process compatibility and remarkable energy efficiency.
Ferroelectricity in these systems has been attributed to the stabilization of a polar orthorhombic phase. However, the remnant polarization and the overall device performance depends strongly on several parameters such as the nature of the bottom and top electrodes, the presence of interfacial layers (whether intentional or not), and the oxygen defect content.
In this study, we discuss the role of processing conditions of double layer FTJ devices consisting of 10 nm $Hf_{0.5}Zr_{0.5}O_2$ (HZO) / 3 nm Al_2O_3 with bottom TiN and top W electrodes on the chemistry of interfaces, on the crystallinity and the ferroelectric polarization in HZO. The latter is crystallized at a low temperature of 400C for full CMOS back-end of-line compatibility.
First, as observed in electrical characterization, processing of the ultrathin Al_2O_3 tunneling barrier plays a key role in the ability to stabilize and switch the electrical polarization in the HZO layer. Moreover, a strong dependence of the remnant polarization with the voltage pulse width is observed, which points to the major role of charge traps in minimizing the depolarizing field. Soft and hard X-ray photoelectron spectroscopy techniques were therefore used to probe the physical chemistry of the different buried interfaces and to quantify the oxygen vacancy content across the stack. We performed measurements at

different synchrotron X-ray energies and beam angles to probe various depths of the HZO layer while the top alumina/W layers were investigated by combining laboratory XPS with low energy Ar ion sputtering. In addition, scanning transmission electron microscopy and electron energy loss spectroscopy (EELS) were performed to further investigate the chemistry of the films and interfaces. Based on the electrical, XPS and STEM/EELS measurements, we will discuss the influence of the processing conditions on providing the needed amount of electronic traps for sufficient screening charges, essential to maintain the non-volatile property of the device.

SYMPOSIUM

April 11 - April 26, 2023

Symposium Organizers
Matthew Brahlek, Oak Ridge National Laboratory
Yue Cao, Argonne National Laboratory
Brian Skinner, The Ohio State University
Liuyan Zhao, University of Michigan

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* Invited Paper
\+ Distinguished Invited

SESSION QM03.01: Emergent Properties from In-Plane Superstructures
Session Chairs: Matthew Brahlek and Yue Cao
Tuesday Morning, April 11, 2023
Marriott Marquis, Fourth Level, Pacific C

10:30 AM *QM03.01.01
Superconducting Four-Fold Fe(Te,Se) Films on Six-Fold Topological Insulator Bi2Te3 and Magnetic MnTe via Hybrid Symmetry Epitaxy
Seongshik Oh; Rutgers Univ, United States

It is challenging to grow an epitaxial four-fold compound superconductor (SC) on six-fold topological insulator (TI) platform due to stringent lattice-matching requirement. Here, we demonstrate that Fe(Te,Se) can grow epitaxially on a TI (Bi_2Te_3) layer as well as magnetic MnTe due to accidental, uniaxial lattice match, which is dubbed as “hybrid symmetry epitaxy”. This new growth mode is critical to stabilizing robust superconductivity with T_C as high as 13 K. Furthermore, the superconductivity in this system survives in Te-rich phase with Se content as low as x = 0.03 but vanishes at Se content above x = 0.56, exhibiting a phase diagram that is quite different from that of the conventional Fe(Te,Se) systems. This unique heterostructure platform that can be formed in both TI-on-SC and SC-on-TI sequences opens a route to unprecedented topological heterostructures. Furthermore, this result opens another possibility of combining topological superconductivity of Fe(Te,Se) with the rich physics of topological magnetism in the $(MnTe)_n(Bi_2Te_3)_m$ family, a recently emerging platform as intrinsic (anti)ferromagnetic topological insulators.

11:00 AM *QM03.01.02
Quantum Non-Reciprocal Responses in Moire Matter Justin Song; Nanyang Technological University Singapore, Singapore

Nonreciprocity lies at the heart of device technology, allowing means to differentiate between forward and backward flows of signals and information. I will describe how the pronounced quantum geometry found in moire quantum matter lead to large non-reciprocal quantum responses that go beyond that of classical means. One striking example is non-reciprocal plasmonics. While traditionally non-reciprocity is traditionally effected using a magnetic field, I will describe how the large quantum metric dipole in twisted bilayer graphene heterostructures enables non-reciprocal bulk plasmons. Strikingly, the strong non-reciprocity persists even for relatively narrow bands underscoring its wavefunction quantum geometric origins. This non-reciprocity of a quantum origin grants a magnetic-field free and passive platform for plasmonic manipulation and opens the door to host of other non-reciprocal responses.

Funding Information: This work was supported by Singapore MOE Academic Research Fund Tier 3 Grant MOE2018-T3-1-002.

11:30 AM *QM03.01.03
Electron Correlation in Graphene/hBN Moire Superlattices Long Ju; Massachusetts Institute of Technology, United States

ABC-stacked trilayer graphene/hexagonal boron nitride moiré superlattice (TLG/hBN) has emerged as a playground for correlated electron physics. A spectroscopy study of this system is, however, challenging due to the device configuration. In this talk, I will introduce our recent efforts on FTIR photocurrent spectroscopy measurements of dual-gated TLG/hBN. We observed strong gate-tunable optical transitions that originated from the moire flat band. At half-filling of the valence flat band, a broad absorption peak emerges at ~18 meV, indicating direct optical excitation across an emerging Mott gap. Furthermore, I will talk about a unique moire-enabled interlayer electron-phonon coupling in this system and its implications.

SESSION QM03.02: Spin and Orbital Effects in Correlated Oxides

Session Chairs: Seongshik Oh and Justin Song
Tuesday Afternoon, April 11, 2023
Marriott Marquis, Fourth Level, Pacific C

1:30 PM *QM03.02.01
The Orbital Degree of Freedom in High Entropy Perovskites RVO_3 Jiaqiang Yan; Oak Ridge National Laboratory, United States

The extreme local compositional disorder in high entropy compounds can be employed to induce novel phenomena such as tunable magnetism, coherent symmetry breaking, metal-insulator transition and superconductivity. This has attracted intense attention in the last decade. However, how this strong local disorder affects the orbital degree of freedom has not been studied in transition metal oxides. In this talk, I will use RVO_3 perovskite as an example to show how the cooperative Jahn-Teller distortion of t-electrons reacts to the local disorder of the rare earth site.

2:00 PM *QM03.02.03
Nonlinear Terahertz Emission Spectroscopy on Chiral Multifold Semimetals Liang Wu; University of Pennsylvania, United States

The absence of mirror symmetry, or chirality, is behind striking natural phenomena found in systems as diverse as DNA and crystalline solids. A remarkable example occurs when chiral semimetals with topologically protected band degeneracies are illuminated with circularly polarized light. Under the right conditions, the part of the generated photocurrent that switches sign upon reversal of the light's polarization, known as the circular photogalvanic effect (CPGE), is predicted to depend only on fundamental constants. The conditions to observe quantization are non-universal, and depend on material parameters and the incident frequency. In my talk, I will discuss nonlinear terahertz emission spectroscopy with tunable photon energy from 0.2 eV - 1.1 eV in the chiral topological semimetals CoSi and RhSi. Particularly, we identify a large longitudinal photocurrent peaked at 0.4 eV reaching around 550 $\mu A/V^2$ at room tempreture in CoSi , which is much larger than the photocurrent in any chiral crystal reported in the literature. Using first-principles calculations we establish that the peak originates from topological band crossings, reaching 3.3 ± 0.3 in units of the quantization constant. Our calculations indicate that the quantized CPGE is within reach in CoSi upon doping and increase of the hot-carrier lifetime. Finally, I will present our most recent experiments to explore the quantization and interaction effects in these chiral crystals with doping at low temperature.

SESSION QM03.03: Tuning the Electronic Structure and Magnetism

Session Chairs: Antia Botana and Liang Wu
Tuesday Afternoon, April 11, 2023
Marriott Marquis, Fourth Level, Pacific C

3:30 PM *QM03.03.01
Topological Switch in a van der Waals Ferromagnet Ming Yi; Rice University, United States

Symmetries are fundamental to how we define phases of matter. More recently, symmetries and the active tuning of which have played an important role in realizing and tuning topological phases of matter. Previously, such tuning in quantum materials have been realized via the application of magnetic field, uniaxial strain, and pressure. Here we report the observation of quantum phase switching between a Weyl nodal line phase and a topological flat band phase in a van der Waals ferromagnet via a thermal annealing process. We further demonstrate that the switching of the electronic properties to be associated with a crystal symmetry change driven by an site ordering that is modified in the thermal annealing process. The presence or absence of the ordering modifes the global symmetry of the crystal and give rise to either magnetic Weyl nodal lines in one case and geometrically frustrated flat bands in the other. We further demonstrate that this topological switching is reverseably controlled via the thermal annealing and quenching method. Our work not only reveals a rich range of quantum phases emergent in 2D van der Waals ferromagnets, but also uncovers the potential of utilizing site occupancy as a novel degree of freedom for tuning symmetry and therefore topology in quantum materials for the realization of exotic emergent phases.

4:00 PM *QM03.03.02
Optical Creation and Probing of Non-Equilibrium Superconductors and Topological Semimetals Joel Moore[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

The high intensity and versatility of optical pumping allows the creation of new states in a material that may not exist anywhere in the equilibrium phase diagram. This talk focuses on electronic phases and on pump pulses, or alternately current drives, that are chosen to modify the symmetry of a material. For example, circularly polarized light provides a means to induce broken time-reversal symmetry in a non-magnetic material, while current drive breaks both time-reversal and inversion symmetries. Examples discussed include current-induced linear optical effects in semimetals and superconductors, where they provide important probes of topological band structure and order parameter symmetry respectively. These effects can be viewed as part of the nonlinear optical tensor, and we then turn to other kinds of nonlinear optical effects and a unique quantization effect obseved in certain Weyl semimetals. The closing discussion will attempt to illustrate the value that the general class of beyond-linear-response measurements is bringing to the investigation of quantum materials.

(The work reported includes previous collaborations with Michal Papaj, Kazuaki Takasan, Takahiro Morimoto, Tianrui Xu, and others, as described in the talk.)

4:30 PM *QM03.03.03
Layer-by-Layer Disentanglement of Bloch States via Frequency-Domain Photoemission Shuolong Yang; The University of Chicago, United States

Layer-by-layer material engineering has enabled exotic quantum phenomena such as interfacial superconductivity and the quantum anomalous Hall effect. Meanwhile, deciphering electronic states layer-by-layer remains a fundamental scientific challenge. This is exemplified by the difficulty in understanding the layer origins of topological electronic states in magnetic topological insulators, which is key to understanding and controlling topological quantum phases. Here, we report a layer-encoded frequency-domain ARPES experiment on a magnetic topological insulator $(MnBi_2Te_4)(Bi_2Te_3)$ to characterize the layer origins of electronic states. Infrared laser excitations launch coherent lattice vibrations with the layer index encoded by the vibration frequency; photoemission spectroscopy tracks the electron dynamics, where the layer information is decoded in the frequency domain. This layer-frequency correspondence reveals a surprising wavefunction relocation of the topological surface state from the top magnetic layer into the buried second layer, reconciling the controversy over the vanishing broken-symmetry energy gap in $(MnBi_2Te_4)(Bi_2Te_3)$ and its related compounds. The layer-frequency correspondence can be harnessed to disentangle electronic states layer-by-layer in a broad class of van der Waals superlattices.

SESSION QM03.04: Poster Session
Session Chairs: Matthew Brahlek and Yue Cao
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM QM03.04.01
Blockades on Spin-to-Charge Conversion Signal in MoS_2 ML Inserted NM/FMI Heterostructures Chanho Park, Sang Kwon Lee, Jae Won Choi, No-Won Park, Si-Hoo Kim and Yun Ho Kim; Chung-ang University, Korea (the Republic of)

In analogy to charge current, spin current carries information with its spin components polarized. This has been already observed in materials via spin-orbit coupling, separating up and down spin-polarized electrons transverse to electric current. Many papers in spintronics have suggested schematics with normal metal (NM) deposited on ferromagnetic (FM) substrate, such that one makes the magnetization out of the equilibrium state, generating quantum properties for magnetization distribution called magnons.[1] The injection of magnons to the interface of the NM/FM heterostructures is usually referred to as injection of the spin current, since the magnons themselves contain spin-polarized quantities for each component.[1] The injected spin current transverse to the interface plane, then converted into voltage signal, named as inverse spin hall effect signal. (E_{ISHE}).
From our previous work, the 2D WSe_2 interlayers between Pt and YIG were discussed in the longitudinal spin Seebeck voltage scheme, indicating that the effect of TMDC monolayers (ML) is substantial in the spin Seebeck effect (SSE) measurement in a Pt/YIG structure.[2] In this paper, we conducted SSE signal-detecting experiments on basic well-known Pt/YIG structure and Pt/MoS_2 ML/YIG structure, and observed their temperature dependence ranging from 190K ~ 300K. In particular, the Pt/MoS_2 ML/YIG structure is adequate for discussing the origin of the signal, i.e. Rashba Edelstein effect (REE) or SSE, since the Pt/TMDC ML layer is considered as an intermediate between Pt /YIG and Pt/multilayer MoS_2/YIG. In other word, The Pt/YIG structure exhibits a perfect 3D spin-to-charge conversion, whereas the Pt/multilayer MoS_2/YIG tends to possess more other magnetic proximity effects (MPE) [3] and magnetoresistance (MR), due to the blockage of spin current from MoS_2 with more thickness.
We firstly assumed both samples (i.e., Pt/YIG structure, Pt/MoS_2 ML/YIG) to obey 3D spin-to-charge conversion. In order to observe the maximum SSE voltage on both samples, out of plane temperature gradient (ΔT) is maintained at 1K. Our results show that Pt/MoS_2 ML/YIG yields much less spin Seebeck voltage than that of Pt/YIG. This is attributed to the significant block of the injection of spin current in the MoS_2 monolayer. Interestingly, wavy signals are observed in the Pt/MoS_2 ML/YIG structure even though MR effects were excluded. This phenomenon is related to the different magnetic properties of MoS_2 crystals in previously reported literature.[4]
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5:00 PM QM03.04.02
Analyzing the Effects of Atomic Reconstruction on CDW Behavior in TaX_2 Moiré Bilayers Nikita Dowlatshahi, Madeline Van Winkle and Kwabena Bediako; University of California, Berkeley, United States

Two-dimensional (2D) moiré bilayers are constructed by stacking two monolayers with an interlayer rotation (or "twist") and/or lattice constant mismatch. In moiré materials with a relatively small lattice misalignment, spontaneous periodic deformations, also known as lattice reconstruction/relaxation, occur to reduce the interlayer stacking energy. In turn, this lattice reconstruction has significant effects on the electronic band structure of the system. While reconstruction has been well-studied in moiré superlattices of bilayer graphene and those of semiconducting transition metal dichalcogenides (TMDs), there is minimal information on lattice relaxation in metallic TMD systems, such as H- and T-phase TaX_2 (X = S, Se). In addition, members of the TaX_2 family can exist in a charge density wave (CDW) state, where there are electronically driven periodic lattice distortions, raising the question of how reconstruction might affect CDW behavior in moiré superlattices of these materials. In this work, we demonstrate how changing the interlayer twist angle or lattice mismatch tunes emergent CDW properties in TaX_2 moiré bilayers using a combination of electron microscopy, optical spectroscopic methods, and electronic transport measurements. This project provides insight into the correlation between atomic and electronic structure in moiré superlattices of metallic TMDs as well as the interplay between different types of lattice deformations in 2D moiré materials more broadly.

SESSION QM03.05: Light Induced Lattice Dynamics
Session Chairs: Shuolong Yang and Ming Yi
Wednesday Morning, April 12, 2023
Marriott Marquis, Fourth Level, Pacific C

8:30 AM *QM03.05.01
Light-induced Ultrafast Phase Transformation Study using X-ray Free Electron Laser Hyunjung Kim; Sogang University, Korea (the Republic of)

A significant challenge in understanding the phase transformation of materials is whether one can identify and characterize the fine details of the complex ultrafast dynamics of molecules and materials. Many existing techniques only measure the initial and final states of the material transformations. The recent advance of X-ray free electron laser makes it possible to obtain critical information on the intermediate states or pathways during the phase transformation. In this talk, we show the recent results of a transition from a topological insulator to a standard insulator in Bi_2Se_3 followed by carrier-induced contraction and vibration modes and the crystalline-amorphous phase transformation of a phase change material as examples.

This research was supported by the National Research Foundation of Korea (NRF-2021R1A3B1077076).

9:00 AM QM03.05.03
Evidence of Opto-Mechanical-Driven Topological Phase Transition in SnSe Jiaojian Shi[1,2], Yijing Huang[2,1,2], Christian Heide[1,2], Carl-Friedrich Schön[3,4], Haowei Xu[5], Yuki Kobayashi[1,2], Andrew May[6], Pooja Donthi Reddy[1], Duan Luo[1,2], Eamonn Hughes[7], Kunal Mukherjee[1], Mariano Trigo[2,2], Ju Li[5,5], Jian Zhou[8], Shambhu Ghimire[2], Matthias Wuttig[3,4], David Reis[2,1,2] and Aaron Lindenberg[1,2,2]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States; [3]RWTH Aachen University, Germany; [4]Forschungszentrum Jülich GmbH, Germany; [5]Massachusetts Institute of Technology, United States; [6]Oak Ridge National Laboratory, United States; [7]University of California Santa Barbara, United States; [8]Xi'an Jiaotong University, China

Important advances have been recently made in the search for materials with complex multi-phase landscapes that host photoinduced metastable collective states with exotic functionalities, such as high-temperature superconductivity or topological switches. In almost all cases so far, the desired phases are accessed by exploiting light-matter interactions via the imaginary part of the dielectric function, through above-bandgap or resonant mode excitation. Recently, inspired by optical tweezers, a novel non-resonant optomechanical driving force was theoretically proposed to drive topological phase switching in tin selenide (SnSe) by using off-resonant light excitation, mediated by the real part of the dielectric function. The absence of direct absorption via the imaginary part signifies the potential of this approach over traditional methods in selectively driving transitions with reduced energy consumption and ultrafast switch speed. Here we study mid-infrared-excited SnSe with time-domain Raman scattering and a suite of advanced spectroscopies sensitive to the dynamic structure and symmetry of the light-induced phase. The abrupt suppression of A_g Raman modes above a critical MIR field strength without discernible softening is consistent with a structural distortion towards a higher symmetry phase with dramatically modified optical properties via a non-thermal driving mechanism. The high reflectivity contrast emphasizes the potential of harnessing these phase control handles for telecommunication applications. Further corroborated with transient reflectivity measurements and state-of-the-art first-principles calculations, our study provides evidence for an opto-mechanical-driven topological phase transition, defining novel opportunities for inducing hidden quantum phases with unique functional properties.

9:15 AM QM03.05.04
Band-Selective Electron-Phonon Couplings in an Excitonic Insulator Probed by Ultrafast Broadband Extreme-Ultraviolet Absorption Spectroscopy Michael Zuerch[1,2], Alfred Zong[1,2], Sheng-Chih Lin[1,2], Shunsuke Sato[3], Sasawat Jamnuch[4], Emma Berger[1,2], Yun Cheng[5], Wei Xia[6], Yanfeng Guo[6], Dao Xiang[5], Jie Zhang[5] and Tod Pascal[4]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]University of Tsukuba, Japan; [4]University of California, San Diego, United States; [5]Shanghai Jiao Tong University, China; [6]ShanghaiTech University, China

The strength of electron-phonon couplings (EPC) constitute one of the most fundamental physical quantities in solids, accouting for a wide range of phenomena from superconductivity to polaronic transport. However, experimental determination of its value is challenging, which heavily depends on the theoretical model used. Recently, a model-free measurement of band-selective EPC becomes possible based on excitation of coherent phonons by a femtosecond laser pulse, which is in turn probed by time-resolved photoemission and diffraction. However, only the coupling between occupied electronic bands and phonons is accessible due to constraints of photoemission, whereas information for unoccupied bands, which play an important role in determining carrier relaxation pathways, is missing. Here, we provide a new method to quantitatively measure electron-phonon coupling strength using ultrafast broadband extreme-ultraviolet absorption spectroscopy, where phonon-induced shifts of unoccupied electronic states can be accurately determined in a band-, mode-, and element-resolved fashion. Using the putative excitonic insulator $1T$-TiSe_2 as a model system, we discovered disctinct coupling strengths of its A_{1g} phonon to unoccupied Ti and Se bands, where the coupling vanishes completely for select electronic states. Our approach provides a robust methodology for determining EPC of previously inaccessible states in a wide range of solids, opening new ways for unbiased evaluation of the role of EPC in emergent phenomena in quantum materials.

9:30 AM BREAK

SESSION QM03.06: Driven Dynamics on the Nano and Mesoscale
Session Chairs: Hyunjung Kim and Haidan Wen
Wednesday Morning, April 12, 2023
Marriott Marquis, Fourth Level, Pacific C

10:30 AM *QM03.06.01
Phase Transition Dynamics in $\mathrm{SrCoO}_{3-\delta}$ Heterostructures Dillon D. Fong[1], Qingteng Zhang[1], Guoxiang Hu[2], Vitalii Starchenko[3], Gang Wan[1], Eric Dufresne[1], Yongqi Dong[1], Huajun Liu[4], Hua Zhou[1], Hyoungjeen Jeen[3], Kayahan Saritas[3], Jaron Krogel[3], Fernando Reboredo[3], Ho Nyung Lee[3], Alec Sandy[1], Irene C. Almazan[1] and Panchapakesan Ganesh[3]; [1]Argonne National Laboratory, United States; [2]The City University of New York, United States; [3]Oak Ridge National Laboratory, United States; [4]Institute of Materials Research and Engineering, A*STAR, Singapore

The brownmillerite phase of strontium cobaltite ($\mathrm{SrCoO}_{2.5}$) is an insulating antiferromagnet while the perovskite phase (SrCoO_3) is a ferromagnetic metal. Relatively small changes to the oxygen concentration can drive a reversible, topotactic phase transition, making $\mathrm{SrCoO}_{3-\delta}$ a material of interest for neuromorphic applications. While the redox behavior of such oxides has been the subject of considerable interest, much concerning the kinetics and dynamics of these materials remain unknown.

Utilizing in situ coherent X-ray scattering at the Advanced Photon Source, we monitored speckle from epitaxial $\mathrm{SrCoO}_{3-\delta}$ thin films grown on both $\mathrm{SrTiO}_3(001)$ and $(\mathrm{LaAlO}_3)_{0.3}(\mathrm{Sr}_2\mathrm{TaAlO}_6)_{0.7}(001)$ as oxygen was incorporated and evolved (switching the environment from O_2 to N_2) to gain insight into the dynamics of oxygen-induced phase evolution in complex oxide materials. We found that the kinetics of the brownmillerite to the perovskite phase transition could be varied from tens of minutes to several hours over a small temperature range (300°C to 350°C), observing pronounced differences between the oxidation and reduction behaviors, the latter involving substantial incubation times to re-nucleate the brownmillerite phase. From X-ray photon correlation spectroscopy performed at the brownmillerite superlattice reflection, we find that the two-time correlation function differs greatly between the two different substrates. We will discuss the kinetics and dynamics of the oxygen ion / vacancy-ordering phase transition and the methods used to distinguish the different atomic and electronic mechanisms taking place.

11:00 AM QM03.06.02
Probing Non-Equilibrium Nucleation Processes During Phase Transitions with X-Ray Photon Correlation Spectroscopy Anudeep Mangu[1,2], Vladimir A. Stoica[3], Hao Zheng[4], Huaiyu Wang[3], Quynh L. Nguyen[2], Ramamoorthy Ramesh[5], Lane Martin[5], Eric Dufresne[4], Haidan Wen[4], John Freeland[4], Long-Qing Chen[3], Diling Zhu[2], Venkatraman Gopalan[3], Yue Cao[4] and Aaron Lindenberg[1,2]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States; [3]The Pennsylvania State University, United States; [4]Argonne National Laboratory, United States; [5]University of California, Berkeley, United States

X-ray photon correlation spectroscopy (XPCS) offers insight into materials dynamics at the mesoscale by the analysis of speckles, but has been largely limited to equilibrium or steady-state dynamics. In this work we extend XPCS by conducting experiments at the Advanced Photon Source (APS) and Linac Coherent Light Source (LCLS) on materials undergoing dynamics induced by external pumps. In this work, we describe work done on $SrTiO_3/PtTiO_3$ (STO/PTO) superlattices. This material system offers a platform with a large phase space of configurations, including polar vortices, supercrystals, and skyrmions. With the high brilliance, high degree of coherence, and short pulse duration available at LCLS we observed novel time scales emerging from mesoscale dynamics during an irreversible phase transition in $SrTiO_3/PtTiO_3$ superlattices from the vortex phase to the supercrystal phase. We then conducted experiments investigating the dynamics of polar vortices and skyrmions in STO/PTO under voltage excitation. Together, these measurements reveal the spatial pinning nature during the transition and the formation and growth of domains as a function of time and voltage excitation. These experiments also revealed the effect of excess charge in the system. These measurements extend XCPS towards probing functionality in materials as it relates to mesoscale structural order.

11:15 AM QM03.06.03
Imaging Light-Induced Metastable Nanostructures in $PbTiO_3/SrTiO_3$ Superlattices Marc Zajac[1], Tao Zhou[1,1], Sujit Das[2], Tiannan Yang[3], Yue Cao[1], Burak Guzelturk[1], Vladimir A. Stoica[3], Mathew Cherukara[1], John Freeland[1], Venkatraman Gopalan[3], Ramamoorthy Ramesh[4], Lane Martin[4], Long-Qing Chen[3], Martin V. Holt[1,1], Stephan Hruszkewycz[1] and Haidan Wen[1,1]; [1]Argonne National Laboratory, United States; [2]Indian Institute of Science, India; [3]The Pennsylvania State University, United States; [4]University of California, Berkeley, United States

Ultrafast light-matter interactions can synthesize novel metastable states of matter [1,2]. For example, when nanoscale phase mixtures of polar vortices and a_1/a_2 ferroelectric domains in $(PbTiO_3)/(SrTiO_3)$ (PTO/STO) superlattices are driven by a 400 nm wavelength optical excitation with sufficient fluence, a metastable 3D ordered phase or “supercrystal” is created [2]. It remains unknown how this photoinduced metastable state nucleates, grows, and is affected by the initial heterogeneity in real space. To gain microscopic insight, we used the recently enabled laser-pump, nano x-ray diffraction imaging capability with 25 nm spatial resolution to perform in-situ hard x-ray diffraction with controlled optical excitation [3].
We show that an intermediate phase characterized by in-plane ordered stripe domains forms when excited by an optical excitation with a wavelength of 343 nm at a repetition rate of 54 kHz. The nanoscale x-ray diffraction imaging reveals that this intermediate phase nucleates within the a_1/a_2 ferroelectric domains after five seconds of optical exposure at a fluence of 3 mJ/cm^2. Upon longer exposure times, the intermediate phase expands into and consumes the polar vortex domains, and after about 1000 seconds of exposure, finally transforms into a 3D nanostructure consistent with the previously reported supercrystal phase. Because 343 nm light excites both PTO and STO layers while 400 nm light only excites the PTO layer, the distinct intermediate phase can arise from different charge screening dynamics at the superlattice interface. Our work of imaging nanoscale phase evolution shows how new light-induced ferroelectric phases with unique optical and electronic properties form and transform in real space. This will lead to new ways of optically controlling phase transformations in emerging ferroelectric technologies.

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11:30 AM QM03.06.04
Mesoscale Inhomogeneity Across Morphotropic Phase Boundary in Relaxor Ferroelectrics Hao Zheng[1], Tao Zhou[1], Dina Sheyfer[1], Travis Frazer[1], Zhonghou Cai[1], Martin V. Holt[1], Eric Dufresne[1], Jieun Kim[2], Zishen Tian[2,3], Jiyeob Kim[2], Lane Martin[2,3] and Yue Cao[1]; [1]Argonne National Laboratory, United States; [2]University of California, Berkeley, United States; [3]Lawrence Berkeley National Laboratory, United States

Relaxor ferroelectrics have drawn much attention due to the intriguing physics underneath their giant piezoelectric properties. The extraordinary electromechanical responses are facilitated by metastable polarization states around the morphotropic phase boundary between rhombohedral and tetragonal symmetries. The highly frustrated lattice distortions give rise to a hierarchical evolution of polar order and make mesoscale mechanism especially important for relaxor ferroelectrics. In this talk, I will provide a comprehensive picture of the spatial ordering heterogeneities in the canonical relaxor ferroelectric $0.68PbMg_{1/3}Nb_{2/3}O_3\text{-}0.32PbTiO_3$ (PMN-PT) film epitaxially synthesized on $SmScO_3$ substrate. Combining X-ray nanodiffraction and X-ray photon correlation spectroscopy (XPCS), we resolved the detailed lattice distortions of both strain and lattice tilt in the nanoscale. Our result showed a continuous distribution of entangled polarization without hard domain walls. The in-operando evolution of the strain and lattice under applied electric field further revealed an inhomogeneous evolution of polarization rotation enhanced by local structural variation across the morphotropic phase boundary. I will also discuss how nanoprobe and XPCS could work cooperatively in probing the polar order distribution and providing a more comprehensive picture of domain response under applied electric fields.

SESSION QM03.07: Realizing the Floquet and Topological States of Matter
Session Chairs: Long Ju and Joel Moore
Wednesday Afternoon, April 12, 2023
Marriott Marquis, Fourth Level, Pacific C

1:30 PM *QM03.07.01
Optical Control of Band Topology and Magnetism in Correlated Two-Dimensional Materials Gregory Fiete; Northeastern University, United States

In this talk I will discuss recent theoretical developments in the Floquet engineering of two-dimensional materials, including those with a “twist” between the layers. With the scenario of a laser driving the material in mind, I will focus on two distinct regimes: (1) A "direct" regime where the dominant coupling of the laser is to the electronic degrees of freedom and (2) and "indirect" regime where the dominant coupling of the laser is to the lattice degrees of freedom. In regime (1), I will present some methods to describe low-frequency drives (where a Magnus expansion typically fails), an approach to change the interlayer hopping in a twisted material using a waveguide, and a treatment of electronic and lattice coupling on equal footing. In regime (2), I will present a non-linear phononics approach to modifying magnetism and electronic band topology in two-dimensional materials through direct coupling of the light to IR phonons that couple non-linearly to Raman modes which in turn induce magnetic and band topology transitions. I will focus on the examples of CrI3 for magnetism change, and MnBi2Te4/MnSb2Te4 for a magnetism combined with band topology change induced via non-linear phononics. Our theoretical study includes a symmetry-based component as well as first principles calculations. I will conclude with an outlook on the field, including challenges for both theory and experiment in the optical control of correlated two-dimensional materials.

We gratefully acknowedge funding from NSF DMR-1720595 and NSF DMR-2114825.

2:00 PM *QM03.07.02

Floquet-Engineered Topological Transport in Quantum Materials B. Schulte[1], M.W. Day[1], K. Kusyak[1], F. Sturm[1], D. Shin[1], H. Bretscher[1], G. Jotzu[1], T. Matsuyama[1], G. Meier[1], A. Cavalleri[1], D. Kennes[1,2], M.A. Sentef[1], A. Rubio[1] and J.W. McIver[1,3]; [1]Max Planck Institute for the Structure and Dynamics of Matter, Germany; [2]RWTH Aachen University, Germany; [3]Columbia University, United States

Quantum materials exhibit remarkable phenomena when driven by the strong fields in femtosecond pulses of light. Examples range from the emergence of metastable hidden phases in complex oxides [1] and dichalcogenides [2] to signatures of light-induced superconductivity in cuprates [3] and fullerides [4]. Recent years have seen a surge of interest in using long-wavelength laser pulses to create photon-dressed “Floquet-Bloch” states in quantum materials [5]. Much of this excitement is driven by the predictive power of Floquet theory, which has been used, for example, to correctly predict the formation of topological edge states in periodically-driven systems that exhibit no topological properties in equilibrium [6-7]. Many of these proposals have been verified in quantum simulation settings [8-9], but are only just beginning to be explored in quantum materials [10].

In this talk, I will present results on the electrical transport properties of quantum materials driven by ultrafast pulses of mid-infrared light. These results were achieved using a device architecture based on laser-triggered photoconductive switches and waveguides, which allows transport measurements on microstructured quantum materials to be performed on femtosecond timescales. In monolayer graphene, we observe an anomalous Hall effect induced by circularly polarized light in the absence of an applied magnetic field [11]. The dependence of the effect on a gate potential used to tune the Fermi level reveals multiple features that reflect a Floquet-engineered topological band structure. The results are a critical first step towards realizing and controlling light-induced topological edge states in quantum materials.

In the second part of the talk, I will discuss our recent results on the Weyl semimetal $MoTe_2$. We observe a rectified, circular dichroic photocurrent response that scales linearly (as opposed to quadratically) with the applied laser field, which is consistent with the formation of Floquet-Bloch states in this material. Furthermore, we find that when pumping the material strongly enough, the interlayer shear phonon mode couples to the transport properties of the out-of-equilibrium states. Pumped above a certain threshold, this phononic motion induces a permanent structural phase transition that changes the band structure topology, which we directly probe in the nonlinear transport sector. Our results demonstrate multiple ways in which ultrafast light-matter interaction can manipulate the topological responses of quantum materials via the breaking of symmetry.

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2:30 PM *QM03.07.03

Order-by-Disorder and Potts-Nematicity in the MPX3 van der Waals Magnets Jörn Venderbos; Drexel University, United States

The family of layered transition-metal trichalcogenides (MPX3) has recently attracted much attention as a versatile platform for exploring magnetism in van der Waals materials, and offer a potential venue for realizing intrisinc two-dimensional magnetism. This talk will discuss the magnetic phases observed in these honeycomb magnets, highlighting in particular the accidental degeneracy of classical ground states in a frustrated honeycomb lattice Heisenberg model. Fluctuations lift this degeneracy via the order-by-disorder mechanism, which is demonstrated by developing a systematic spin wave theory. As a result of the accidental degeneracy at the classical level, linear spin wave theory is insufficient to accurately describe the spin wave dispersion---an experimentally relevant characterstic. Indeed, at the quadratic level pseudo-Goldstone modes are present, which are gapped by higher order quantum corrections. This talk will further address the nature of the quantum phase transition between a paramagnet and a rotation symmetry broken ordered state of the kind observed in some members of MPX3 family. In particular, this talk will show that this transition can proceed in two steps, with the rotation symmetry broken first as the ordered state is approached, thus giving rise to a Potts-nematic phase.

3:00 PM BREAK

SESSION QM03.09: Optically Induced Topological Phenomena
Session Chairs: Youngjun Ahn and Matthew Brahlek
Thursday Morning, April 13, 2023
Marriott Marquis, Fourth Level, Pacific C

9:00 AM *QM03.09.02
Light Induced Ultrafast Phenomena in Quantum Materials Matteo Calandra[1] and Giovanni Marini[1,2]; [1]Università di Trento, Italy; [2]Istituto Italiano di Tecnologia, Italy

The successful prediction and design of broken symmetry states induced by femtosecond laser light could lead to an unprecedented control and manipulations of the physical properties of materials. To phase this challenge, we developed a constrained density-functional perturbation theory scheme [1] for the calculation of structural (energy, forces and stress tensor) and harmonic vibrational properties (phonon frequencies and electron-phonon coupling) of insulators in the presence of an excited and thermalized electron-hole plasma. In this talk we present the application of the methods and comparison with TDDFT calculations for the case of low dimensional materials, thermoelectrics and phase change materials.

We show that irradiation of the insulating 2H phase in MoTe2 stabilizes multiple transient charge density wave orders with light-tunable distortion, periodicity, electronic structure and bandgap. Moreover, optical pumping of the semimetallic 1T' phases generates a transient charge ordered metallic phase composed of 2D diamond clusters. For each transient phase we identify the critical fluence at which it is observed and the specific optical and Raman fingerprints to directly compare with future ultrafast pump-probe experiments.
Moreover, we demonstrate that ultrafast pulses can be used to induce a magnetic state in the non-magnetic compound V2O5. We show which criteria must the materials satisfy to show the occurrence of ultrafast magnetization, a much less common effect that the widely studied ultrafast demagnetization.

Finally we present applications to phase change materials and demonstrate that ferroelectricity in GeTe can be easily tuned with fs pulses[4].

This project has received funding from the European Union ERC Advanced Grant

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9:30 AM QM03.09.03
Rational Design of Materials with Coexisting Delocalized and Localized States via Extrinsic Polarons Shuaishuai Yuan and Kirk H. Bevan; McGill University, Canada

Free and self-trapped electrons usually coexist in intrinsic polaronic materials. The transition between delocalized and localized states is of great interest to both theoretical and experimental efforts in the field. However, it is difficult to tune the transition between coexisting delocalized and localized states within intrinsic polaron materials. In this study, we provide an innovative approach for designing extrinsic materials in which the coexistence between delocalized and localized states may be engineered. Through comprehensive ab initio calculations, utilizing hybrid functionals and supporting tight-binding insights, trapping properties in this class of tailored materials are investigated with respect to variations in the lattice strain and doping concentration. In this regard, the energy level of the defect and its bandwidth are shown to play a dominant role in the associated transition barrier and the relative stability between delocalized and localized states. Overall, this work explores the means by which the coexistence of free and trapped carriers can be tuned at the atomic scale, with direct applications in resistive switching, memristive, and related computing devices.

SESSION QM03.10: The Collective Dynamics of Magnetism
Session Chairs: Gregory Fiete and Wanzheng Hu
Thursday Morning, April 13, 2023
Marriott Marquis, Fourth Level, Pacific C

10:30 AM *QM03.10.01
Engineering Magnetic Excitations and Entanglement in Quantum Materials Yao Wang; Clemson University, United States

The rapidly evolving quantum material research calls for precise control of collective electronic properties. Among various control knobs, an ultrafast laser pump is a promising approach due to its rich degrees of freedom. Unlike equilibrium spectroscopies, ultrafast pump-probe spectra involve more theoretical complexity and are limited by more experimental constraints. In this talk, I will discuss the application of time-resolved resonant inelastic x-ray scattering (trRIXS) in quantum magnets. Specifically, I will introduce how one can engineer magnetic excitations with and without long-range orders. The transient states driven by laser pulses exhibit more entanglement than equilibrium states, which can be witnessed by trRIXS.

11:00 AM *QM03.10.02
Engineering Magnetic Ground States in Iridium Oxides Alberto De la Torre[1,2]; [1]Brown University, United States; [2]Northeastern University, United States

Competing exotic phases of matter emerge in quantum materials due to complex interactions between charge, lattice, spin, and orbital degrees of freedom. The control of their macroscopic properties via external perturbations is essential to achieving new technological applications [1]. Traditional approaches include hydrostatic pressure, strain, and chemical doping. Most recently, ultrafast light-matter coupling enables unique mechanisms to access new out-of-equilibrium phases of matter in a controlled and reversible manner [2].

In this talk, I will focus on two strategies to control the magnetic interactions and ground state of two 5d5 iridium oxides: α-Li_2IrO_3 and Sr_2IrO_4. In the former, we use resonant x-ray spectroscopy measurements to study how the introduction of intralayer H atoms ($H_3LiIr_2O_3$) nudges this material toward a Quantum Spin Liquid phase [3]. In the latter, by using resonant ultrafast excitations, we discover new nonthermal critical behavior, which has potential implications for future THz spintronic technology [4]. These results highlight the unique potential of quantum materials for future technological applications.

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SESSION QM03.11: THz and Strain Control Over Quantum Phenomena
Session Chairs: Yue Cao and Keith Nelson
Thursday Afternoon, April 13, 2023
Marriott Marquis, Fourth Level, Pacific C

1:30 PM *QM03.11.01
Toward Multimodal Control Over Quantum Phenomena Keith A. Nelson; Massachusetts Institute of Technology, United States

Quantum phases and phase transitions are exquisitely sensitive to coupled degrees of freedom that mediate key properties and dynamical behavior. Control over the relevant modes through applied pulsed fields can provide fundamental mechanistic insights and offer intriguing prospects for applications involving either transient or persistent induced responses. Electromagnetic and strain fields, applied through optical and acoustic pulses respectively, can exert profound effects on quantum materials.

Terahertz light fields are extremely well matched to the excitations and dynamics characteristic of many cooperative systems. Strong THz fields can induce responses that may reveal important mode-mode couplings, hidden quantum phases, and other phenomena of interest. Recent results involving collective electronic, vibrational, and spin degrees of freedom will be presented. A THz-induced transition into a topological insulator phase of the transition metal dichalcogenide $MoTe_2$ will be discussed. A single THz pulse drives the phase transition electronically, after which the new phase persists indefinitely [1]. A persistent optically-induced change in TaS_2 will also be discussed briefly. The transition is monitored on a single-shot basis with both optical and THz probe light [2]. Strong THz fields drive a “soft” lattice vibrational mode to induce a transition from the quantum paraelectric phase of $SrTiO_3$ to a transient ferroelectric phase [3]. Recent ultrafast x-ray diffraction measurements provide information beyond what could be determined through optical probes. Finally, THz-induced nonlinear responses of collective spin waves (magnons) have revealed coupling that is inherent in canted antiferromagnetic materials [4]. Two-dimensional THz spectroscopy, conducted using single-shot readout of the time-dependent signal field, reveals the coupled spin responses.

Many quantum (and other crystalline) phase transitions involve changes in the lattice parameters. In such cases, strain can play a key role in controlling which phase is present. We have developed a facile method for laser generation of compressional or surface acoustic wave (SAW) shocks [5] that focus in the plane of a sample to reach stresses sufficient to cause material fracture, chemical decomposition, and other effects [6-8]. We have demonstrated a SAW-induced insulator-to-metal persistent phase transition in V_2O_3, extending prior study of a reversible transition induced by quasi-static high pressure [9]. In very recent work, we have developed a method for non-destructive generation of large-amplitude acoustic waves [10]. The approach permits repeated shocks to be delivered to the same sample region, and has been used to observe cumulative effects (i.e. fatigue) caused by hundreds or thousands of shocks. The shocks also may be used to drive phase transitions by themselves or in conjunction with THz or optical excitation. The combination of multimodal excitation and control with probing from THz to x-ray spectral ranges and with real-time single-shot measurement capabilities offers fascinating prospects for fundamental study and potential practical applications of collective quantum dynamics.

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2:00 PM QM03.11.02
A Thermodynamic Framework to Establish Phase Diagrams for Strain Engineering Bo Wang[1,2] and Long-Qing Chen[1]; [1]The Pennsylvania State University, United States; [2]Lawrence Livermore National Laboratory, United States

Strain engineering has been established as a viable way to stabilize hidden phases and induce exotic phenomena in many low-dimensional solid-state materials. A phase diagram describing the equilibria of phases and domain variants as a function of strains and other thermodynamic variables is invaluable to guide the strain engineering. Here, we propose a universal theoretical framework based on thermodynamics to establish the strain phase diagrams of any solid-state functional materials, without *a priori* assumptions on the multi-phase/multi-domain coexistence or substantial computational workload. We apply this approach to establish the strain phase diagrams of various functional materials that undergoes structural transformations, including ferroelectric and multiferroic perovskite oxides (e.g., $BaTiO_3$, $PbZr_{1-x}Ti_xO_3$, and $BiFeO_3$), unconventional HfO_2-based ferroelectrics, and strongly correlated electronic materials such as VO_2. Based on the strain phase diagrams, we discuss the generalized Gibbs phase rules, critical and multi-critical points, universal topological characteristics of the diagrams, and demonstrate a graphical approach to determine the content fractions of the coexisting phases/domain variants. Our theoretical approach offers a universal understanding of the phase equilibria of solid-state materials subject to arbitrary anisotropic strains, enabling efficient construction of strain phase diagrams in high dimensions that would be tremendously useful for strain engineering of quantum materials. Part of this work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

SESSION QM03.12: Emergent Phases Viewed Through Electron Scattering
Session Chairs: J.W. McIver and Yao Wang
Thursday Afternoon, April 13, 2023
Marriott Marquis, Fourth Level, Pacific C

3:30 PM *QM03.12.01
Classification of Nonequilibrium Phase Transitions in Quantum Materials Using Ultrafast Electron Microscope Platform Chong-Yu Ruan, Shuaishuai Sun and Xiaoyi Sun; Michigan State University, United States

The quantum materials are featured by their complex phase diagrams where multiple electronic phases often occur adjacently. The rich variety of ordered states —including superconductivity, electronically and magnetically ordered phases—emerge as a consequence of the astounding properties of quantum many-body physics. Harnessing the collective behavior thus may lead to functionalities beyond the conventional semiconductors. In particular, recent discoveries of the quantum phases strongly interacting with light fields gave rise to a new dimension of emergent phases, including the light-induced metastable or even long-lived hidden phases brought in with properties never seen under equilibrium conditions.

Bridging the connections between different microscopic initiations and macroscopic responses is central toward elucidating the organizing principle behind the light-induced phases. Here, we present a path toward such understanding using a joint experiment-theory framework to explore the nonequilibrium states of quantum materials. The investigations leverage a new ultrafast electron microscope, which gives a unified platform to cross-examine the microscopic dynamics and the outcomes in a control-feedback fashion, thus establishing a mapping between the microscopic tuning knobs and emergent functions. The predictive framework is based the phenomenological mean-field theory (Landau-Ginzburg equation) modelled on the dynamics of the order parameter fields . In a generic pump-probe scheme, the ultrafast control is enacted upon pumping the nanostructured materials where optical interference effect shapes the excitation profile. Three classes of materials (RTe_3, TaS_2 and VO_2) were thus investigated to offer valuable insights on different broken-symmetry systems. The ultrafast electron microscopy setting gathers information by judiciously selecting the scattering channels: with coherently scattered electrons, one captures the evolution of order parameter (diffraction and dark-field imaging), whereas collecting the inelastically scattered electrons, sensitivity falls primarily on incoherently excited electronic dynamics directly connected with the pump laser field control. Alternatively, bright-field imaging of local fields, strain profiles or morphology plays a role to inform the potential feedback mechanism. These different modalities, executed over the same incident beams and the pump fields, offer causality-linked sequences pertaining to nonequilibrium phase transitions which are crucial to establish the mechanistic insight.

We can categorize the nonequilibrium phase transitions based on the dynamical behavior of symmetry breaking in respond to different triggers as a mean to classify controls. In the studies of $CeTe_3$, we observe dynamical critical phenomena associated with the emergence of a hidden order parameter field. The new broken-symmetry state appears by suppressing the predominant order over a critical level, thus revealing the competitive nature between the two. In TaS_2, we witness an entirely different scenario where the laser pulses lead to a transient vestigial order without breaking the existing order parameter, i.e., no order-disorder phase transition involved, to obtain a new topological arrangement. The dynamics are mediated by amplitude modes and the transformation does not suffer from extended criticality and so maintain a high degree of coherence in transitions from one energy basin to another. In VO_2, the quasi-1D nature of the active system subjects its phase change behavior to the presence of light-induced defects. The new form of instabilities offers a mechanism for feedback control. The insulator to metal transition in the excited dynamical system becomes self-regulating and exhibit memory effect.

The work was funded by the U.S. Department of Energy, Grant DE-FG0206ER46309. The experimental facility was supported by U.S. National Science Foundation, Grant DMR 1625181.

4:00 PM *QM03.12.02
Ultrafast Electron Microscopy Studies of Quantum Materials Yimei Zhu; Brookhaven National Laboratory, United States

In this presentation I will give an overview of our recent work on symmetry-guided, photoinduced manipulation and control of transient and metastable quantum states and phenomena in strongly correlated quantum materials using ultrafast electron diffraction and microscopy. Several examples will be given. 1) Using fs temporal gating via photoinduced nearfield electron microscopy (two-color PINEM) to achieve 10^{-21} m×s spatiotemporal resolution to probe nanoscale-femtosecond dielectric response and metal-to-insulator transition in VO2 [1,2]. 2) Probing photoinduced electronic transition from a topological insulating state to a Dirac semimetal state in ZrTe5 [3] using MeV ultrafast electron diffraction. 3) Analyzing photoinduced transient and metastable states based on time-resolved diffuse scattering in thermoelectric SnSe and manganites [4,5]. I will also report our latest development on the laser-free electron pulser that can be retrofitted into a commercial transmission electron microscope for ultrafast stroboscopic diffraction, imaging and GHz excitations. I will show an example of the interdigitated comb device that is widely used as an antenna or sensor in mobile platforms for direct visualization of its interactions with microwave and electromagnetic wave dynamics [6]. The ability to probe materials dynamic responses under RF and microwave excitations has promising applications for qubit devices and quantum information science.

Collaborations with X. Fu, T. Konstantinova, W. Wang, J. Li, L. Wu, and other co-authors listed in the references below are acknowledged. Work at BNL was supported by the DOE-BES-MSE grant DE-SC0012704.

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4:30 PM QM03.12.03
Understanding the Phase Transformation Dynamics in NiTi using *In Situ* 4D-STEM Jennifer Donohue[1], Didier Perrodin[2], Colin Ophus[2], Sean Mills[1], Benjamin Savitzky[2], Steven Zeltmann[1] and Andrew M. Minor[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

There has been much focus on the development of caloric cooling technologies as an environmentally-friendly alternative to conventional vapor compression technologies owing to their use of benign solid-state refrigerants[1]. Elastocaloric materials (eCMs) in particular have garnered much interest for this application due to its ability to produce high temperature and entropy changes when subjected to an external mechanical stress while not utilizing expensive or toxic elements[1]. Shape memory alloys (SMAs) are well known to exhibit the elastocaloric effect by undergoing a stress-induced martensitic phase transformation. This has made SMAs, binary NiTi alloys in particular, some of the most well studied and most promising eCMs. While NiTi demonstrates a respectable adiabatic temperature change of ~25K with possible improvements, short fatigue life and hysteresis losses limit practical applications. Much research has been done into functional fatigue and high hysteresis in NiTi supplying many theories, however, the origin of these phenomena still remains unclear.

Current theories state that the origin of hysteresis and functional fatigue in NiTi is microscopic strain incompatibility at the interface of the parent and product phase and potential residual martensite. This strain incompatibility causes the accumulation of defects at the phase boundary[2-4] which then stabilize martensite above the transition temperature. Understanding how the nanoscale strain landscape develops at and before the transformation front in these materials is necessary to fully understand the origin of the high hysteresis and short fatigue life in these systems. This understanding could be critical to the design of improved fatigue-resistant low-hysteresis materials with high recoverable strains.

Here we use four-dimensional scanning transmission electron microscopy (4D-STEM) with high precision bullseye apertures[5] to map the nanoscale structure of NiTi during *in situ* cooling through the phase transformation from the high temperature B2 austenite to the low temperature B19' martensite. Using 4D-STEM and advanced data processing tools, we map the nanostructure of NiTi as it approaches and proceeds through the phase transformation during cooling, demonstrating the first structurally-resolved imaging of the local transformation in this system. With this method, we map the phase distribution of austenite & martensite variants during the transformation. We also map the development of local diffuse streaking, and the local strain landscape at the transformation front. With continued cycling, we observe the variation in the resulting martensite structure. Finally, we correlate diffuse scattering, strain, and phase distribution granting insight into the phase transformation dynamics in the eCM NiTi.

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4:45 PM QM03.12.04
Disentanglement of Electronic and Structure Orders in Photoinduced Phase Transition of VO_2 Xiaoyi Sun[1], Shuaishuai Sun[2], Ian Gonzalezafanador[1], Gerardo T. Morales[1], Nelson Sepulveda[1] and Chong-Yu Ruan[1]; [1]Michigan State University, United States; [2]Institute of Physics, Chinese Academy of Sciences, China

The insulator-to-metal transition (IMT) in vanadium dioxide with a resistivity change of more than three orders of magnitude is typically accompanied by a structural phase transition (SPT) from the monoclinic phase (M) to the rutile phase (R). This cooperative phase transition is well established in the equilibrium states under monotonic tuning parameters, such as applying pressure or chemical doping, or change in temperature. However, recently intriguing evidences for decoupling between IMT and SPT emerged when the systems were exposed to strong ultrashort laser pulses, casting in doubt the fundamental nature of this cooperativity both in and out of equilibrium.
Here, to address this issue we examine the emergences of cooperativity or its lack thereof through a dual-probe setting employing ultrafast electron diffraction (UED) and optical transmittance (TR-OT) measurements to obtain simultaneously the structural and electronic responses to the static and transient perturbations. To set the stage for comparing equilibrium and nonequilibrium phase transitions we benchmark the VO2 system reaching metallic status while gaining the rutile (R) structural motif from the initial monotonic (M) state under the steady-state heating (and cooling) where we invariably confirmed the cooperativity based the same critical temperature obtained for IMT and SPT. The same VO2 system is then subject to the optical excitation for the nonequilibrium investigations where we switch the control parameter from temperature to laser fluence (F).
Our results unambiguously show the two transitions characterized in the fashion defined in the equilibrium studies are decoupled in the observation of two thresholds respectively assigned to IMT and SPT. The first threshold, Fc1 ~ 4 mJ/cm2, defines the IMT based on TR-OT reaching the equilibrium metallicity, which is distinctly below the threshold, Fc2 ~ 7 mJ/cm2, for SPT, as identified by the UED structure factor losing monoclinic. This classification is based on the intermediate time behavior (+ 500 ps) where one expects the thermal energy provided by the optical excitation is sufficiently redistributed. While this apparent decoupling might confirm some of the earlier studies regarding the establishment of a distinct electronic order status away from SPT, we also found subtle structural distortion closely accompanying the IMT dynamics in all ranges of the excitation. This surprising result points to yet a new type of cooperativity on the microscopic level without the conventional motif changes observed in equilibrium, namely M-to-R. Judging from the early onset of the distinct light-induced electronic order (< 1 ps), the process is clearly nonthermal, likely mediated by the photo-hole generation. Based on the simultaneous structural data, the hole dynamics are heavily dressed by the ambient lattice field, resulting in a polaronic-like response leading to transient cooperativity with IMT on the local level. Separately, the structured ordering to obtain the R phase requires the development of a long-range correlation in the new motif along the V-V chain, which is not a critical ingredient for the IMT. Although, on the thermodynamical timescale, or in the strongly driven regime (over a much higher fluence than FC2) the IMT and SPT may seem to proceed simultaneously. The research conducted here points out the importance of non-equilibrium physics and the different collective behaviors in order to comprehensively address the multi-faceted aspects of the VO2 phase-change phenomena.
The authors acknowledge S. Kunjir, S. Zhao for the low-level RF phase-locked system used in the UED experiment. The work was funded by the U.S. Department of Energy, Grant DE-FG0206ER46309. The experimental facility was supported by U.S. National Science Foundation, Grant DMR 1625181.

SESSION QM03.13: Emergent Phenomena in Quantum Material Devices
Session Chairs: Dillon Fong and Qiang Li
Friday Morning, April 14, 2023
Marriott Marquis, Fourth Level, Pacific C

8:30 AM *QM03.13.01
Ultrafast Spin-Shear Coupling in van der Waas Antiferromagnets Haidan Wen; Argonne National Laboratory, United States

The symmetry of magnetic order and underlying lattice structures in van der Waals magnets intertwines and mutually gives rise to a plethora of exotic phenomena that are absent in 3D materials. However, among multiple structural degrees of freedom, it remains elusive which structural parameters primarily couple to magnetism and the impact of this coupling on the ultrafast dynamics of vdW magnets. Here, we discover a strong coupling between interlayer shear and magnetic orders using a set of ultrafast measurements including ultrafast electron diffraction and microscopy, ultrafast x-ray diffraction and optical linear dichroism. On the picosecond time scale, a seesaw-like rotational motion was observed in the reciprocal lattice of $FePS_3$, which exhibits a thirty-fold amplification of its gigahertz structural resonance upon cooling below the Neel temperature [1]. The rotation in reciprocal space manifests as an unusually large interlayer shear in real space, where individual micro-patches of the film behave as synchronized shear oscillators that are phase-locked and deform along the same in-plane axis. On nanosecond time scales, we found the recovery of the lattice shear and magnetic order exhibit concurrent slowing down at the Neel temperature with the same critical components [2]. The time-dependent Ginzburg-Landau theory shows that this concurrent critical slowing down arises from a linear coupling of the interlayer shear to the magnetic order, which is dictated by the broken mirror symmetry intrinsic to the monoclinic stacking. Our work not only offers the first microscopic view of the spin-mediated mechanical motion of an antiferromagnet, it also identifies a new route towards realizing high-frequency resonators up to the millimeter band, where the capability of controlling magnetic states at the ultrafast timescale can be readily transferred to engineering the mechanical properties of nano-devices.

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This work is primarily supported by the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, under award no. DE-SC-0012509.

9:00 AM *QM03.13.02
Magnetic Proximity Effects Between Topological Insulators and Insulating Antiferromagnet Ryan T. Van Haren and David Lederman; University of California, Santa Cruz, United States

Magnetic proximity effects between topological insulators and insulating antiferromagnets can open the way to new spintronic functionalities, including THz communication and data storage technology. Here we report on magnetotransport measurements of $MnF_2/(Bi,Sb)_2Te_3$ antiferromagnetic/ topological insulator heterostructures. MnF_2 is a canonical uniaxial antiferromagnet with a tetragonal crystal structure, whereas $(Bi,Sb)_2Te_3$ is a topological insulator whose Fermi level can be brought into the bulk gap to access the topologically-protected surface states by varying the Sb concentration. The samples were grown using molecular beam epitaxy on MgF2 (110) substrates. The MnF_2 layer was grown epitaxially the substrate using a $(Mn,Ni)F_2$ graded layer to reduce the strain on the MnF_2, resulting in (110) growth with the [001] crystallographic direction in the plane of the sample, corresponding to the magnetic anisotropy easy axis. We find evidence for coupling between the MnF_2 layer and the $(Bi,Sb)_2Te_3$ surface states by measuring the planar Hall effect with the external magnetic field applied parallel to the MnF_2 easy axis, where a sudden change is measured at the MnF_2 spin-flop field. We will also present measurements with the field perpendicular to the plane of the samples, where the Hall effect is observed. Possible interpretations of these measurements and the influence of the topological nature of the surface state carriers will be discussed.

This work was supported in part by the Air Force MURI program, grant number FA9550-19-454963.

9:30 AM QM03.13.03
Electrical Gating of the Quantum Condensate Phases in Two-Dimensional Charge-Density-Wave Materials Maedeh Taheri[1], Jonas Brown[1], Adil Rehman[2], Nicholas R. Sesing[3], Fariborz Kargar[1], Tina T. Salguero[3], Sergey Rumyantsev[2] and Alexander A. Balandin[1]; [1]University of California, Riverside, United States; [2]Institute of High-Pressure Physics, Poland; [3]University of Georgia, United States

The charge-density-wave (CDW) phase is a macroscopic quantum state consisting of a periodic modulation of the electronic charge density accompanied by a periodic distortion of the atomic lattice. The early work on CDW effects, performed with bulk samples of the quasi-one-dimensional (1D) metallic crystals, revealed many spectacular phenomena — nonlinear electron transport, oscillating electric current for constant voltages, and giant dielectric response. Recent years witnessed a rebirth of the field of CDW materials and devices, partially driven by an interest in layered quasi-2D van der Waals materials where CDW phases can manifest themselves at room temperature (RT) and above [1-3]. However, despite numerous attempts, the electrical gating of the CDW phases remained elusive. The main difficulty of electrical gating of the CDW phases van der Waals materials is associated with the fact that different phases still have a rather high concentration of charge carriers. We succeeded in electrical gating of the CDW phases and currents in *h*-BN capped three-terminal $1T\text{-}TaS_2$ heterostructure devices. It was demonstrated that the application of a gate bias can shift the source-drain current-voltage hysteresis associated with the transition between the nearly commensurate and incommensurate CDW phases [4]. The evolution of the hysteresis and the presence of abrupt spikes in the current while sweeping the gate voltage suggest that the effect is electrical rather than self-heating. We attributed the gating to an electric-field effect on the commensurate CDW domains in the atomic planes near the gate dielectric. The transition between the nearly commensurate and incommensurate CDW quantum phases can be induced by both the source-drain current and the electrostatic gate. Since the CDW phases are persistent in $1T\text{-}TaS_2$ at room temperature, one can envision memory applications of such devices when scaled down to the dimensions of individual commensurate domains and few-atomic plane thicknesses.

A.A.B. acknowledges the support from the U.S. DOE, Basic Energy Sciences, under the contract DE-SC0021020 "Physical Mechanisms and Electric-Bias Control of Phase Transitions in Quasi-2D Charge-Density-Wave Quantum Materials" and Vannevar Bush Faculty Fellowship, under the ONR contract N00014-21-1-2947 "One-Dimensional Quantum Materials".
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9:45 AM QM03.13.04
Iontronics—Control of Lattice Symmetry and Hidden Phases in Oxide Thin Films Hyeon Han and Stuart S. Parkin; Max Planck Institute, Germany

Transition metal oxide thin films reveal intriguing physical phenomena by control of their lattice symmetry, as their physical and structural properties are strongly intertwined. Iontronics has emerged as a novel concept to tailor lattice symmetry and the associated physical properties of oxide thin films [1]. Here, we demonstrate ionic liquid gating of $T\text{-}Nb_2O_5$ thin films, revealing multi-step hidden phase transitions by intercalation of lithium ions into the lattice [2]. We realize growth of single crystalline $T\text{-}Nb_2O_5$ thin films critically with vertical ionic transport channels, leading to a fast and colossal insulator-metal transition with an eleven orders of magnitude change in resistivity. A change in lattice symmetry from orthorhombic to monoclinic along with electronic phase transitions are revealed by various *in situ* characterizations. Furthermore, by employing a hydrogen spillover method, we present itinerant ferromagnetic $SrRuO_3$ (SRO) thin films whose resistivity and magnetism are extensively tuned by hydrogen ion intercalation [3]. The hydrogenated SRO films reveal a reversal of the sign of the anomalous Hall effect coupled with a distinct lattice symmetry change from orthorhombic to tetragonal via octahedral tilting. These studies open a new path towards the exploration of hidden phases and suggest a new approach to tailor lattice symmetry and emergent physical phenomena via iontronics.

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SESSION QM03.14: Optically Induced Topological Phases and Nonlinear Phenomena
Session Chairs: Jiaqiang Yan and Yimei Zhu
Friday Morning, April 14, 2023
Marriott Marquis, Fourth Level, Pacific C

10:30 AM *QM03.14.01
Nonlinear Optical Detection of Dual Magnetic Ground States in a Magnetic Weyl Semimetal $Co_3Sn_2S_2$ Youngjun Ahn[1], Xiaoyu Guo[1], Rui Xue[2], Kejian Qu[2], Kai Sun[1], David Mandrus[2,2,3] and Liuyan Zhao[1]; [1]University of Michigan–Ann Arbor, United States; [2]The University of Tennessee, Knoxville, United States; [3]Oak Ridge National Laboratory, United States

The symmetry properties of ground states of material systems lie at the essence of condensed matter physics. Nonlinear second harmonic generation techniques have successfully characterized crystallographic point groups, but mostly on systems without inversion symmetry using the leading-order electric dipole contribution. The symmetry studies of recently realized topological centrosymmetric semimetal systems are in demand to provide a clear understanding of their ground states and electronic band topology. In this talk, rotational anisotropy (RA) second harmonic generation (SHG) study of the magnetic Weyl semimetal $Co_3Sn_2S_2$ will be presented to resolve the debate on its magnetic ground state. In this study, the RA SHG patterns of this centrosymmetric compound are identified to contribute from the leading-order electric quadrupole. By tracking temperature dependence of the RA SHG with the focus on the intensity (time-reversal invariant) and orientation (time-reversal broken), out-of-plane ferromagnetism at $T_{C,1}$ = 175 K and in-plane antiferromagnetism at $T_{C,2}$ = 120 K are revealed, both belonging to -3m' magnetic point group. Finally, the critical exponents of ferromagnetic and antiferromagnetic order parameters are extracted from the intensity and orientation of the RA SHG, which are represented by even and odd powers of order parameters, respectively, providing insight into the characteristics of these two phase transitions.

11:00 AM *QM03.14.02
New Synthesis Pathways Through High-Pressure Floating Zone Growth Stephen D. Wilson; University of California-Santa Barbara, United States

High-pressure floating zone growth can provide nonequilibrium synthesis pathways capable of creating an array of new functional and quantum materials. The ability to access ultrahigh processing temperatures in high pressure reactive gas environments can, in many cases, provide a unique processing environment for realizing new materials. In this talk, I will discuss some of our group's recent work in the growth of quantum materials via high pressure floating zone techniques. Select examples of our recent research will be given and potential opportunities for driven states enabled by advances in high pressure floating zone instrumentation will be highlighted.

11:30 AM *QM03.14.03
Switching Topological Phases in Quantum Materials by Phonons Qiang Li; Stony Brook University/Brookhaven National Laboratory, United States

Zirconium pentatelluride ($ZrTe_5$) is a material at the phase boundary between topological insulator and Dirac semimetal. It was shown theoretically that atomic displacements corresponding to five of the six zone-center A_g (symmetry-preserving) phonon modes can drive a topological transition from a strong to a weak topological insulator with a Dirac semimetal state emerging at the transition.[1] Experimentally, a few-cycle THz-pulse-induced phase transition was demonstrated by the excitation of the lowest Raman active mode.[2] Above a critical THz-pump field threshold, there emerges a long-lived metastable phase, approximately 100 ps, with unique Raman phonon-assisted topological switching dynamics. Using first-principles and effective Hamiltonian methods, it is shown that lattice distortions corresponding to all three types of zone-center infrared optical phonon modes can drive the system from a topological insulator to a Weyl semimetal.[3] Experimentally, the light induced switching to Weyl phase was dynamically created by B_{1u} phonons that led to helicity-dependent current, orthogonal to the dynamical inversion symmetry breaking axis, via circular photogalvanic effect. Such phononic control breaks ground for coherent manipulation of Weyl nodes and robust quantum transport without application of static electric or magnetic fields, which is desirable for high-temperature fault-tolerant multi-qubit computation and communication.

The work at Brookhaven National Laboratory was supported by the U.S. Department of Energy (DOE) the Office of Basic Energy Sciences, Materials Sciences, and Engineering Division under Contract No. DESC0012704.

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2) C. Vaswani et al Phys. Rev. X 10, 021013 (2020)
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SESSION QM03.15: Virtual Session: Optically Induced Phases in Quantum Materials
Session Chairs: Matthew Brahlek and Yue Cao
Tuesday Morning, April 25, 2023
QM03-virtual

8:00 AM *QM03.15.01
Ultrafast Dynamics and Floquet Engineering Enabled by Ultrafast Time- and Angle-Resolved Photoemission Spectroscopy Shuyun Zhou; Tsinghua University, China

Revealing the ultrafast dynamics of quantum materials and further controlling the transient electronic states by ultrashort laser pulses can extend our understanding of the fundamental physics to the nonequilibrium state, with the intriguing possibility to manipulate material properties in the picosecond (ps) to femtosecond (fs) time scale. Time-resolved ARPES (TrARPES) is a powerful tool for capturing the nonequilibrium electronic structures and for investigating possible light-induced new electronic states with energy-, momentum- and time-resolved information. In this talk, I will present our recent progress in developing cutting-edge TrARPES instrumentation, with particular efforts focusing on extending the pump and probe photon energy ranges. I will also present our recent progress on the ultrafast dynamics and Floquet engineering of quantum materials which are made possible by such instrumentation development.

8:30 AM *QM03.15.02
Light Induced Symmetry Reduction in Cr2O3 by Time Resolved Second Harmonic Generation Anshul Kogar; University of California, Los Angeles, United States

Intense light pulses offer the ability to manipulate materials on ultrafast timescales using various protocols. In this talk, I will outline some work our group has undertaken in inducing novel optical effects in magnetoelectric compounds. I will present some data on parity-breaking antiferromagnet, Cr2O3, in which the magnetoelectric effect was first discovered. We demonstrate that by pumping the system below the electronic gap, that the original threefold symmetry of the crystal can be reduced. The symmetry changes are monitored by rotational anisotropy second harmonic generation (SHG), which is a sensitive tool of electronic symmetry breaking. Pumping below the gap gives the ability to manipulate the optical phase, which we demonstrate using second harmonic interferometry. Two anti-ferromagnetic domains, which are indistinguishable at equilibrium with linearly polarized light, give different responses to the pump. Additionally, the rotational anisotropy of the second harmonic light can be controlled with the incident pump polarization. Our work points towards a new dissipationless scheme by which to manipulate the properties of materials on ultrafast time scales.

SESSION QM03.16: Virtual Session: Optical Spectroscopy of Transient and Moire Properties
Session Chairs: Matthew Brahlek and Yue Cao
Wednesday Morning, April 26, 2023
QM03-virtual

8:00 AM *QM03.16.02
Raman Spectroscopy of Twisted Double Bilayer CrI3 Moiré Superlattices and Nematicity in 2D XY-Type Magnet NiPS3 Rui He; Texas Tech University, United States

Two-dimensional (2D) materials with intrinsic ferromagnetism/antiferromagnetism have attracted strong interest because of their potential applications in data storage and spintronic devices. In the first part of this talk, I will present our magneto-Raman and magnetic circular dichroism (MCD) spectroscopy studies of twisted double bilayer (tDB) CrI_3. We identify Raman signatures of a new magnetic ground state that is distinct from those in natural two-layer (2L) and four-layer (4L) CrI_3. Results from Raman and MCD both reveal the emergence of finite net magnetization that originates from spin frustrations and noncollinear spin texture introduced by moiré superstructures in tDB CrI_3. In the second part of this talk, I will show our studies of spin-induced nematicity in few-layer XY-type magnet $NiPS_3$. Our findings suggest that spin fluctuations in few-layer $NiPS_3$ at low temperature are so strong that they destroy the static, long-range antiferromagnetic order for 3D, but instead, introduce a nematic state in 2D $NiPS_3$. Our studies offer an unprecedented venue for realizing novel magnetic states and phases in 2D magnets.

Funded by NSF Grant No. DMR-2104036 and NSF CAREER Grant No. DMR-1760668.

8:30 AM QM03.16.03
Ultraweak Electron-Phonon Coupling Strength in Cubic Boron Arsenide Unveiled by Ultrafast Dynamics Jimin Zhao; Institute of Physics, Chinese Academy of Sciences, China

We report a time-resolved ultrafast quasiparticle dynamics investigation of c-BAs, which is a recently discovered highly thermally conducting material. The excited-state ultrafast relaxation channels dictated by the electron-phonon coupling (EPC), phonon-phonon scattering, and radiative electron-hole recombination have been unambiguously identified, along with their typical interaction times. Significantly, the EPC strength is obtained from the dynamics, with a value of $\lambda_{T2}= 0.008$ (corresponding to $\lambda\langle\Omega^2\rangle = 1.18 \pm 0.08\ ps^{-2}$), demonstrating an unusually weak coupling between the electrons and phonons. As a comparison, an ultraweak EPC strength for graphene is also expected. We propose that preserving an ultrasmall EPC strength may be a prerequisite for exhibiting an ultrahigh thermal conductivity. Our investigation provides insight for searching and designing ultrahigh thermal conductivity materials. Notably, during our analysis we have generalized the fluence-dependence method for obtaining the EPC strength to room temperature, which can be applied to many other types of quantum materials in the future.

8:45 AM QM04.10.02
Ferroelastic Twin-domain Patterns and Polar Domain Walls in $BiVO_4$ Films via Phase-field Simulations Ren-Ci Peng[1], Fei Xue[2], Xiaoxing Cheng[2], Pao-Wen Shao[3], Ying-Hao Chu[3] and Long-Qing Chen[2]; [1]Xidian University, China; [2]The Pennsylvania State University, United States; [3]National Yang Ming Chiao Tung University, Taiwan

Polar domain walls in centrosymmetric ferroelastics (e.g., $BiVO_4$ films) give rise to inhomogeneity and offer promises for energy conversion applications via inducing charge-carrier separation. However, the origin of polar domain walls and the relationship between them and spontaneous strain during the phase transition remain elusive at the mesoscale. Here, from the perspective of the phenomenological thermodynamics, the relationship between the four variants of monoclinic (M) phase and the corresponding lattice constants during the tetragonal-monoclinic (T-M) phase transition is revealed. Using phase-field simulation, it suggests that the formation of four variants of ferroelastic twin domains originates from spontaneous strain during phase transition from T phase to M phase in $BiVO_4$ films. It also reveals that variant 1 and variant 2 forms a striped-like twin-domain pattern while variant 3 and variant 4 form the other twin; every variant has two perpendicular orientations, resulting from mechanically compatible ferroelastic domain walls. The orientation angle of ferroelastic twin domain walls from phenomenological thermodynamics is in agreement with that of phase-field simulation, which is also consistent with the experimental results. Moreover, the phase-field simulations demonstrates that (1) the origin of polar domain walls in $BiVO_4$ films arises from strain gradient across the domain walls during phase transition process; (2) especially shear strain gradient mainly contributes to the magnitudes of polarization vectors and the polarization orientations depend on the relative magnitude ratio of two types of shear strain gradient. Our results not only provide in-depth insights on the formation mechanisms of ferroelastic twin-domain patterns but also reveal the origin of polar domain walls induced by strain gradient at the ferroelastic domain walls.

9:00 AM *QM03.09.01
Epitaxial Growth of 2D van der Waals Magnets and Heterostructures with Topological Insulators Roland Kawakami; The Ohio State University, United States

I will discuss our latest advances on the epitaxial growth of 2D van der Waals (vdW) magnets and their integration with topological insulators (TI). This work is motivated by the realization of topological phases such as the quantum anomalous Hall effect and highly efficient spin-orbit torque produced by TIs.
Our initial studies of $MnSe_2$ growth on Bi_2Se_3 showed a tendency for the interdiffusion of Mn into the Bi_2Se_3. This ultimately led to the synthesis of $MnBi_2Se_4$ (MBS), a new magnetic TI. Interestingly, the vdW phase is not the thermodynamically stable phase and bulk crystals do not exist, so the epitaxial stabilization of MBS creates the opportunity to explore the magnetic and topological properties of this material. We find that MBS is a layered antiferromagnet, similar to $MnBi_2Te_4$, but a difference is that the magnetic moments lie in the plane of the film. Angle resolved photoemission experiments show the presence of a topological surface state with Dirac dispersion.
For bilayers of 2D magnets and TIs, we have developed FGT films on Bi_2Te_3. We first optimized FGT by studying its growth on Ge(111) substrates, where we find that kinetic considerations play a major role. Using cross-sectional scanning transmission electron microscopy and scanning tunneling microscopy, we optimize the FGT films to have atomically smooth surfaces and abrupt interfaces with the Ge(111). Subsequently, we have developed the growth of FGT on Bi_2Te_3 for the integration of 2D magnets with TIs. Interestingly, we observe room temperature ferromagnetism in FGT/Bi_2Te_3 heterostructures by varying the growth conditions.

SYMPOSIUM

April 11 - April 27, 2023

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SESSION QM04.01: Frontiers of Charged Topological Defects
Session Chairs: Rohan Mishra and Jayakanth Ravichandran
Tuesday Morning, April 11, 2023
Marriott Marquis, Fourth Level, Pacific E

11:00 AM *QM04.01.01
Three-Dimensional Twistronic Photogalvanic Effect - A New Paradigm of Light-Matter Interaction Ritesh Agarwal; University of Pennsylvania, United States

We will start by discussing nonlocal photogalvanic spectroscopies where the photon momentum of engineered optical beams can be utilized to probe quantum materials (e.g., Weyl semimetals and supertwisted spirals of 2D materials) uncovering new aspects of light-matter interactions.Specifically, we will discuss the nonlinear optical Hall effect in self-assembled supertwisted WS_2 system formed by a screw-dislocation-driven mechanism. The optical Hall current reflects the structural handedness of the supertwisted system, and an unusual photon-momentum dependence of the nonlinear optical response in the moire potential was observed. Furthermore, signatures of thickness-dependent exciton-polaritons and the associated strong photon momentum-lattice interaction dependent photocurrent response were measured, which suggest a fundamentally altered light-matter interaction in 3D moire systems. Our response function theory can explain the origin of the photon momentum dependent nonlinear response, revealing new observables of the system going beyond Berry curvature and other conventional band geometrical quantities. Our study seamlessly connects 2D and 3D twistronics and provides a bridge connecting the electrons and photons by overcoming their significant length scale differences in conventional systems. These measurements also demonstrate the versatility of 3D moire systems for exploring new aspects of light–matter interaction phenomena in condensed matter systems, which are important in realizing extreme large optical nonlinearities for a variety of quantum and classical photonic applications.

11:30 AM *QM04.01.02
Chiral Spin Textures Stuart S. Parkin; Max Planck Institute of Microstructure Physics, Germany

Chiral domain walls are just one member of an ever-expanding family of chiral spin textures that are of great interest from both a fundamental as well as a technological perspective [1]. Recently a zoology of complex spin textures stabilized by volume or interface Dzyaloshinskii-Moriya interactions have been discovered including, in our work, anti-skyrmions [2], elliptical Bloch skyrmions [3], two-dimensional Néel skyrmions [4] and fractional antiskyrmions [5]. Such nano-objects are potential candidates as magnetic storage bits on the racetrack [6]. Recently we have observed Néel skyrmions in two distinct but closely related 2D van der Waal's ferromagnetic compounds that should not allow for such structures. We show that the crystal structures are substantially modified by self-intercalation, lowering their symmetry and thereby allowing for chiral spin textures that require acentric structures [7, 8]. Finally we discuss the unusual properties of chiral Kagome antiferromagnets and how their magnetic structures can be manipulated by a previously unobserved seeded spin orbit torque mechanism [9].

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SESSION QM04.02: Modeling and Theoretical Methods for Charged Topological Defects
Session Chairs: Long-Qing Chen and Gwan-Yeong Jung
Tuesday Afternoon, April 11, 2023
Marriott Marquis, Fourth Level, Pacific E

2:00 PM QM04.02.02
Direct Observation of Strain-Induced Ferroaxial Transition in Quasi-1D $BaTiS_3$ Guodong Ren[1], Gwan-Yeong Jung[1], Huandong Chen[2], Chong Wang[3], Boyang Zhao[2], Rama K. Vasudevan[4], Andrew Lupini[4], Miaofang Chi[4], Di Xiao[3], Jayakanth Ravichandran[2], Jordan A. Hachtel[4] and Rohan Mishra[1]; [1]Washington University in St. Louis, United States; [2]University of Southern California, United States; [3]University of Washington, United States; [4]Oak Ridge National Laboratory, United States

The properties of ferroic materials are dictated by their symmetry, particularly, a broken symmetry results in a phase transition that can be represented using an order parameter. Ferroelectricity is characterized by an electric polarization vector that is invariant under time-reversal operation. Ferromagnetism is described by a magnetization vector that is invariant under spatial-inversion operation. In contrast to these two well-studied ferroic orders, the ferroaxial transition — that is characterized by a rotational structural distortion with an axial vector symmetry — is relatively unexplored. The symmetry requirement for a ferroaxial transition is broken mirror symmetry in a plane parallel to the rotation axis, and ferroaxial order is invariant under both spatial- and time-reversal operations. Ferroaxial order has shown an intimate ties with emergent properties, such as magnetoelectric couplings in multiferroicsand chiral materials.[1-2] Here, we report direct, atomic-scale observation of a strain-induced ferroaxial transition in a single crystal of a quasi-1D chalcogenide, $BaTiS_3$. Using a combining aberration-corrected scanning transmission electron microscope imaging and density-functional-theory calculations, we show that a biaxial strain of 2% along a plane perpendicular to 1D chains of TiS_6 octahedra in $BaTiS_3$ transforms it from a higher symmetry $P6_3cm$ phase to a ferroaxial $P6_3$ phase, which is characterized by a rotational distortion of the TiS_6 octahedra along the axis containing the chains.
The global refinement of X-ray diffraction suggests an average structure with a space group of $P6_3cm$. To induce a biaxial strain, we welded a $BaTiS_3$ lamella to two lateral sides of a TEM half-grid. For another lamella, we attached it to a TEM half-grid with only one lateral side fixed such that strain relaxation was possible through the unconstrained side. We performed atomic resolution high-angle annular dark-field imaging of both samples and performed local crystallography by extracting and analyzing the atomic positions from the acquired images. In the biaxially strained sample, we observe a rotational distortion of TiS_6 octahedra accompanied with an outward displacement of the Ba sublattice, suggesting the presence of ferroaxial order. We also observe nanoscale (~10 nm) domains consisting of three ordered distorted Ba sublattice configurations separated by an undistorted Ba sublattice. By comparing the average Ba-Ba distance in the strained $BaTiS_3$ lamella to the unstrained one, we find the presence of ~3.45 % tensile strain in the former $BaTiS_3$ lamella.
We used DFT calculations to gain further insights into the microscopic details of this ferroaxial transition in $BaTiS_3$ under biaxial strain. We find that the ferroaxial transition from $P6_3cm$ to $P6_3$ space group can be accomplished through the freezing of two distortion modes ($\Gamma 1$ and $\Gamma 2$) in the high-symmetry $P6_3cm$ phase. These modes involve the rotational distortion of TiS_6 octahedra and outward displacements of Ba atoms in *ab*-plane, both of which are observed in the STEM images. Using DFT calculations, we show that ferroaxial order in $P6_3$ phase can be stabilized over the $P6_3cm$ phase for biaxial strains >2%, which further supports the STEM observations. We will also discuss the effect of the ferroaxial transition on the electronic and optical properties of $BaTiS_3$.
Acknowledgements: This work was supported by ARO MURI grant # W911NF-21-1-0327 and NSF through DMR-2122070, DMR-2122071 and DMR-2145797. Electron microscopy performed at Oak Ridge National Laboratory's (ORNL) Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility.
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2:15 PM *QM04.02.03
Stochastic Dynamics of Nano-Ferroelectrics Jorge Iniguez[1,2]; [1]Luxembourg Institute of Science and Technology, Luxembourg; [2]U. of Luxembourg, Luxembourg

My group is interested in the behavior of ferroelectric materials that present non-trivial polar orders (vortexes [1], skyrmions [2]) and properties (chirality [3], negative capacitance [4,5]) in situations of reduced dimensionality (ultra-thin layers or films) or subject to suitable electric and mechanical boundary conditions. In this talk I will review our most recent theoretical results for one of the model systems in the field, the $PbTiO_3$/$SrTiO_3$ ferroelectric/dielectric superlattices where many of the above effects were first demonstated. In particular, I will discuss the dynamical behavior of these nano-ferroelectrics, paying especial attention to the state we call "domain liquid" [4], which is characterized by a spontaneous stochastic motion of the domains. I will show quantitative resuls for domain life and diffussion times, illustrate ways in which those
characteristic times can be controlled, and briefly discuss potential applications in unconventional computing.

Work done in collaboration with Hugo Aramberri, from the Luxembourg Institute of Science and Technolgoy. Funded by the Luxembourg National Research Fund through Grants C18/MS/12705883/REFOX and C21/MS/15799044/FERRODYNAMICS.

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2:45 PM QM04.02.04
Dislocations as Natural Quantum Wires in Diamond Sevim Polat Genlik, Roberto Myers and Maryam Ghazisaeidi; The Ohio State University, United States

Dislocations as natural quantum wires in Diamond
The one-dimensional complex bonding environment, within the core region of dislocations, has unique and localized properties that is different from that in bulk. Thus, dislocations and low dimensional (1D) quantum materials should exhibit similar features, except for the fact that dislocations are naturally occurring and environmentally protected by their host material. This makes dislocations advantageous as the fabrication and storage of low dimensional materials has remained challenging over the last two decades.Here we systematically investigate electronic properties of the glide set of partial dislocations in diamond with first principles calculations using hybrid exchange correlation functionals. The electronic band structure of dislocations and the anisotropic carrier mobilities are calculated and compared with the host crystals band structure and carrier mobilities. The results reveal that dislocations create one-dimensional (1D) metallic and semiconducting wires based on the character and position of defect states which heavily depend on the local core structures. 1D metallic bands appeared within the core of unreconstructed 30 partial dislocations, with a characteristic 1D density of states (1/). Map of charge density distribution along the cross-plane of dislocation line reveal that spatially localized 1D chain of overlapping pz orbitals creates conduction pathway for 1D Fermi gas. On the other hand, unreconstructed pure edge dislocation in diamond is found to be semiconducting with a band gap of 3.21 eV. These results open the door for exploitation of dislocations as 1D active components in functional devices.

3:00 PM BREAK

SESSION QM04.03: Phase Transitions and Topological Defects
Session Chairs: Albina Borisevich and Jorge Iniguez
Tuesday Afternoon, April 11, 2023
Marriott Marquis, Fourth Level, Pacific E

3:30 PM *QM04.03.01
Phase-field Method of Mesoscale Polar Topological Transformations and Phase Diagrams of Ferroelectric Thin Film Heterostructures Long-Qing Chen; The Pennsylvania State University, United States

This presentation will discuss the thermodynamic stability and transformations of polar topological structures in ferroelectric thin films and heterostructures. The focus will be on the applications of phase-field method to predicting the mesoscale transformation pathways and mechanisms among the different ferroelectric polar structures such as conventional nanotwins, vortex lattices, skyrmions, supercrystals, etc., under mechanical, electric, and thermal stimuli as well as light. The possibility of establishing the thermodynamic stability and phase diagrams of polar topological structures at different temperature, strain, and film thickness using both classical thermodynamics and phase-field method will be illustrated. One of the main advantages of the phase-field method is the fact that it allows one to analyze the primary strain, electrostatic, and domain wall energy contributions that are responsible for the thermodynamic stability of specific polar structures and thus can be utilized to guide the design and tuning of the polar topological structures and properties.

4:00 PM QM04.03.02
Mechanically Tunable Elastic Modulus of Freestanding $Ba_{1-x}Sr_xTiO_3$ Membranes via Phase-field Simulation Kena Zhang and Ye Cao; The University of Texas at Arlington, United States

The freestanding ferroelectric membranes with super-elasticity show promising applications in flexible electronic devices such as transducers, memories, etc. While there have been recent studies on the effect of mechanical bending on the domain structure evolutions and phase transitions in ferroelectric membranes, its influence on Young's modulus of these freestanding membranes is less explored, which is crucial for the design and application of flexible electronics. Here, a phase-field model is developed to simulate the tunability of Young's modulus of freestanding $Ba_{1-x}Sr_xTiO_3$ membranes under mechanical bending. It is demonstrated that the bent membrane shows a uniform Young's modulus compared with the unbent membrane. By increasing the bending angle, Young's modulus tunability is enhanced, which can be attributed to the vortex-like domain structures induced by mechanical bending. These vortex-like domains with large domain wall energy inhibit the subsequent domain switching under externally applied tensile strain and reduce the eigenstrain variation, which leads to a large Young's modulus. In addition, the formation of vortex domain structure is suppressed with increasing Sr^{2+}

content in $Ba_{1-x}Sr_xTiO_3$ membranes at the same bending degree, resulting in a decrease in Young's modulus tunability. Our work reveals that the tunability of Young's modulus of freestanding ferroelectric membranes can be achieved by mechanical bending, which provides guidance for designing flexible electronic devices.

4:15 PM *QM04.03.03
Anomalous Polar Textures and Exotic Phases in Quasi-1D Chalcogenide Gwan-Yeong Jung[1], Chong Wang[2], Guodong Ren[1], Boyang Zhao[3], Batyr Ilyas[4], Huandong Chen[3], Nuh Gedik[4], Jayakanth Ravichandran[3], Di Xiao[2] and Rohan Mishra[1]; [1]Washington University in St. Louis, United States; [2]University of Washington, United States; [3]University of Southern California, United States; [4]Massachusetts Institute of Technology, United States

Topological structures in ferroic materials have been studied extensively and garnered much attention due to their multiple prospective applications ranging from low-power electronics to high-performance optoelectronic devices. Specifically, topological patterns of electric dipoles such as polar vortices and polar skyrmions have been recently demonstrated in oxide superlattices and thin films. These patterns form a few to tens of nanometer-scale polar textures due to their long-range dipole interactions and geometrically confined boundary conditions. In this work, we explore the anomalous polar textures in quasi-1D $BaTiS_3$, where several competing structural distortions lead to different exotic phases such as charge-ordered phase consisting of atomic-scale polar vortices, a high-mobility ground-state phase, and a strain-induced chiral phase. Starting from high-symmetry room-temperature phase ($P6_3cm$), the quasi-1D $BaTiS_3$ undergoes two phase transitions, (i) second-order transition (240-250 K) to a charge-ordered phase ($P3c1$) and (ii) a first-order transition (150-190 K) to a high-mobility ground-state phase ($P2_1$).[1] Combining the single-crystal XRD and first-principles calculations, we identified the underlying structures of each three phases. Room temperature $P6_3cm$ phase consists of the anti-polar displacements along the *c*-axis with ferrielectric polarization along the out-of-plane direction. In the charge-ordered $P3c1$ phase, the atomic-scale polar vortices emerge with different chiralities on a larger size unit cell. In the ground state high-mobility phase ($P2_1$), striped pattern of antipolar displacements are observed both along in-plane and out-of-plane directions, making the net dipole moment as zero. This high-mobility phase exhibits chiral optical Raman response, implying an anomalous polar textures with optical activity. Notably, using a scanning transmission electron microscope (STEM) imaging, we directly observed a strain-induced ferroaxial transition, which is characterized by rotational distortion of the TiS_6 octahedra and Ba outward movements in the *a-b* plane.
Next, we will focus on the evolution of atomically thin clockwise counter-clockwise (CW-CCW) vortex pairs in the second-order transition. These polar vortices lie on a triangular-lattice network of Ti atoms along in-plane direction, which intrinsically hosts the frustration of electric dipoles in neighboring atoms. This resembles small skyrmions in magnetic materials, which often arises by resolving the exchange frustrations.[2,3] Using the first-principles electronic structure calculations and Monte Carlo simulations, we will discuss the possible mechanism to form the polar vortices on a 2D triangular lattice. We find that the coupling between several collinear antiferroelectric modes is the key to realize the non-collinear dipole textures such as vortices. Using group theoretical methods, we extracted three primary order parameters (K_3, Λ_3, M_2^-), which are all located at zone-boundaries, and developed a Landau model to microscopically understand the couplings between these modes. Based on the results, we find the CW-CCW vortex pairs can be further stabilized with more complex orders, involving non-coplanar orders along the in-plane direction with a finite scale macroscopic polarization along the out-of-plane direction. We expect that these results could pave the way to control the polar textures with multiple functionalities in ferroelectrics.

4:45 PM QM04.03.04
Electron- and Hole-Doped Hexagonal $TbInO_3$ from First Principles Nabaraj Pokhrel and Elizabeth Nowadnick; University of California, Merced, United States

In materials hosting frustrated magnetism, localized spins are acted upon by competing exchange interactions that cannot be satisfied at the same time, leading to a highly degenerate ground state. This can give rise to a fluid-like state of matter with no magnetic ordering known as a *spin liquid*. Spin liquids have been proposed to host exotic properties such as fractionalized charges and superconductivity upon doping, which are both of fundamental interest and may be of potential interest for quantum computing applications. However, the experimental confirmation of spin liquid states remains challenging, and there is a strong need for the identification of more candidate materials that may host spin liquids. Recent research has shown that hexagonal $TbInO_3$, with anisotropic exchange interactions, significant spin-orbit coupling, and f-electron magnetism, may be a spin-liquid candidate. $TbInO_3$ has a hexagonal crystal structure consisting of layers of corner-sharing non-magnetic InO_5 trigonal bipyramids, separated by layers of Tb^{3+} ions in a distorted triangular lattice with two inequivalent Tb sites. In this work, we use density functional theory (including spin-orbit coupling) to investigate the structural, electronic, and magnetic properties of hexagonal $TbInO_3$. We explore both undoped $TbInO_3$ as well as the effect of electron- or hole-doping by adding (removing) electrons from the calculation. By analyzing the density of states and band structure of doped $TbInO_3$, we explore whether added charge carriers are localized or form a metallic conducting state. Our work advances our fundamental understanding of charge-doping spin-liquid candidate $TbInO_3$.

SESSION QM04.04: Poster Session: Topological Defects in Novel Materials

Session Chairs: Gwan-Yeong Jung and Boyang Zhao
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM QM04.04.02
Investigating the Structural and Magnetic Properties of CrxTaS2 when x ≤ 0.25 Cameron Mollazadeh, Lilia Xie and Kwabena Bediako; UC Berkeley, United States

Moore’s Law states that the number of transistors in an integrated circuit will double approximately every two years. Although this trend has held steady since the mid-twentieth century, in the past decade, it was observed that new technologies are needed to maintain this growth while minimizing energy consumption. A promising avenue to address this issue is the field of spintronics, which take advantage of an additional degree of freedom, that is spin, as a way to store and retrieve information.
We propose that Cr-intercalated TaS2 (CrxTaS2) is a promising material for spintronics due to its unique structural and magnetic properties. CrxTaS2 has a layered structure containing Cr3+ions between two-dimensional sheets of TaS2. Typically, TaS2is a nonmagnetic material, but when spin-bearing Cr3+ ions are introduced between layers, the resultant material becomes magnetic. Layered magnets present an exciting alternative to current materials, as one can tune their magnetic properties based on intercalant stoichiometries. Preliminary data shows that when x = 0.25, the Cr intercalants order structurally in a 2 x 2 superlattice, and the material enters a spin glass state below 100 K. A spin glass is a magnetic state in which competition between ferromagnetic (FM) and antiferromagnetic (AFM) interactions causes spins to order randomly.
Several spintronic device designs utilize spin glasses interfaced with FMs or AFMs. Therefore, materials with tunable spin glass properties that can form clean interfaces with other magnetic materials are highly desired. We hypothesize that as the Cr amount decreases below 0.25, the material will exhibit more disorder and glassy behavior.

We aim to study how varying intercalant stoichiometry affects the magnetic and structural properties of CrxTaS2. Three batches of crystals were grown using chemical vapor transport, targeting stoichiometries of 0.25, 0.20, and 0.15. Cr ratios were then confirmed using energy-dispersive X-ray spectroscopy (EDX). Raman spectroscopy was used to probe the structures of the crystals. The x = 0.25 crystals contained a feature at 156 cm-1, demonstrating an ordered 2 x 2 superlattice. However, in the x = 0.20 crystals, this feature was red-shifted, suggesting the presence of a defective superlattice.
The x = 0.15 crystals grew in the expected hexagonal shape, but the Raman spectra were highly disordered. Golden-tinted, ribbon-like crystals were also obtained, which appear to be a side product based on Raman, EDX, and morphology.
Thus, we predict that lower Cr intercalant crystals may have transition temperatures lower than 100K due to enhanced disorder. The results of the x = 0.25 stoichiometry of Cr hold promise for application in next-generation devices. Further structural and magnetic characterization on stoichiometries consisting of x < 0.25 will unveil how these crystals can be tuned to our needs by varying the compositions.

5:00 PM QM04.04.04
Synthesis and Characterization of Polymeric Nanofibers Templated Along Topological Defects in Ultrathin Liquid Crystalline Film Arit Patra and Joerg Lahann; University of Michigan–Ann Arbor, United States

Formation of point defects, line disclinations and vortices are frequent in liquid crystalline materials, however application of these charged topological defects to synthesize materials has been rarely explored. In this work we have utilized substrate supported spin coated ultrathin E7 liquid crystal (LC) film (nematic) as a template to guide synthesis of nanofibers along the defect lines using chemical vapor polymerization (CVP) of [2.2]Paracyclophane based monomers. Such defects take on significant prominence for our system (60-300 nm LC films) because of the higher number density of defects in ultrathin films even after time-dependent annihilation of defects during the polymerization time. We predict that the polymerization would proceed exactly along the defect lines and to avoid artifacts such as changes in the nanofiber orientation after templating, critical point drying (CPD) has been used for removal of the LC phase. We have used polarizing optical microscope to characterize defect structures which allows for direct observation of darker lines or brushes in mixed LC/nanofiber phases (prior to LC removal3) and compared with the scanning electron microscope (SEM) images of the nanofibers to confirm that the defect structures get templated by the CVP process. We have observed that these distinctly identifiable short nanofibers can map 3-dimensional space of defect lines which shows presence of all different kind of LC defects including s = ±1, ±1/2 that appear to align with mathematically predicted defect patterns. We believe, understanding the nature and structure of LC defects will pave the path towards understanding of inducible defects, such as those created by particles immersed in a LC phase and how particle-loaded LC templating phases can be leveraged to design defects that template novel nanofiber patterns during CVD polymerization.

5:00 PM QM04.04.06
Impact of Grain Boundary Atomic Structure on the Formation of Conductive Pathways in Memristive Devices Robert Eilhardt[1], Alexander Zintler[1], Stefan Petzold[1], Eszter Piros[1], Nico Kaiser[1], Tobias Vogel[1], Keith McKenna[2], Lambert Alff[1] and Leopoldo Molina-Luna[1]; [1]Darmstadt University of Technology, Germany; [2]University of York, United Kingdom

One of the most promising emerging non-volatile memory technologies is Resistive Random Access Memory [1]. A major challenge is to improve device reliability and device-to-device variability [2]. Grain boundary (GB) engineering the dielectric layer in oxide thin film resistive switching devices is a novel approach to overcome these flaws [3]. The main objective here is to reveal insight why grain boundaries impact resistive switching properties. By using reactive molecular beam epitaxy (RMBE) and sputter coating stack combinations of a 50 nm TiN bottom electrode, a 10 nm thin HfO_2 layer and a top electrode of Pt (100 nm) were grown on *c*-cut sapphire. By combining ultra-high-resolution experimental and theoretical methods, we established a direct correlation between the grain boundary atomic and electronic structures with the resistive switching behavior of TiN/*m*-HfO_2/Pt memristors with defined HfO_2 textures. First principles calculations reveal that oxygen vacancies readily segregate to grain boundaries in (11-1) textured HfO_2 leading to reduced forming voltages which might also be influenced by local strain states at the grain boundaries [4]. This unique approach of combining advanced atomic-scale imaging and first principles theoretical calculations to understand the resistive switching properties of memristors yields invaluable guidance in improving device performance.

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SESSION QM04.05: Imaging, Diffraction and Spectroscopy of Topological Defects
Session Chairs: Berit Goodge and Petro Maksymovych
Wednesday Morning, April 12, 2023
Marriott Marquis, Fourth Level, Pacific E

8:00 AM *QM04.05.01
Direct Imaging of Charge Distribution at Crystalline Defects by Scanning Transmission Electron Microscopy Naoya Shibata[1,2]; [1]The University of Tokyo, Japan; [2]Japan Fine Ceramics Center, Japan

Differential phase contrast imaging in aberration-corrected scanning transmission electron microscopy (DPC STEM) enables to directly probe local charge distribution around crystalline defects down to the atomic dimensions. In the present study, we introduce recently developed magnetic-field-free STEM with tilt-scan averaging system and demonstrate quantitative imaging of local charge distribution around crystalline interfaces at sub-nm resolution. We further show the possibility of local magnetic structure imaging near crystalline defects by the technique. Several on-going STEM developments and material application results will be also presented.

8:30 AM QM04.05.02
Nano-ARPES Visualization of Chiral Electronic Domains and Defects on Layered Chalcogenides Yi Lin[1], Luca Moreschini[1], Junze Zhou[1], Sushant Behera[1], Sean Mills[2], Steven Zeltmann[2], Cheng Hu[1], Maximilian Huber[1], Alexander Weber-Bargioni[1], Andrew M. Minor[2], Sinead Griffin[1], Aaron Bostwick[1], Chris Jozwiak[1] and Alessandra Lanzara[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

Topological defects have been extensively studied in ferromagnets, liquid crystals and ferroelectric materials. Analogically, it is interesting to understand if charge orders can also form topological structures and how they can be visualized. In this work, we use nano-ARPES to map spatially resolved electronic structure in layered chalcogenides. We find rotational electronic domains that are degenerate in energy. Further characterized by atomic force microscope and electron diffractions, we find these domains are likely on the surface and form defects where chirality can be defined. The observations of the energy degeneracy and the chirality highly resemble the Kibble–Zurek conditions for identifying topological defects.

8:45 AM QM04.05.03
Harnessing Dislocation Motion Using an Electric Field Yu Zou; University of Toronto, Canada

Dislocations, line defects in crystalline materials, play an essential role in the mechanical, electrical, optical, thermal, and phase transition properties of these materials. Dislocation motion, an important mechanism underlying crystal plasticity, is critical for the hardening, processing, and application of a wide range of structural and functional materials. For decades, the movement of dislocations has been widely observed in crystalline solids under mechanical loading. However, the goal of manipulating dislocation motion via a non-mechanical field alone remains elusive. Here, we present real-time observations of dislocation motion controlled solely by an external electric field in single-crystalline zinc sulfide (ZnS). We find that 30{\deg} partial dislocations can move back and forth depending on the direction of the electric field, while 90{\deg} partial dislocations are motionless. We reveal the nonstoichiometric nature of dislocation cores using atomistic imaging and determine their charge characteristics by density functional theory calculations. The glide barriers of charged 30{\deg} partial dislocations, which are lower than those of 90{\deg} partial dislocations, further decrease under an electric field, explaining the experimental observations. This study provides direct evidence of dislocation dynamics under a non-mechanical stimulus and opens up the possibility of modulating dislocation-related properties.

9:00 AM QM04.05.04
Ultrafast Formation of Topological Defects in a 2D Charge Density Wave Alfred Zong[1,2], Yun Cheng[3], Lijun Wu[4], Qingping Meng[4], Wei Xia[5], Fengfeng Qi[3], Pengfei Zhu[3], Xiao Zou[3], Tao Jiang[3], Yanfeng Guo[5], Jasper van Wezel[6], Anshul Kogar[7], Michael Zuerch[1,2], Jie Zhang[3], Yimei Zhu[4] and Dao Xiang[3]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Shanghai Jiao Tong University, China; [4]Brookhaven National Laboratory, United States; [5]ShanghaiTech University, China; [6]University of Amsterdam, Netherlands; [7]University of California, Los Angeles, United States

In solids, transient defects are known to generate a variety of hidden orders not accessible in equilibrium, but how defects are formed at the nanometer lengthscale and femtosecond timescale remains unknown. Here, we employ an intense laser pulse to create topological defects in a 2D charge density wave (CDW), and track their morphology and dynamics with ultrafast electron diffraction. Leveraging its high temporal resolution and sensitivity in detecting weak diffuse signals, we discover a dual-stage growth of 1D domain walls within 1 ps, a process not dictated by the CDW amplitude but instead mediated by a nonthermal population of longitudinal optical phonons. Our work provides crucial insights into ultrafast engineering of topological defects based on selective excitation of collective modes, opening avenues for dynamical control of nonequilibrium phases in correlated materials.

9:15 AM *QM04.05.05
New Methods for Imaging Polar Topological Textures in Oxide Heterostructures Yu-Tsun Shao[1,2], Sergei Prokhorenko[3], Lucas Caretta[4,5], Yousra Nahas[3], Sujit Das[6], Zijian Hong[7], Ruijuan Xu[8], Fernando Gomez-Ortiz[9], Pablo Garcia-Fernandez[9], Long-Qing Chen[10], Harold Y. Hwang[11], Javier Junquera[9], Lane Martin[4], Laurent Bellaiche[3], Darrell Schlom[1], Ramamoorthy Ramesh[4,12] and David A. Muller[1]; [1]Cornell University, United States; [2]University of Southern California, United States; [3]University of Arkansas, Fayetteville, United States; [4]University of California, Berkeley, United States; [5]Brown University, United States; [6]Indian Institute of Science, India; [7]Zhejiang University, China; [8]North Carolina State University, United States; [9]Universidad de Cantabria, Spain; [10]The Pennsylvania State University, United States; [11]Stanford University, United States; [12]Rice University, United States

Polar topological textures such as polar skyrmions and merons in ferroelectric heterostructures emerge resulting from the interplay of elastic, electrostatic and gradient energies. These dipolar textures not only have mathematical beauty but also exhibit exotic functionalities such as emergent chirality and local negative capacitance for potential applications in next generation nanodevices. To understand and explore the microscopic details of such topological textures requires a characterization method which can track their detailed 3D structures at the atomic scale.

A popular approach for mapping polar distortions in ferroelectrics has been to use high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM), which directly image the atomic displacements with a precision of a few picometers. Although conceptually straightforward, because of the small depth-of-field and strong dechanneling of the probe scattered by heavy cations, HAADF-STEM only samples the top surface of the sample, which can have a very different polar order from the middle of a 3D structure such as skyrmion, for example Néel (top) versus Bloch (middle) characters.

Here, by utilizing the full 4-dimensional phase space information collected by a new design of direct electron detector that can measure the momentum transfer distributions at every probe position (4D-STEM), we can solve the inverse multiple scattering problem and retrieve the 3-dimensional electrostatic potential of the sample, yielding a lateral resolution of <20 pm. This allows us to determine both the cation displacements and octahedral tilts. To further improve the sensitivity to polar order, we combine scanning diffraction with dynamical diffraction simulations to robustly image the polarization and chirality in each polar texture. I will show how 4D-STEM-based approach allows us to image dipolar waves, polar skyrmions and merons in ferroelectric thin films that are unable to measure by conventional methods.

Research supported by AFOSR Hybrid Materials MURI (FA9550-18-1-0480) and ARO ETHOS MURI (W911NF-21-2-0162), facilities support from the NSF (DMR-1429155, DMR-1719875, DMR-2039380). Researchers at the University of Arkansas also thank the Vannevar Bush Faculty Fellowship Grant No. N00014-20-1-2834 from the Department of Defense.

9:45 AM QM04.05.06
Emergent Atomic Scale Polarization Vortices Boyang Zhao[1], Gwan-Yeong Jung[2], Chong Wang[3], Huandong Chen[1], Shantanu Singh[1], Guodong Ren[2], Nick Settineri[4], Simon Teat[4], Di Xiao[3,5], Rohan Mishra[2] and Jayakanth Ravichandran[1,1,1]; [1]University of Southern California, United States; [2]Washington University in St. Louis, United States; [3]University of Washington, United States; [4]Lawrence Berkeley National Laboratory, United States; [5]Department of Physics, United States

Topological defects, such as vortices and skyrmions, enable emergent electronic and photonic functionalities in materials [1,2]. Magnetic and dipolar vortex-anti-vortex structures have geometric bounds on their stability [3,4]. Understanding the scaling limits of such topological structures is critical to enable microscopic functional units towards novel device architectures. In this work, we report the existence of atomic-scale vortex-anti-vortex dipolar structures in a quasi-1D hexagonal chalcogenide, $BaTiS_3$, from the refined crystal structures of X-ray synchrotron single-crystal diffraction studies. We observe large displacements of Ti in the TiS_6 octahedra of $BaTiS_3$, comparable to ferroelectric perovskite oxides, along and across the quasi-1D TiS_3 chain.

$BaTiS_3$ undergoes a series of TiS_6 dipole-ordering from a room temperature ferrielectric phase to a intermediate phase with the vortex-antivortex dipolar structures below ~250 K through a second-order phase transition, and then, transforms into a lower symmetry phase below 180 K through a first-order transition. The observation of dipolar vortices in $BaTiS_3$ shows that the ultimate scaling limit for dipolar topological structures is down to the atomic scale. We will discuss the role of different electrostatic interactions and soft-phonon modes in stabilizing the emergent polarization textures in $BaTiS_3$. We will also discuss the accessibility of similar structural and electrical characteristics in charge density wave materials such as $1T$-$TiSe_2$ [5] and $BaTiSe_3$. Our work sets up complex charge density waves with d^0 filling as a playground for realizing and understanding quantum polarization topologies.

Acknowledgements: This work was supported by ARO MURI grant # W911NF-21-1-0327 and NSF through DMR-2122070 and DMR-2122071. Single crystal diffraction works were performed at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, which is a DOE Office of Science User Facility.

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10:00 AM BREAK

SESSION QM04.06: Scanning Probe Methods for Topological Defects
Session Chairs: Yu-Tsun Shao and Naoya Shibata
Wednesday Morning, April 12, 2023
Marriott Marquis, Fourth Level, Pacific E

10:30 AM *QM04.06.01
The Multiwells—Switching Portraits of the Thiophosphate Family Petro Maksymovych; Oak Ridge National Laboratory, United States

Multiwell potentials make ferroelectrics fundamentally interesting, diverse and unique. In particular, multiwells can give rise to metastable states that control ferroelectric switching and the structure of domain walls. In this sense ferroelectric materials gain field-induced functionality by design, which is particularly promising for applications in microelectronic, electrocaloric and energy-storage functions. We have recently come across several distinct multiwell potentials in ferroelectrics comprising P_2S_6 anion building blocks [1]. Although the materials in this family include both van der Waals and continuous solids with very different polarization properties [1], their multiwells share two common features – uniaxiality and substantial tunability with strain and chemical composition. On a fundamental level, the uniaxiality of the potential nearly guarantees new behaviors of domain walls and can give rise to polarization dynamics that may be unachievable in a double-well potential.
In this talk, we will first show how nanoscale microscopy methods play central role in inferring the existence of multiwell potentials in thiophosphates [2-4], through direct and indirect observables. Indeed, despite almost two decade history of $CuInP_2S_6$, many functional properties such as giant negative electrostriction, multiplicity of the domain structure and strongly time-dependent switching, were first revealed with scanning probe techniques. These findings then led to computational predictions of the 4-well with first principles modeling, with subsequent quantitative verificaition by microscopy measurements [2]. Meanwhile unique features of switching hysteresis in $Sn_2P_2S_6$ consituted the first direct evidence of the proposed triple-well in this material, which enables coexistence of antiferroelectric-like switching loops with ferroelectric-like domain structure. Subsequently, we will focus on the interesting aspects of polarization dynamics that can be expected and observed in a multiwell potential, such as volatile and time-dependent polarization switching [3,4], field-induced order-disorder [4] and noise-induced restructuring of domain walls [5]. These properties collectively represent new prospects for ferroelectric applications, particularly in tunable and neuromorphic computing elements, while also posing a fresh frontier for revisiting and further understanding the emergence and dynamics of metastable polarization states. Finally, we will address the need for continued development of scanning probe methods capable of reproducible measurements of relatively more complex switching dynamics in multiwell systems, including combined piezoelectric and microwave microscopy, topological methods for data analysis and atomically-resolved imaging of materials with increased density of domain walls. The experiments were supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division, and conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. Theoretical work at Vanderbilt University was supported by Department of Energy grant DE-FG02-09ER46554 and by the McMinn Endowment.

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11:00 AM QM04.06.02
Towards Spatially Resolved Measurements of Domain Wall Thermal Transport Using Scanning Thermal Microscopy Rebecca Kelly[1,2], Fran Kurnia[1], Amit Kumar[1], Marty Gregg[1] and Ray McQuaid[1]; [1]Queen's University Belfast, United Kingdom; [2]University of Glasgow, United Kingdom

It is now a well-established idea that ferroelectric domain walls can be considered as extended structural defects that affect thermal transport through phonon scattering[1]. Additionally, the fact that some types of domain walls exhibit dramatically enhanced electrical conductivity suggests enhanced thermal transport within the wall due to charge transport might be plausible.
Measurement approaches used to date to investigate domain wall thermal properties, such as time-domain thermoreflectance and steady state heat flow setups, typically measure large sample areas and domain wall contributions to the overall sample response must be back extracted. Direct, local measurements of domain wall thermal transport properties have not yet been reported and would require thermal imaging with sufficiently nanoscale spatial resolution.
Scanning Thermal Microscopy is a promising technique for mapping thermal properties of a sample with nanoscale spatial resolution. Here, we describe an

approach for locally mapping variations in thermal properties associated with microstructural heterogeneity. A thin gold bar is deposited on the sample surface and is periodically Joule heated, allowing lock-in measurements of temperature to be mapped locally using the scanning probe as a temperature sensor[2]. To validate that spatial heterogeneity in thermal properties can be imaged, a multilayer ceramic capacitor was used due to the expected variation in thermal response between the metal electrode and ceramic layers. We find that temperature contrast between the metal and ceramic layers can indeed be resolved and that the lock-in temperature measurements help mitigate against topographical crosstalk issues seen in static temperature measurements. Exploratory measurements are also currently underway to image thermal signal contrast associated with electrically conducting domain walls in ion-sliced $LiNbO_3$ thin films.

[1] Wang, J. J., Wang, Y., Ihlefeld, J. F., Hopkins, P. E. & Chen, L. Q. Tunable thermal conductivity via domain structure engineering in ferroelectric thin films: A phase-field simulation. *Acta Mater.* **111**, 220–231 (2016).
[2] Menges, F. *et al.* Temperature mapping of operating nanoscale devices by scanning probe thermometry. *Nat. Commun.* **7**, 1–6 (2016).

11:15 AM QM04.06.03
Confinement-Driven Inversion of the Domain Scaling in Polycrystalline $ErMnO_3$ Jan Schultheiß[1,2], Fei Xue[3], Håkon Ånes[2], Frida Danmo[2], Sverre M. Selbach[2], Long-Qing Chen[3] and Dennis Meier[2]; [1]Universität Augsburg, Germany; [2]Norwegian University of Science and Technology, Norway; [3]The Pennsylvania State University, United States

The functionality and physical properties of ferroelectric materials are intimately coupled to their domain morphology. Recently, precipitates and dislocations have been identified as an effective mean to control the domain pattern in ferroelectrics. In addition, more complex topological structures have drawn interest, giving a new dimension to the control of ferroelectric domains and their responses.
Here, we demonstrate that topologically protected vortex/anti-vortex cores can be used to engineer the domain structure in polycrystalline improper ferroelectric $ErMnO_3$. We find a one-to-one correlation between the grain size and the type of domain structure, allowing us to induce mono-, vortex-like- or stripe-like domain states on demand. Interestingly, and in contrast to proper ferroelectrics, such as $BaTiO_3$ and $Pb(Zr,Ti)O_3$, we observe an inverted domain-size / grain-size dependence, leading to the formation of smaller domains in larger grains. Phase field simulations show that this unusual behavior originates from the interaction of topologically protected vortices with elastic strain fields. The topology-driven inverted scaling behavior is intriguing as it provides a conceptually new handle for tuning the electromechanical and dielectric performance of ferroelectrics, giving a new dimension to capacitor applications and domain wall-based nanoelectronics.

11:30 AM QM04.06.04
Novel Scanning Probe Investigations of Domains and Domain Walls in Lithium Niobate Jesi Maguire[1], Hamza Waseem[1], Charlotte Cochard[2], Ray McQuaid[1], Amit Kumar[1] and Marty Gregg[1]; [1]Queen's University Belfast, United Kingdom; [2]University of Dundee, United Kingdom

Over the last 25 years, scanning probe microscopy techniques have revolutionised the way in which we understand ferroelectric domains and domain walls. This trend shows no sign of stopping. Here, for example, we have used two key imaging modes to investigate new characteristics of charged (head-to-head) conducting domain walls in single crystal $LiNbO_3$: Kelvin Probe Force Microscopy (KPFM) and Charge Gradient Microscopy (CGM).

In detail, newly configured “high-voltage” in-situ KPFM (imaging relatively large voltages while driving current) has allowed us to explicitly determine the resistivity of conducting lithium niobate domain walls for the first time (without the confounding influence of contact resistance): conducting domain walls were written in x-cut lithium niobate films by partial poling between coplanar thin film electrodes. In-situ KPFM mapping of the interelectrode region was then performed, while driving current along the conducting walls. Knowing the current density and the potential gradient developed allowed room temperature "four-probe" wall conductivity to be explicitly determined.

Equally, the combination of KPFM and CGM has revealed interesting surface potential profiles, associated with the microstructure around the charged walls, and forced us to reconsider the fundamental imaging mechanism responsible for CGM contrast [1]: KPFM scans revealed a triangular potential profile perpendicular to a head-to-head wall, which was an almost perfect match to the integrated CGM signal obtained in the same region. This strongly suggests that CGM does not actually measure charge gradients, but rather potential gradients.

[1] Maguire, J.R., Waseem, H., McQuaid, R.G., Kumar, A., Gregg, J.M. and Cochard, C., 2022. Imaging Ferroelectrics: Reinterpreting Charge Gradient Microscopy as Potential Gradient Microscopy. *Advanced Electronic Materials*, p.2101384.

11:45 AM QM04.06.05
Deep Tomographic Piezoresponse Force Microscopy—A New Approach to Unveil Novel Topological Structures in Uniaxial Ferroelectrics Conor J. McCluskey[1], Jesi Maguire[1], Yurii Tikhonov[2], James McConville[1], Haidong Lu[3], Dennis Meier[4], Anna Razumnaya[5], Alexei L. Gruverman[3], Valerii Vinokur[5], Igor Lukyanchuk[2], Amit Kumar[1] and Marty Gregg[1]; [1]Queen's University Belfast, United Kingdom; [2]University of Picardie, France; [3]University of Nebraska–Lincoln, United States; [4]Norwegian University of Science and Technology, Norway; [5]Terra Quantum AG, Switzerland

With the development of scanning probe microscopy and related techniques (piezoresponse force microscopy, conductive atomic force microscopy), we now have access to nanoscale images of ferroelectric domain structure and in-situ electrical, mechanical or magnetic properties with unprecedented resolution. While representing an incredible leap forward in our understanding of these systems, the information available is quite literally superficial: the entire subsurface structure is traditionally inaccessible by these techniques. Recently, researchers have been interested in experimentally revealing the third dimension of ferroelectric domain structures [1,2] to understand the complex networks that exist below the surface.

Here, we develop tomographic piezoresponse force microscopy to reveal and reconstruct the subsurface ferroelectric domain structure in two well-known uniaxial ferroelectrics: lead germanate and triglycine sulfate. Pioneered by Huey et al. [3], tomographic atomic force microscopy methods involve scanning the surface of a sample with an atomic force microscopy tip in contact with a sample, while employing a significant compressive force from tip to sample. This “machines” the surface of the material, meaning subsequent images are collected at different depths into the material. If carried out in conjunction with standard piezoresponse force microscopy imaging of the ferroelectric domain structure, the 3D domain structure can be recreated. We take this tomographic method to new depths, milling in excess of 5 microns into the surface of the ferroelectric, where previously 100’s of nanometres had been typical [3].

In the case of lead germanate, we find evidence for the theoretically predicted domain wall saddle point features. Models suggest that this is the consequence of the mutual bifurcation of head-to-head domains, and accompanying rotation of polarisation away from the singular polarisation axis. This prevents the build-up of bound charge at head-to-head or tail-to-tail sections of domain walls, and gives the polarisation network a topological character[4]. In triglycine sulphate, we find charged sections of domain walls, which contradicts the notion that domain walls in this material are uncharged, fully penetrating the crystal along the polar axis. Tomographic atomic force microscopy adds a new dimension to scanning probe studies on ferroelectrics, and can reveal topological features which may have been previously unexpected, especially in uniaxial ferroelectrics.

[1] Roede, E. D., *et al.*, The Third Dimension of Ferroelectric Domain Walls, *Advanced Materials* **34**, 2202614 (2022).
[2] Kirbus, Benjamin, et al. "Real-time 3D imaging of nanoscale ferroelectric domain wall dynamics in lithium niobate single crystals under electric stimuli: implications for domain-wall-based nanoelectronic devices." *ACS Appl. Nano Mater.,* **2.9,** 5787-5794. (2019).
[3] Steffes, J. J., Ristau, R. A., Ramesh, R., & Huey, B. D., Thickness scaling of ferroelectricity in BiFeO3 by tomographic atomic force microscopy. *Proc. Natl Acad. Sci.*, **116,** 2413-2418, (2019).
[4] Tikhonov, Yurii, et al. "Polarisation Topology at the Nominally Charged Domain Walls in Uniaxial Ferroelectrics." *Adv. Mater.,* 2203028, (2022).

SESSION QM04.07: Physical Properties and Applications I

Session Chairs: Huandong Chen and Han Wang
Wednesday Afternoon, April 12, 2023
Marriott Marquis, Fourth Level, Pacific E

1:30 PM QM04.07.01
Imaging the Emergent Functionality in Bulk Ferroelectrics Trygve M. Ræder and Hugh Simons; Technical University of Denmark, Denmark

Emergent behaviour in ferroelectrics can be imaged at surfaces by scanning probe microscopy (SPM), and in thin lamella by transmission electron microscopy (TEM). Despite tremendous advances in these techniques over the past decades, SPM and TEM remain unsuitable for investigation of the bulk. X-ray-based techniques, on the other hand, penetrate through the material and are well suited for investigation of the bulk. Multiple X-ray techniques are now able to image strain and orientation deep in the bulk. Dark-field X-ray microscopy (DF-XRM) is one such technique, which has previously been applied to ferroelectrics and has produced images of domains and strain deep in the bulk [1]. Here, we present our efforts to functionalize DF-XRM and image the polarization in addition to strain. Functionalized DF-XRM will allow us to image exotic topological structures deep inside the sample or at a buried interface. A more expansive analysis of the interplay between strain, stress, and polarization can then be explored in the 3D bulk of the material. The interplay between ferroelectric domain walls, line defects, and vacancies in the bulk is of particular interest, and this is difficult to approach using other techniques.

We will present proof-of-concept experimental results from our ongoing efforts to image the polarization of $BaTiO_3$ in-situ using DF-XRM. Our experimental work is guided by a theoretical framework, which we will also present together with simulations of realistic experimental conditions. Furthermore, we will describe how a stroboscopic configuration can be used to image material dynamics. Finally, this work has implications for any material imaged in DF-XRM with an applied electric field. In a general case, the electric field will perturb the X-ray structure factor, which is assumed to be constant when calculating strain maps from a DF-XRM image series. We will show how this perturbation can be quantified and addressed, so that accurate strain maps may still be produced in the presence of an electric field.

[1] Simons, Hugh, et al. "Long-range symmetry breaking in embedded ferroelectrics." Nature materials 17.9 (2018): 814-819.

1:45 PM *QM04.07.02
Stripes, Gaps and Orderly Disorder—Tuning Magnetic Textures in Intercalated TMDs Berit H. Goodge[1,1], Oscar Gonzalez[1], Lilia Xie[1] and Kwabena Bediako[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Intercalated transition metal dichalcogenides (TMDs) have been proposed as promising platforms for next-generation spintronic devices based on a wide range of electronic and magnetic phases which can be tuned by varying the host lattice or the species, amount, and ordering of intercalants [1]. Several compounds have been shown to host chiral magnetic order, namely a helical winding of in-plane magnetic moments along the *c*-axis of the layered crystal structure. Previous studies have shown that different intercalant concentrations can have a dramatic impact on, for example, chiral domains [2] and magnetic properties [3], but a deeper and more predictive understanding of these effects will be necessary for any future applications of these materials. Here, we leverage a combination of imaging modes in the (scanning) transmission electron microscope (S/TEM) to directly probe (dis)order across multiple length scales and show how subtle changes in the atomic lattice can have dramatic impact on mesoscale magnetic textures.

1. Xie, L. S. et al. Structure and Magnetism of Iron- and Chromium-Intercalated Niobium and Tantalum Disulfides. *J. Am. Chem. Soc.* **144**, 9525−9542 (2022).
2. Horibe, Y. et al. Color Theorems, Chiral Domain Topology, and Magnetic Properties of Fe_xTaS_2. *J. Am. Chem. Soc.* **136**, 8368−8373 (2014).
3. Kousaka, Y. et al. An emergence of chiral helimagnetism or ferromagnetism governed by Cr intercalation in a dichalcogenide $CrNb_3S_6$. *APL Mater.* **10**, 090704 (2022).

* This work supported by University of California President's Postdoctoral Fellowship Program, the National Science Foundation (DMR-2039380, DMR-1719875, MRI-1429155, DMR-1539918), and the Air Force Office of Scientific Research (FA9550-20-1-0007).

2:15 PM QM04.07.03
A Class of Magnetic Topological Material Candidates with Hypervalent Bi Chains Jason F. Khoury[1], Bingzheng Han[1], Milena Jovanovic[1], Ratnadwip Singha[1], Xiaoyu Song[1], Raquel Queiroz[2], Nai-Phuan Ong[1] and Leslie Schoop[1]; [1]Princeton University, United States; [2]Columbia University, United States

The link between crystal and electronic structure is crucial for understanding structure–property relations in solid-state chemistry. In particular, it has been instrumental in understanding topological materials, where electrons behave differently than they would in conventional solids. Herein, we identify 1D Bi chains as a structural motif of interest for topological materials. We focus on Sm_3ZrBi_5, a new quasi-one-dimensional (1D) compound in the Ln_3MPn_5 (Ln = lanthanide; M = metal; Pn = pnictide) family that crystallizes in the $P6_3/mcm$ space group. Density functional theory calculations indicate a complex, topologically nontrivial electronic structure that changes significantly in the presence of spin–orbit coupling. Magnetic measurements show a quasi-1D antiferromagnetic structure with two magnetic transitions at 11.7 and 10.7 K that are invariant to applied field up to 9 T, indicating magnetically frustrated spins. Heat capacity, electrical, and thermoelectric measurements support this claim and suggest complex scattering behavior in Sm_3ZrBi_5. This work highlights 1D chains as an unexplored structural motif for identifying topological materials, as well as the potential for rich physical phenomena in the Ln_3MPn_5 family.

2:30 PM BREAK

SESSION QM04.08/QM02.05/QM03.08: Joint Session: Frontiers in Characterization Methods for Topological Defects
Session Chairs: Yue Cao, Dennis Meier and Jayakanth Ravichandran
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2008

3:30 PM *QM04.08/QM02.05/QM03.08.01
Ultrafast Dynamics and Dispersion of Collective Modes in Polar Skyrmions Haidan Wen; Argonne National Laboratory, United States

Collective excitation is important for understanding many-body interactions as well as inspiring new functionalities in condensed matter systems. Novel collective excitations can arise from competing interactions in ferroelectric nanostructures. For example, polar vortex stabilized in $PbTiO_3/SrTiO_3$ superlattices can host collective atomic motions involving hundreds of unit cells, emerging as a vortexon mode [1]. However, the collective excitation of topologically nontrivial polar skyrmions [2] is not yet known. Here, using terahertz-field excitation and femtosecond x-ray diffraction probe technique, we discover the collective dynamics of polar skyrmions, featuring a 0.3-THz mode with coherent vibrating domain walls and a stable core. The Pb atomic displacement forms a transient vortex structure in skyrmions. The broad diffuse scattering satellite peaks from polar skyrmions allow us to probe the dispersion of this collective mode. The distinct dispersion relations for skyrmion cores and domain walls evident the significant phononic properties of $PbTiO_3$ layer, indicating possible phonon localization. The dynamical response is significantly reduced at the sample temperature of 360 K, corresponding to the loss of skyrmion topological charge due to the deformation of skyrmions at high temperatures. The dynamical phase-field modeling reproduces the key experimental observations and gives microscopic insight into the polar skyrmion modes. Our work opens opportunities for engineering phononic properties and controlling collective dynamics in topological nanostructures.

[1] Li et al. "Subterahertz collective dynamics of polar vortices", Nature, 592, 376 (2021)
[2] Das et al. "Observation of room-temperature polar skyrmions", Nature, 568, 368 (2019)

This work is primarily supported by the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, under award no. DE-SC-0012375.

4:00 PM *QM04.08/QM02.05/QM03.08.02
Unconventional Properties of Nominally Charged Domain Walls in Uniaxial Ferroelectric Lead Germanate Alexei L. Gruverman; University of Nebraska-Lincoln, United States

Application of the scanning probe microscopy techniques, such as Piezoresponse Force Microscopy (PFM), opens a possibility to re-visit the ferroelectrics previously studied by the macroscopic electrical testing methods and establish a link between their local nanoscale characteristics and integral response. Here, we report the nanoscale PFM studies and phase field modeling of the static and dynamic behavior of the domain structure in the well-known ferroelectric material - lead germanate, $Pb_5Ge_3O_{11}$ (PGO). Several unusual phenomena were revealed: (1) domain formation during the paraelectric-to-ferroelectric phase transition, which exhibits an atypical cooling rate dependence; (2) unexpected electrically-induced formation of the oblate domains due to the preferential domain walls motion in the directions perpendicular to the polar axis, contrary to the typical domain growth behavior observed so far; (3) absence of the bound charges at the head-to-head (H-H) and tail-to-tail (T-T) domain walls, which typically exhibit a significant charge density in other ferroelectrics due to the polarization discontinuity. This strikingly different behavior is rationalized by the phase field modeling of the dynamics of uncharged H-H and T-T domain walls. Our results provide a new insight into the emergent physics of the ferroelectric domain boundaries, revealing unusual properties not exhibited by conventional Ising-type walls.

4:30 PM *QM04.08/QM02.05/QM03.08.03
Ultrafast Manipulation of Multiferroic $BiFeO_3$ Through Light-Driven Phonons Wanzheng Hu; Boston University, United States

Manipulating coupled orderings by external fields, or exploring methodologies to achieve ultrafast control of ferroic orderings have driven significant research activities for understanding the physics of multiferroicity. $BiFeO_3$ shows strong couplings of the lattice structure, electronic and magnetic properties to external fields, which make it appealing for potential applications to encode and access information using a multiferroic bit.
Nonlinear phononics is an emerging approach, in which intense mid-infrared or teraherz laser pulses are used to resonantly excite optical phonons. The high peak electric fields drive phonon oscillations to large amplitudes. This leads to quasistatic lattice distortion due to strong anharmonic couplings between phonons. The lattice deformation modifies the microscopic Hamiltonian of the system on average, offering a unique platform to engineer novel functionalities which may not exist in equilibrium, and to achieve selective control of quantum phases such as ferroelectric polarization and magnetic orderings. In this talk, I will present our recent results on the ultrafast manipulation of multiferroic $BiFeO_3$ by nonlinear phononics.

Funding Acknowledgement: This material is based upon work supported by the U.S. Department ofEnergy, Office of Science, Office of Basic Energy Sciences Early Career Research Program under Award Number DE-SC-0021305.

SESSION QM04.09: Physical Properties and Applications II
Session Chairs: Jayakanth Ravichandran and Haidan Wen
Thursday Morning, April 13, 2023
Marriott Marquis, Fourth Level, Pacific E

8:00 AM *QM04.09.01
A New Era in Ferroelectrics Ramamoorthy Ramesh and Peter Meisenheimer; Rice University, United States

Complex topological configurations are a fertile playground to explore novel emergent phenomena and exotic phases in condensed-matter physics. I will describe the discovery of polar skyrmions in a lead-titanate layer confined by strontium-titanate layers by atomic-resolution scanning transmission electron microscopy (STEM). Phase-field modeling and second-principles calculations reveal that the polar skyrmions have a skyrmion number of +1 and resonant soft X-ray diffraction experiments show circular dichroism confirming chirality. Such nanometer-scale polar skyrmions exhibit a strong signature of negative permittivity at the surface of the skyrmion, which is furthermore highly tunable with an electric field. They are a new state of matter and electric analogs of magnetic skyrmions, and may be envisaged for potential applications in information technologies.

8:30 AM QM04.09.02
Topological States in Nanostructured Ferroelectrics of Different Dimensions Igor Lukyanchuk; University of Picardie, France

Past decade marked breakthrough discoveries of novel topological polarization structures in nanostructured ferroelectrics. These findings lie at the crossroad of the forefront of the physics of nanostructured materials, advanced topological concepts, and cutting-edge industrial nanotechnologies. The observed polarization structures have been interpreted in terms of the real-space vector field topology as multiple combinations of vortices, skyrmions, merons, and other topological formations. This topological approach was successfully used in the physics of dislocation, liquid crystals, and magnetism. Ferroelectricity has been viewed as an electric dual of magnetism; however, this visible analogy misses ferroelectricity's cornerstone, the dominant role of the long-range electrostatic forces. We establish a topological foundation of ferroelectricity arising from its electrostatic essence and discuss the observed topological phenomena. We point out at the shortcomings of the existing topological approaches widely utilized for the description of the polarization vector fields. We establish that the physics of ferroelectrics can be constructed in the framework of topological hydrodynamics, an advanced formalism of the topology of an incompressible flow of the vector fields, introduced by Arnold. Based on the introduced topological identity of the electrostatics of ferroelectrics and hydrodynamics of the incompressible liquid, we set up a unified approach for the explanation of topological states in ferroelectrics. We give a comprehensive description of the observed polarization topological structures and show that their rich variety can be exhaustively described by the foundational Arnold theorem in terms of fundamental formations of topological hydrodynamics, vortices, and Hopfions. We outline the prospects of implications of topological hydrodynamics to the physics of ferroelectrics and their diverse applications to the related emergent technologies.

8:45 AM QM04.09.03
Emergent Energy Storage and Conversion in Polar-Topology-Contained Oxide Multilayers Yiqian Liu, Junfu Liu, Ce-Wen Nan and Yuan-Hua Lin; Tsinghua University, China

Polar topologies such as vortices, skyrmions and merons in multilayered ferroelectrics have attracted enormous attention recently as a promising alternative for high-density storage media. However, polar-topology-contained multilayers as ferroelectrics themselves have not been well explored. Herein, using phase-field simulations, we report that polarization hysteresis profiles of these multilayers can be flexibly tailored from ferroelectrics (FE) to relaxor ferroelectrics (RFE), antiferroelectrics (AFE) and paraelectrics (PE), and render potentials to outperform in many ways conventional ferroelectric materials. In bismuth ferrite/strontium titanate trilayers, strain-engineered polar vortices and spirals possess distinct electric coercivity, generating RFE-, AFE- and PE-like behaviors. Ultimately, an ultrahigh energy density of 178 J cm^{-3} with an efficiency of over 95% is achieved. Similarly, simultaneously high energy density and efficiency can be realized in oxide superlattices. These tremendous energy storage performances are owing to the triple-well energy landscape as a result of the extra eigenstate of polar topologies.
In potassium niobate/potassium tantalate oxide superlattices, a continuous FE-AFE-PE phase transition is observed, along with a drastic change in polarization across the AFE-PE boundary. Therefore, an ultrahigh pyroelectric figure of merit of ~10^4 C^2 m^{-4} K^{-2} at an electric field of 2 MV cm^{-1} and an equivalent zT of nearly 6.0 at a temperature difference of 50 K near room temperature. Symmetrically, the inverse effect, electrocaloric cooling, is also remarkable, with a ΔT of nearly 40 K per MV cm^{-1}. This excellent electro-thermal interconversion is caused by the ample polarization profile of polar topologies.
Our findings have indicated that polar-topology-contained multilayers are utilizable in miniaturized energy devices, serving as a possible substitution for RFEs. We hope that our simulations can beget more experimental attempts and realizations.

9:00 AM *QM04.09.04
Ferroelectric Domain Patterns for Brain-Inspired Information Processing Beatriz Noheda; University of Groningen, Netherlands

Ferroelectric thin fims can be engineered to combine several key features of relevance for efficient information processing: they provide non-volatile memory addresasble by electric fields and they self-organize in domain patterns, whose periodicity can be made of the order of nanometers for ultra-thin layers. In addition, in ferroelectric oxides, the domain walls have been often found to be conducting and memristive due to ion migration driven by strain gradients and internal bias field, therefore, showing multistate resistance and synaptic functionality. In addition, these materials can be tuned to exist the verge of a phase transition, by means of chemical composition or epitaxial strain. As shown by Kinouchi and Copelli (Nature Physics 2006), the dynamical range is maximized at non-equilibrium phase transitions and, it is well known that the dynamics of a system slows down by many orders of magnitude near critical points, where the correlation lengths reach the size of the entire system. Therefore, materials that undergo phase transitions are of great interest to achieve the largest sensitivity to input signals, the greatest non-linearities in their responses and, at the same time, the largest variations in the time scales of their output signals, all of these very useful ingreients for efficient learning. Here I will show two examples of ferroelectric systems with domain patterns that show some of these aspects: $BaTiO_3$ films at a boundary between two differently modulated domain phases that show signatures of edge-of-chaos dynamics and $BiFeO_3$ films that provide a dense network of interconnected (conducting) domain walls intersecting memory bits.

9:30 AM QM04.09.05
Observation of Surface Superconductivity in Planar Honeycomb Layer Structured AeCuBi (Ae = Ca and Sr) Nahyun Lee and Sung Wng Kim; Sungkyunkwan University, Korea (the Republic of)

Planar honeycomb layer structured materials have received much attention in the past decades due to their unique physical properties such as massless Dirac state, three-dimensional (3D) topological Dirac semimetal (TDS), thermoelectricity, and superconductivity. In particular, the recently reported 3D TDS KZnBi (space group P6$_3$/*mmc*) showed the surface superconductivity at 0.8 K. Herein, we report the superconductivity of newly synthesized AeCuBi (Ae = Ca and Sr) composed of CuBi planar honeycomb layers, analogous to 3D TDS KZnBi [1]. It is demonstrated from the magnetic susceptibility and heat capacity measurements under ambient pressure, the superconductivity exclusively occurs at the surface region, showing the T_c of 2.1 K for SrCuBi compound. Furthermore, the superconducting transition temperature of the SrCuBi compound was largely enhanced, showing the T_c of 4.8 K at 6.18 GPa. Compared to the high-pressure superconductivity of 3D TDS Cd_3As_2 [2] and KZnBi [3], we found a common feature, which is the linear temperature dependence of the upper critical field, suggesting that the surface superconductivity is of non-s-wave character. Our discovery serves a distinctive platform to study the interplay between 3D TDS and superconductivity, anticipating possible topological superconductivity.

Reference
[1] J. S. Song et al., Phys. Rev. X, 11, 021065 (2021).
[2] He, L. et al., npj Quant. Mater. 1, 1057 (2016).

[3] Unpublished

9:45 AM QM04.09.06
Exploring Topological Insulating Perovskite Oxides Grown on Silicon Substrate Towards Quantum Applications Clement Merckling[1,2], Islam Ahmed[1,2], Luca Ceccon[1,2], Moloud Kaviani[1] and Stefan De Gendt[1]; [1]imec, Belgium; [2]KU Leuven, Belgium

With the slowing down of Moore's law, related to conventional scaling of integrated circuits, alternative technologies will require research effort for pushing the limits of new generations of electronic, photonic and quantum devices. Perovskite oxides with the ABO_3 chemical formula have a very wide range of interesting intrinsic properties such as metal-insulator transition, ferroelectricity, pyroelectricity, piezoelectricity, ferromagnetic and superconductivity. For the integration of such oxides, it is of great interest to combine their properties with traditional electronic, memory and optical devices on the same silicon-based platform.

In this work, we will discuss the use of perovskites oxide in the field of topological based qubits which is one of the promising methods for realizing fault-tolerant computations. It is recognized that superconductor/topological insulator heterostructure interfaces may be a perfect host for the exotic "Majorana" particles. These have relevant topological protection nature as required for processing information. Therefore, the physics at the superconductor/topological insulator heterostructure interface need to be studied further, starting at the material level. In this work, a candidate material Barium Bismuthate (BBO) is studied utilizing the Oxide Molecular Beam Epitaxy (MBE) process. The perovskite structure provides opportunity for easily tailored functionality through substitutional doping. Incorporation of potassium into the lattice of BBO results in a superconducting phase with Curie temperature as high as ~ 30K. In addition, BBO is according to DFT based studies, predicted to form topological surface states when doped with Fluorine. In our work, we integrate BBO perovskite on Si(001) substrate, using an epitaxially grown strontium titanate (STO) single-crystalline buffer layer and discuss the structural and chemical properties of the heterostructure will be established by utilizing physical characterization techniques such as AFM, Raman, XRD, TEM and ARPES in later stages. This will go hand in hand with the understanding of related surface reconstruction of BBO observed by RHEED as a criterion for the high-quality films.

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreements N° 864483 and 742299)".

10:00 AM QM04.09.07
Methods for Characterization of Dislocations in 3 Dimensions Zachary J. Barringer, Edwin Fohtung, Nimish P. Nazirkar, Xiaowen Shi and Skye Williams; Rensselaer Polytechnic Institute, United States

Dislocations are an important class of crystal defects that have a significant impact on the mechanical, chemical, kinetic, and electronic properties of materials. The study of dislocations has historically been rooted in Transmission Electron Microscope based approaches. However, TEM gives limited information about the 3-dimensional nature of dislocations and has strict geometric and experimental constraints on the sample size. To overcome this limitation, other methods of characterization have been employed to probe dislocations in 3 dimensions. In this paper we will review methods used to probe dislocations in 3 dimensions, including both x-ray and electron-based techniques. The applications and limitations of the techniques will be discussed, and some future prospects will be presented. Particular attention will be paid to the ability of techniques to distinguish charged dislocation cores in ionic crystals.

SESSION QM04.10: Virtual Session: Advances in Probing and Realizing Topological Defects in Functional Materials
Session Chairs: Albina Borisevich and Rohan Mishra
Thursday Morning, April 27, 2023
QM04-virtual

10:30 AM *QM04.10.01
Novel Phases and Applications of Ferroelectric Perovskite Oxide Membranes Yuefeng Nie; Nanjing University, China

The synthesis of high-quality freestanding oxide membranes provides unprecedented opportunities for the exploration of novel phases and applications of transition meatal oxides[1,2]. In this talk, I will present the synthesis of freestanding perovskite membranes with high crystalline quality and discuss their great potential electronic applications. By integrating freestanding $PbTiO_3/SrTiO_3$ bilayers with silicon wafer, we obtained high-density skyrmion-like polar nanodomains. Moreover, an external electric field can reversibly switch these nanodomains into the other type of polar texture, which substantially modifies their resistive behaviours[3]. We also explored the ferroelectric size effects in ultrathin $SrTiO_3$ membranes[4] and the integration of conducting charged domain walls of $BaTiO_3$ membranes on silicon wafers[5]. All these new advances demonstrate the great potential of ferroelectric oxide membranes in nonvolatile memory and related electronic applications.

References
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11:00 AM *QM04.10.03
Enhanced or Tailored Superconductivity in 2D Materials via Ionic Liquid Cation Intercalation Shuyun Zhou; Tsinghua University, China

Dimensionality and carrier concentration have been two most important control knobs for engineering the electronic properties of layered materials and inducing novel properties. So far, the control of the interlayer interaction is mainly achieved by reducing the sample thickness to atomic scale, however, such atomically thin samples are usually difficult to obtain, unstable in air and with extremely low T_c. In this talk, I will report our recent experimental progress to control both the interlayer coupling and carrier concentration in layered materials through intercalation of organic cations from ionic liquids to transition metal dichalcogenides. The intercalated organic-inorganic hybrid materials exhibit tailored properties beyond the bulk crystals and monolayer films. I will provide a few examples for enhanced or tailored superconductivity in topological semimetals $MoTe_2$ and WTe_2 [1,2], semiconducting $SnSe_2$

[3] and $NbSe_2$ [4].

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11:30 AM *QM04.02.01
From Bound to Topological Charges in Ferroelectric Flatlands Sergei Prokhorenko, Yousra Nahas and Laurent Bellaiche; University of Arkansas, United States

Ultra-thin ferroelectrics represent a paradigmatic materials platform for realizing nontrivial polar topologies. Owing to strong electrostatic interactions, the local electric dipoles in these systems are oftentimes forced to adopt swirling configurations in order maintain the right balance of bound charges both within the material and at its interfaces. As a result, one observes formation of such topological defects as electric vortex tubes and polar disclinations or skyrmion-like bubble solitons.

While sharing many similarities with their magnetic counterparts, these polar states have a fundamentally different, *electric*, nature which opens new opportunities to control ferroelectric topologies but also poses a question of their possible technological applications. Here, we explore these questions using effective Hamiltonian simulations of ultra-thin $Pb(Zr,Ti)O_3$ films under residual depolarizing fields. On the one hand, our results reveal how the screening and local electric fields can be tuned to induce topological transitions and control the dynamical behavior of polar topological defects and solitons. On the other hand, we inquire into the role of bound electric charges intrinsically associated with polar disclinations and bubbles. Namely, we explore the effect of such charges on interactions between electric topological defects and discuss possible implications of such charge on functional properties of polar topologies.

Research supported by the Vannevar Bush Faculty Fellowship Grant No. N00014-20-1-2834 from the Department of Defense.

SYMPOSIUM

April 13 - April 25, 2023

Symposium Organizers
Marie-Eve Aubin-Tam, TU Delft
Maneesh Gupta, U.S. Air Force Research Laboratory
Srikanth Singamaneni, Washington University
Taylor Ware, Texas A&M University

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* Invited Paper
\+ Distinguished Invited

SESSION SB01.01: Session I
Session Chairs: Marie-Eve Aubin-Tam and Srikanth Singamaneni
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2012

9:00 AM *SB01.01.01
Polymer Platforms for 3D Printing Engineered Living Materials Alshakim Nelson; University of Washington, United States

The convergence of synthetic biology with polymer science has led to the rapid emergence of engineered living materials (ELMs), which are composite materials of engineered cells encapsulated within a polymeric matrix. ELMs have the potential to attain a level of precision, control, and sustainability that is not achieved with traditional abiotic materials. While the minimum requirements for fully living ELMs are cell viability and metabolic activity, the integration of ELMs at their fullest potential in future biomanufacturing also requires processing into desired form factors and spatial control over multiple engineered cell populations.
Additive manufacturing (or 3D printing) has re-emerged into the spotlight in the last 10 years driven by the rapid progress in hardware and software. While off-the-shelf polymeric materials have been utilized as inks and resins for additive manufacturing, there is still a need to develop functional materials that are specifically designed for these processes. In this seminar, I will present two different polymer platforms that we have developed to 3D print ELMs. In the first part of my seminar, I will discuss the development of stimuli-responsive triblock copolymer hydrogels for fabricating immobilized cell bioreactors.

These hydrogels were used to incorporate engineered microbes that served as cellular factories for the on-demand bio-production of chemical products. In the second part of my seminar, I will discuss a two-step additive manufacturing process to fabricate protein-based constructs using a commercially available laser-scanning SLA printer. Methacrylated bovine serum albumin (MA-BSA) was synthesized and formulated into aqueous resins that was used to print complex 3D geometrical constructs with a resolution comparable to a commercially available resin. Compression studies of hydrated and dehydrated constructs demonstrated a broad range of compressive strengths and Young's moduli that could be further modulated by adjusting the type and amount of co-monomer. These protein-based matrices served as biodegradable scaffolds for 3D printing ELMs, and I will present strategies for fabricating bio-augmented and bio-sustained ELMs.

9:30 AM SB01.01.02
Optimizing *Sporosarcina pasteurii* Biology and Growth for Shelf-Stable Preparations for Biocement Applications Michael Carter, Matthew J. Tuttle, Adriana Joson, Joshua Mancini, Rhett L. Martineau, Chia-Suei Hung and Maneesh Gupta; Air Force Research Lab, United States

Contemporary concrete production, which accounts for ~8% of the world's CO_2 production, relies on Portland cement to bind aggregates. Biocement is an environmentally friendly material that relies on biological structures (enzymes, cells, and/or cellular superstructures) and/or biologically generated structures ($CaCO_3$ crystals) to bind aggregates. Current biocementation protocols require addition of living cultures to aggregates, which requires on-site culturing expertise and infrastructure. We have developed a strategy for producing a shelf-stable preparation of *Sporosarcina pasteurii*, a biocementation workhorse bacterium, that can be combined on-site with feedstocks and aggregates to form biocement. Scaling up and enhancing the efficacy of our novel biocementation protocol will require optimization of *S. pasteurii* growth and biology. Here, we discuss our progress toward improving the growth and biology of *S. pasteurii*, an alkaliphile with distinct nitrogen requirements, and our progress toward understanding relevant physiological characteristics of *S. pasteurii*.

9:45 AM SB01.03.08
Tailoring the Growth of Living Materials Towards Sustainable Manufacturing Suitu Wang, Manivannan Sivaperuman Kalairaj, Mustafa Abdelrahman and Taylor H. Ware; Texas A&M University, United States

Traditional manufacturing of polymer composites relies on valuable precursors derived from fossil fuels and energy-intensive processes. Innovation in polymer composites manufacturing strategies should focus on resource recyclability and low carbon footprint procedures. Here, a new paradigm of polymer composite manufacturing valorizing local wastes and using biological growth of living materials to dictate the final product form has been proposed. Living materials comprised of living *Saccharomyces cerevisiae* (baker's yeast) within a hydrogel matrix cultured in media derived from bread waste can achieve volume and mass increase through in-situ cell proliferation. The final object shape can be tailored through controlled growth of living materials. For example, by digitally programming the cell viability through UV irradiation or photodynamic inactivation, growth-induced shape control can be achieved. This growth-dictated manufacturing process can be powered by wasted chemical energy present in substances such as food waste, which stands in stark contrast to the energy-intensive processes used for synthetic material manufacturing. After growth, the final material is up to 96 wt% biomass and 590% larger in volume than the initial object. Subsequent enzymatic hydrolysis and regeneration of yeast cell walls within the grown structures enable shape reconfiguration. The proposed biomanufacturing strategy utilizing the growth of living materials with food waste may pave the way for future ecologically friendly manufacturing of materials.

10:00 AM SB01.01.03
Iridescent Biofilms of Bacteria: Versatile Platforms for Functional Materials Claretta J. Sullivan; AFRL/RXA, United States

Abstract not available.

SESSION SB01.02: Session II
Session Chairs: Rhett Martineau and Srikanth Singamaneni
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2012

1:30 PM *SB01.02.01
From Bones to Stones—Towards Surmounting Challenges in Designing Engineering Living Building Materials Chelsea Heveran; Montana State University, United States

Microbial induced calcium carbonate precipitation (MICP) is commonly used to seal cracks, stabilize soils, and sequester contaminants. Increasingly, MICP is used to engineer living building materials. These biomineralized structures have the potential for greater functionality and sustainability than conventional building materials. However, several challenges persist in efficiently and precisely manufacturing these biomineralized materials and in keeping the living component alive for a prolonged time. We look to bone, which maintains living cells within a load-bearing stiff matrix for decades, as an inspiration for surmounting these obstacles. Bone tissue is strong, tough, and lightweight, and both self-assembles and self-repairs at body temperatures. Bone achieves these remarkable properties through scaffolds secreted by bone cells that dictate where, when, and how the structure is biomineralized. We are working towards engineering biomineralized building materials that utilize several strategies inspired by bone. In this talk, we will focus on several bone-inspired scaffolding approaches that influence bacterial biomineralization. In a first strategy, we functionalize aggregate surfaces to form a bacterial monolayer that scaffolds the initial biomineralization and improves the efficiency of strength development. In a second strategy, we use fungal mycelium as a scaffold for biomineralization. These scaffolds are either self-mineralized by the living mycelium or mineralized by bacteria that attach to the scaffold surface. Finally, we will explore ongoing efforts and next steps in producing bone-inspired sustainable living building materials.

2:00 PM SB01.02.02
Production of Biocement Using a Shelf-Stable Formulation of the Soil Bacterium *Sporosarcina pasteurii* at Laboratory and Field-Scales for Ground Improvement Matthew J. Tuttle[1,2], Brandon M. Bradow[1,2], Rhett L. Martineau[1], Michael Carter[1,2], Joshua Mancini[1,2], Chia-Suei Hung[1] and Maneesh Gupta[1]; [1]Air Force Research Laboratory, United States; [2]UES, Inc., United States

Manufacturing of traditional cementitious materials is an energy-intensive and unsustainable process. Cement is the third largest source of anthropogenic carbon dioxide emissions globally, accounting for an estimated 8% of emissions. To help mitigate the environmental impacts of cement and concrete, more environmentally-friendly materials are needed. Biocement shares many similar physical properties with traditional cement and may be useful as an alternative material for a variety of applications in construction and the development of infrastructure. It is produced via microbially-induced biomineralization of calcite. *Sporosarcina pasteurii* is a soil bacterium that has emerged as the model organism for biocement production. While there has been considerable interest in biocement as a green material, producing it at industrial scales is challenging and there is a lack of ready-mix formulas similar to those that exist for traditional cement. Here we developed a shelf-stable preparation of *S. pasteurii* that has been preserved via lyophilization. At the laboratory-scale, we see that this formulation performs similarly to live cell cultures, precipitating an equivalent amount of calcite and resulting in biocement with the same level of mechanical strength. We further demonstrate the applicability of this formulation at precipitating calcite under non-ideal conditions in the field, leading to *in situ* production of biocement with increased bearing capacity of the ground. The strength and depth of cementation achieved using this formulation can be modulated by altering the treatment regime used in biocement production. Altogether, these results indicate that stabilized preparations of bacteria are a viable means by which biocement may be manufactured. This is advantageous as it has the potential to be used as a ready-mix formula for the creation of biocement that is accessible to nontechnical professionals. Shelf-stable formulas such as this will make the process of biocement production easier, paving the way for more widespread adoption of biocement as a construction material as the technology surrounding it continues to mature.

2:15 PM SB01.02.03
Multiplex Genome Editing in Diatoms for Sustainable Production of Designer Mesoporous Silica Jernej Turnsek[1,1] and Krishna K. Niyogi[1,1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Evolutionary and ecological success of diatoms—ubiquitously distributed photosynthetic single-celled algae and dominant primary producers in the contemporary ocean—has been attributed to their silica-based cell wall called a frustule. Diatoms exhibit a dazzling variety of frustule morphologies. How they construct this ornate organic-inorganic hybrid material at mild temperatures and pressures is a fascinating question, a bridge between nanoscale and planetary scale biological and geological processes. Additionally, the biocompatibility and hierarchical mesoporous structure of naturally produced diatom silica represents a basis for applications in drug delivery, biosensing, industrial catalysis, energy storage, and bioremediation.

To advance our understanding of diatom cell wall biogenesis and to facilitate our ability to control diatom silica morphogenesis, we implemented a straightforward multiplex genome editing technique in the model marine diatom *Thalassiosira pseudonana*. We first present successful use of bacterial conjugation as an emerging genetic transformation method in *T. pseudonana*. We then describe SpCas9- and tRNA-gRNA array-expressing vectors for bacterial conjugation-based multiplex genome editing. Here, a single transcript, which is processed into sgRNAs by endogenous tRNA nucleases, can be scaled to simultaneously target any number of loci. We applied this molecular engineering system to edit a nitrogen and silicon metabolism-related urease-encoding gene in *Thalassiosira pseudonana*, which led to a clean genome excision event. Finally, we show that urease-deficient *T. pseudonana* cell lines cannot grow on urea as the sole nitrogen source and discuss our strategy to simultaneously edit two *T. pseudonana* genes.

Facile multiplex genome editing gives fresh momentum to studying molecular mechanisms of complex multigene metabolic processes in diatoms such as cell wall biogenesis. It paves the way for new biomedical, industrial, and environmental diatom-based applications rooted in tuning silica properties and structure (e.g., pore size) via precise targeted genome manipulations.

2:30 PM BREAK

3:30 PM *SB01.02.04
Improving Engineering Resilience and Sustainability with Engineered Living Materials Qiming Wang; University Southern California, United States

Modern society demands engineering materials with high resilience and sustainability; however, most of the existing engineering materials exhibit undesirable resilience and sustainability. For example, typical materials used in the urban infrastructure are continuously aging and failing under environmental hazards (www.engineeringchallenges.org/challenges/infrastructure.aspx). Most of the widely-used commodity plastics feature extremely low biodegradability, leading to a long-standing sustainability issue. On the other hand, biological living materials naturally exhibit extraordinary resilience and sustainability. For example, biological living materials consist of living cells to support their metabolisms, thus enabling self-growing, self-remodeling, self-healing, and self-strengthening in response to environmental hazards. Biological living materials typically feature rapid biodegradation, without leaving environmental pollution. In this talk, we present a strategy by integrating living components, such as living microorganisms and plants, into traditional engineering materials to design several types of engineered living materials. The vision is that these engineered living materials will differ from traditional engineering materials, but behave like biological living materials to enable extraordinarily high resilience and sustainability in response to environmental hazards. For example, assisted by living bacteria, 3D-printed polymers can self-grow into structural composites with extremely high toughness like shells. Assisted by living chloroplasts, 3D-printed polymers can behave like a tree to harness carbon dioxide to enable photosynthesis for self-remodeling and self-strengthening. Assisted by living microorganisms, commodity plastic waste can be upcycled into a class of new materials that feature full recyclability and giant energy generation.

4:00 PM *SB01.02.05
DIY 3D Printing of Complex Living Materials for Degrading Bioplastic Anne S. Meyer; University of Rochester, United States

3D printing of engineered bacteria is an evolving field that employs the tools of synthetic biology to express desired proteins and peptides while maintaining control over the shape and spatial organization of the resultant biomaterials. Previous bacterial 3D printers have been limited to producing low aspect ratio prints that become unstable and collapse under their own weight at greater heights. By leveraging open-source hardware and software, we have designed and modified a low-cost, commercial 3D printer into a bacterial bioprinter that can print complex, free-standing structures with high aspect ratios. To print complex structures with sharply defined edges, a novel syringe mount was designed with retraction functionality that pauses bio-ink extrusion during non-printing periods. Our new printer deposits bio-ink within gel slurries with viscoplastic properties, allowing delivery of bio-ink gellification agents immediately upon printing. This technique allows us to print stable, high aspect ratio (15:1), free-standing structures with sharper resolutions and internal cavities. We have applied our 3D bacteria printers to construct living materials containing marine microbes that can metabolize the bioplastic poly-3-hydroxybutyrate (PHB). These printed materials can act as living stickers that degrade bioplastics in oceanic conditions, a notoriously difficult environment for carrying out plastic biodegradation. These materials will pioneer a new way of thinking about material design by explicitly incorporating microbial metabolism and degradability at the outset, with potential to transform the plastics industry as a whole.

4:30 PM SB01.02.06
Towards the Development of Engineered Living Carbon Materials Monsur Islam[1], Mohammadreza Taale[2], Jan G. Korvink[1], Christine Selhuber-Unkel[2] and Andrés D. Lantada[3]; [1]Karlsruhe Institute of Technology, Germany; [2]Universität Heidelberg, Germany; [3]Universidad Politécnica de Madrid, Spain

Engineered living materials (ELMs) is considered to be one of the most relevant contemporary revolutions in the field of materials science. ELMs aim to outperform current examples of “smart”, active, or multifunctional materials, enabling countless industrial and societal applications [1]. Current examples of ELMs have mostly focused on either cell-derived biofilms or polymer-based hybrid living materials (HLMs) [2]. Here we postulate carbon as an ideal material for the abiotic counterpart in an HLM system due to its unique properties, including excellent biocompatibility, adjusted electromechanical properties, and tunable electrochemical properties [3]. 3D printing of carbon structures allows the fabrication of customizable geometrical features, which can further facilitate the printing of shape-morphing carbon structures, leading to 4D architectures. Upon culturing living cells, 3D and 4D carbon structures can work synergically with the cells to express novel functionalities, which can be highly important for several biomedical and biotechnological applications. Here, we aim to develop a hybrid living carbon material by integrating a novel 4D printing approach for glassy carbon and the self-beating properties of living muscle cells.

To date, we have demonstrated the capability of fabricating 4D printed glassy carbon and their capability to host muscle cells leading to improved proliferation and differentiation. Here, 4D printing refers to the shape-morphing capabilities of a 3D printed structure. The 4D printing of glassy carbon included 3D printing of unique mechanically shape-morphing precursor epoxy structures using laser microstereolithography, followed by carbonization at 900°C in an argon environment. Upon pyrolysis, 60-75% geometrical shrinkage of individual microlattices occurred, leading to even smaller features. For example, a printed lattice diameter of 100 µm shrank to ~35 µm after carbonization. The shape-morphing capability of the structures was retained despite such significant shrinkage. C2C12 myoblast cells were cultured on the 3D/4D printed carbon structures to investigate the biocompatibility of the carbon scaffolds. The cells adhered to the carbon scaffold and populated within the pores between adjacent lattices, leading to 3D cell colonization. Furthermore, the cultured myoblast cells fused to myotubes on the carbon scaffolds after 14 days. This is highly promising as the presence of myotubes suggests the possibility of the beating motion of the cells on carbon scaffolds. Our current efforts are towards synergizing the beating movement of the cells on the 4D carbon scaffolds leading to a stimuli-responsive motion of the biohybrid structures, the genesis of a novel family of living carbon materials.

References:

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4:45 PM SB01.02.07

Pattern Formation and Stability of Algae-Laden Hydrogels due to Differential Growth Nakhiah Goulbourne; University of Michigan, United States

There is an emerging class of engineered living materials that can grow, self-heal, sense, and adapt to their surroundings similar to biological organisms. Recent reports have repeatably demonstrated successful 3D printing of hydrogels containing microorganisms, such as, algae, yeast, and bacteria. The 3D printed living materials support growth once manufactured. Growth within a hydrogel matrix can generate stress due to interactions of the living matter with the surrounding nonliving matter. These stresses can induce shape instabilities in the growing medium. The changes in the 3-dimensional shapes will vary depending on the morphology and composition of the hydrogel, and the morphology of the living material. We seek to gain mechanistic insights into the pattern formation and stability of algae-laden hydrogels. To gain better insight into growth-induced instabilities due to algae-hydrogel interactions, we study the growth of an elastic shell embedded in a soft elastic medium. The contact stress from the hydrogel interaction is calculated as a function of geometric and growth parameters. We obtain critical values for instabilities and the modes of instability.

SESSION SB01.03: Session III: Poster Session
Session Chairs: Marie-Eve Aubin-Tam and Srikanth Singamaneni
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SB01.03.02

Tissue-Attachable Intestinal Organoids as Injectable Therapeutics for Reconstruction of Intestinal Injuries Myeong Jae Baek, Min Beom Kim and Yun Kee Jo; Kyungpook National University, Korea (the Republic of)

Crohn's disease, a type of inflammatory bowel disease, can often lead to loss of intestinal function due to impaired intestinal barrier performance and exposure to noxious antigens that cause chronic inflammation. Organoids transplantation has emerged as a promising strategy for restoration of the damaged intestinal epithelial barrier in treating several intestinal diseases. However, most organoids culture commonly relies on the use of an ill-defined tumor-derived basement membrane extract, Matrigel, which restricts practical applications to transplantation with aim of regenerating tissues *in vivo*. Here, we develop tissue-adhesive hyaluronic acid (HA) hydrogels for generation and *in vivo* transplantation of intestinal organoids as an alternative substitute to Matrigel. The morphological and functional features of intestinal organoids cultured in the well-defined, biocompatible HA hydrogels are comparable to those in Matrigel by providing extracellular matrix-mimetic microenvironments. Moreover, superior tissue-adhesion ability of catechol-functionalized HA facilitates their use in transplantation of intestinal organoids to target tissues even under wet conditions. These results suggest the possiblity of only a single hydrogel in generating and transplanting intestinal organoids to accomplish an effective recovery of small intestinal wounds. Therefore, our chemically-defined, tissue-adhesive HA hydrogels can be a novel, simple therapeutic platform for organoids-based regeneration of intestinal injuries with further expansion to general tissue recovery.

5:00 PM SB01.03.03

Tissue Extracellular Matrix-based Microribbon Scaffolds for Bone Regeneration via Immunomodulation Cassandra Villicana, Andrew Yang, Ni Su, Xinming Tong and Fan Yang; Stanford University, United States

Introduction: The immune system plays a critical role in bone regeneration as the mediator of the body's inflammatory response to injury. Previous biomaterials research on bone tissue engineering has largely focused on enhancing stem cell osteogenesis rather than modulating immune cell responses. Tissue-derived extracellular matrix (ECM) has been used in nanoporous hydrogels and demonstrated advantages over synthetic hydrogels in promoting regenerative immune responses when injected in muscle [1]. However, previous tissue ECM-based research has been limited to soft tissue models and nanoporous hydrogels. How ECM modulates immune cell response and bone regeneration in macroporous scaffolds have not been investigated before. Our lab has reported gelatin microribbon (µRB) scaffolds that contain macroporosity and enhance endogenous bone regeneration *in vivo* compared to nanoporous gelatin hydrogels [2]. We hypothesize that incorporating ECM into µRB scaffolds would modulate immune responses and bone regeneration. To test this hypothesis, the present study seeks to develop µRB scaffolds containing tissue-derived ECM, and assess the effect of varying ECM dosage and tissue type on immunomodulation and bone regeneration *in vitro* and *in vivo*.

Materials and Methods: To derive ECM from multiple tissue types (bone, muscle, articular cartilage, and meniscus cartilage), juvenile bovine stifles were used. Bone was first demineralized, and all tissues were decellularized and digested following previous protocols. Gelatin µRBs were synthesized by wet spinning as we previously reported [2]. To incorporate ECM, two methods were evaluated including co-spinning a mixture of bone ECM (bECM) containing gelatin solution, or coating ECM from various tissue types onto gelatin µRBs through physical adsorption. To characterize ECM incorporation, immunostaining of various tissue markers was performed. For *in vitro* studies, mouse MSCs or macrophages were encapsulated in µRB scaffolds with varying ECM dosages or tissue types. To assess immunomodulation, macrophage phenotype was assessed using gene expression and ELISA. MSC osteogenesis was assessed using histology of bECM markers. Leading compositions that led to regenerative immune responses and enhanced osteogenesis were further validated *in vivo* using a mouse critical size cranial defect model. Samples were harvested at weeks 1 and 6. Immunomodulation and bone formation *in vivo* were assessed using histology and microCT imaging.

Results and Discussion: Immunostaining confirmed both co-spinning and coating methods enable successful incorporation of tissue ECM into macroporous µRB scaffolds. The coating method induces more homogenous ECM presentation relative to the co-spinning method. Incorporating bECM promotes macrophage polarization towards the regenerative M2 phenotype while promoting MSC osteogenesis in a dose-dependent manner *in vitro*. We found intermediate bECM concentration led to enhanced MSC osteogenesis, yet further increase of bECM inhibited osteogenesis. Adding tricalcium phosphate particles synergized with a low dosage of bECM to accelerate bone formation *in vivo*. Varying tissue ECM further enhances MSC osteogenesis *in vitro*, with the most mineralized bone formation found in meniscus cartilage and muscle-derived ECM-coated groups. Together, these results support our hypothesis, and future studies will evaluate the effect of varying ECM type on immunomodulation *in vitro* and bone formation *in vivo*. While the present study focuses on bone as a target tissue for regeneration, the ECM-coated macroporous µRB scaffolds may be broadly applied to enhance regeneration of other tissue types.

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5:00 PM SB01.03.04
Sensory Artificial Octopus Suckers with Highly Adaptive Soft Micro-Denticles Gui Won Hwang[1], Heon Joon Lee[1], Sangyul Baik[1], Da Wan Kim[1], Tae-Heon Yang[2] and Changhyun Pang[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Korea National University of Transportation, Korea (the Republic of)

Geometric and material adhesion mechanisms inspired by natural organisms have been shown to be effective and useful by providing adaptive switchable adhesion and versatile applications. Several biologically inspired devices with high adaptability and robust dry and wet adhesion have been reported. However, it is still difficult to achieve stable and switchable attachments to objects with curved, rough, and irregular surfaces, especially in dry and aquatic environments. Here, an electronically sensory switchable adhesive device with an adaptable soft microstructure inspired by the geometric and material properties of micro-denticles on the surface of an octopus sucker is presented. The contact interface of artificial octopus suckers (AOS) is imprinted with soft micro-denticles that interact appropriately with very rough or curved surfaces. AOS with soft micro-denticles (AOS-sm) provides strong and controllable attachment to dry and wet surfaces of various shapes and conformal attachment to highly rough curves and soft objects. The carbon nanotube-based strain sensor with a three-dimensional structure formed to mimic nerves-like functions of an octopus in the AOS architecture does decision-making capabilities to predict the weight and center of gravity for samples with diverse shapes, sizes, and mechanical properties through machine learning. Also assembled with octopus-arm-inspired soft actuators, the AOS-sms reliably grips and transports complex polyhedrons, rough objects, and soft, delicate, and slippery biological samples.

5:00 PM SB01.03.05
Graphically-Encoded Biodegradable Microspheres with Hydrogel Shell for Sustained Release of Drugs at Controlled Rates Yoonjin Oh and Shin-Hyun Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Biodegradable microparticles have been widely used as an efficient drug delivery platform. Several biocompatible and biodegradable polymers, including polylactic acid (PLA), poly(lactic-co-glycolic acid) (PLGA), and polycaprolactone (PCL), have been used as matrix materials to encapsulate lipophilic drugs and control their release. To create microparticles containing the drugs, polymers are dissolved in a volatile organic solvent in conjunction with drugs, then emulsified and consolidated. Lipophilic drugs are released from the microparticles over a sustained period of time. As the polymer matrices biodegrade from the surface by the hydrolysis of ester groups in the backbones of the polymers, the microparticles impede an initial burst of drugs which can exert damaging effects on the biological integrity of the protein.

These microparticles are generally in the form of oil-in-water emulsion templated microbeads. When the polymeric microbeads are implanted into tissue, however, the surfaces can undergo uneven degradation and the rate of drug release will vary particle by particle. It deteriorates the controllability over a consistent rate of release.

Here, we microfluidically produce PLA microspheres enclosed by a hydrogel shell for sustained release at controlled rates. As the PLA microspheres do not directly contact with other microspheres due to the presence of the hydrogel shell, it reduces particle-by-particle variation regarding the degradation rate. Also, the hydrogel shell slows down the release rate as the degradation of the PLA core proceeds only by slow diffusion through the hydrogel shell. In this regard, we control the density of the hydrogel shell to elaborately alter the degradation rate of PLA. As the density of the hydrogel shell increases, the rate of degradation decreases so that the encapsulants can be released for an extended period of time. Therefore, the release rate can be adjusted to suit the type and dose of the drugs. To distinguish each microsphere with a different concentration of encapsulants and shell density, we graphically encode the PLA microspheres with different types of photolithographically featured SU-8 particles. These particles work as an indicator to readily recognize the content of the PLA microspheres and the release behavior of the drugs with the naked eye.

Using a glass capillary microfluidic device, monodisperse oil-in-water-in-oil (O/W/O) double-emulsion droplets are produced. PLA and alpha-tocopherol (aTOC), which is an antioxidant that supports the immune system and reduces the risk of blood clots, are dissolved in toluene and used as the innermost phase of double-emulsion droplets. As the toluene evaporates completely, PLA is consolidated to form a solid microsphere. To enclose the PLA microspheres with a hydrogel, an aqueous solution of biocompatible sodium alginate and a complex of calcium-ethylenediaminetetraacetic acid (Ca-EDTA) is used as the middle water phase. When the double-emulsion droplets are collected in the mineral oil containing acetic acid, alginate is crosslinked by calcium ions dissociated from the Ca-EDTA complexes, forming the hydrogel shell. To further crosslink the alginate gel and make the hydrogel shell denser, the microcapsules are transferred to an aqueous solution of calcium chloride which can provide additional calcium ions to the alginate chains.

We disperse different types of alphabet-shaped SU-8 particles in the innermost phase depending on the concentration of aTOC in the core and calcium chloride in the aqueous medium. For example, the microcapsules containing 1, 5, and 10 w/w% of aTOC in the core are encoded with ‘a’, ‘b’ and ‘c’ particles, respectively. When the microcapsules are transferred to 0, 20, 50 w/w% of aqueous calcium chloride solutions, they are encoded with ‘A’, ‘B’ and ‘C’ particles. Therefore, we can easily and precisely differentiate the composition and release rate of each microcapsule even if they are all mixed.

5:00 PM SB01.03.06
Nutrient Transport for Increasing the Active Lifespan of Engineered Living Materials Ellen van Wijngaarden and Christopher Hernandez; Cornell University, United States

Engineered living materials (ELMs) are materials synthesized and/or populated by living cells. While early examples of ELMs have been promising, prior demonstrations have a short service life, often single use, due to the limited lifespan of resident cells. To replace traditional engineering materials that require longer service lives, methods of maintaining the viability of resident cells inside the ELM are needed.

Bone is a living material in which resident cells survive for decades, receiving nutrients through micro-scale pores networks, connected to one another and free surfaces by nanoscale channels. Cyclic mechanical loading applied to bones causes deformations of the pores, forcing fluid through the connecting channels and back, thereby allowing for transport and mixing even when there is no net fluid transport through the pore network [1-3]. Nutrient delivery through this mechanism has so far only been examined for the pore geometries specific to bone. Here we perform an analysis to identify pore/channel network geometries that allow for nutrient distribution. The microfluidic pore networks (0.05 -1 mm) were modelled and analyzed via hydraulic circuit simulations and fluid flow modelling using COMSOL.

In the absence of cyclic loading, transport to peripheral pore networks is negligible and limited to diffusion. In contrast, cyclic mechanical loading, results in volumetric strain in the network, causing fluid mixing in the material pores, allowing for transport far exceeding that achieved through diffusion. The fluid displacement through the channels during a loading cycle is determined as: $D = \sigma V / BnA$, where D is the fluid displacement, σ is the stress applied to the material, V is the undeformed pore volume, B is the material bulk modulus, n is the number of connecting channels and A is the cross-sectional area of a single channel. To achieve any nutrient transport, the value of must exceed the length of the channel so that upon unloading, nutrients are transported from one pore to the next. Increasing the loading magnitude resulted in greater volumetric strain and more solute transport per cycle. Higher loading frequencies resulted in decreased transport by limiting the time for fluid to flow through channels. The effects of applying a cyclic pressure, sufficient to induce deformation within the material pores and channels, was also investigated. The cyclic fluid pressure results in volumetric strain within the porous network similar to mechanical loading. However, lower solute transport was observed for pores further from the source channel during cyclic flow, relative to cyclic mechanical loading.

Maintaining the viability of resident cells is the key challenge to applications of engineered living materials beyond single use. Here we demonstrate that regular mechanical stress and strain has the potential to extend the viability of living cells within an ELM.

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5:00 PM SB01.03.09
Enhancing Microbially-Induced Calcite Precipitation (MICP) Using Protein and Peptide Additives Joshua Mancini[1,2], Matthew J. Tuttle[1,2], Brandon M. Bradow[2], Rhett L. Martineau[1], Karen A. Holley[2], Michael Carter[1,2], Chia-Suei Hung[1] and Maneesh Gupta[1]; [1]Air Force Research Lab, United States; [2]Biological and Nanoscale Technologies Division, UES Inc, United States

Sporosarcina pasteurii is a soil bacterium capable of cementing soils using an enzymatic reaction that hydrolyzes urea into ammonium and bicarbonate ions. The elevated pH caused by ammonia accumulation causes calcium ions to interact with carbonate to form a crystalline precipitate (calcite). These crystals can form bridges between soil particles, resulting in high-strength biocement. This processes is known as microbially induced calcite precipitation (MICP). Cementation by S. pasteurii in this manner shows promise for the erection of cemented structures in an environmentally-friendly, non-energy-intensive manner. Features of the cementation process include an aqueous reaction environment and harnessing of microbial activity from native soil microbes. At the Air Force Research Laboratory, we are employing microbial and protein engineering strategies to enhance MICP for the production of biocements. This presentation details our efforts using recombinant proteins to assist with calcite nucleation and promotion of desirable crystal morphology to reduce the amount of urea required and to improve the mechanical properties of the material.

5:00 PM SB01.03.10
Controlling Shape Morphing and Cell Release in Engineered Living Materials Laura Rivera Tarazona[1], Manivannan Sivaperuman Kalairaj[1], Tyler Corazao[1], Mahjabeen Javed[1], Philippe Zimmern[2], Sargurunathan Subashchandrabose[3] and Taylor H. Ware[1,1]; [1]Texas A&M University, United States; [2]The University of Texas Southwestern Medical Center, United States; [3]Texas A&M College of Veterinary Medicine & Biomedical Sciences, United States

Engineered living materials (ELMs) are a class of materials that incorporate living organisms into biomaterial matrices to derive functions from both living and non-living components. By combining and tuning the properties of both living and non-living components, desired functionalities can be achieved for biosensing, therapeutic, self-healing, and shape-morphing applications. Here, we introduce a method to control the delivery of bacteria from ELMs by varying the cell loadings and matrix stiffnesses. Controlling the long-term delivery of bacteria could potentially be used in biomedical applications to modulate microbial communities within the human body. We fabricate ELMs by encapsulating *E. coli* DH5α within a non-degradable crosslinked acrylic hydrogel matrix. Growing these ELMs for 1-day results in a volume change of >100%, due to cell proliferation. The forces that drive these shape changes can also release the cells found on or near the surface of the ELMs to the surrounding growth media. When the ELM was introduced to fresh growth media every 24 h for 10 days, the ELM was able to release ~10^4 colony forming units / mL to the surrounding media within 30 min. Finally, with controlled cell delivery from ELMs, we demonstrated a potential therapeutic material by releasing a probiotic *E. coli*, asymptomatic bacteriuria (ABU 83972), which could then modulate the proliferation of a uropathogenic E. coli strain, CFT073, *in vitro*. The ELMs will also be implanted in the urinary bladder of a mouse model and the therapeutic performance will be studied.

5:00 PM SB01.03.11
Manufacturing a Three-Dimensional Bioprinted and Oriented Electrospinning Dual-Scale Scaffold to Promote Cellular Alignment and Enhance Structural Elasticity for Muscular Functioning Evan Fair, Elizabeth Ricci, Eliza Hogan, Ryan jaworski, Naser Haghbin, Isaac Macwan and Shelley Phelan; Fairfield University, United States

Every day, at least 22 people pass away while waiting for a vital organ donation. Biomanufacturing artificial organs have the potential to address the organ scarcity crisis and save lives. This study investigates muscle tissue engineering by combining 3D bioprinting and electrospinning methods to create a dual-scale scaffold (a porous block of 10 mm × 10 mm × 3.5 mm). The dual-scale scaffold contains multiple layers of 3D bioprinted microstructures and an integrated polycaprolactone (PCL) electrospun nanofiber matrix. The most significant limitation of using 3D-printed scaffolds relates to the ineffectiveness of cellular elongation resulting in resistance to the adsorption of muscle bundles. Synthetic nanofibers used in this study have the potential to influence the alignment of the cells in a specific direction, which improves the effectiveness of holistic muscle functioning through cooperative contraction and relaxation of the muscle cells. The 3D bioprinted microstructures serve as a gap collector and a flexible structure to allow extension and contraction of the cellular structure. Electrospun nanofibers form aligned mesh networks within the 3D printed scaffold's pores and are deposited perpendicular to the direction of the 3D bioprinted scaffold layer lines. The three-dimensional dual scaffold will be manufactured, characterized, sterilized, and then used as a scaffold for muscle cell culturing. The attachment, growth, viability, proliferation, and alignment of muscle cells are examined using fluorescence microscopy, scanning electron microscopy, and cellular assays to verify these characteristics.

5:00 PM SB01.03.12
3D Bioprinting Human Blood Vessel Using a Collagen Bioink to Optimize Growth Conditions of Two Primary Cell Lines of HUVEC and HASMC
Alana Hayes, Grace Lombardi, Elia Haghbin, Elizabeth Ricci, Eliza Hogan, Naser Haghbin, Isaac Macwan and Shelley Phelan; Fairfield University, United States

Traditional vein grafts are a complicated surgery as doctors should deeply cut a patient's legs and neck to harvest a vein, which puts patients at risk of additional traumatic surgery. Therefore, creating a personalized vein using their body cells is essential. This research will create a simulated blood vein using collagen bioink as a scaffold for cell growth. Collagen (i.e., an abundant protein) is the main structural element of the Extracellular Matrix (ECM) found in the vessel wall. Collagen provides a support structure with a tensile strength that controls the cell growth direction as cells adhere and elongate. Our preliminary study showed collagen bioink does not lose its structural integrity when submerged in DMEM (Dulbecco′s Modified Eagle′s Medium) cell media. Human umbilical vein endothelial cells (HUVEC) and Human Aortic Smooth Muscle Cells (HASMC) are two primary cell lines used in blood vessel research. The HUVEC and HASMC will be co-cultured, mixed with collagen-based bioink, and printed in a tube-like arrangement to simulate the geometry of an actual blood vessel. A step-by-step procedure for cell co-culturing on a 3D-printed scaffold with the collagen bioink is being developed. The two cell lines' attachment, viability, and proliferation are examined using fluorescence and scanning electron microscopy.

5:00 PM SB01.03.15
Engineered Extracellular Vesicles for Safe and Efficient Chemo-Sonodynamic Cancer Therapy via Stimuli-Responsive Drug Release Thuy Giang Nguyen Cao[1], Ji Hee Kang[2], Wangyu Kim[3], Su Jin Kang[1], Quan Truong Hoang[1], Jun Min[1], Won Jong Rhee[1], Chulhong Kim[3], Young Tag Ko[2] and Min Suk Shim[1]; [1]Incheon National University, Korea (the Republic of); [2]Gachon University, Korea (the Republic of); [3]Pohang University of Science and Technology (POSTECH), Korea (the Republic of)

Sonodynamic therapy (SDT) is a novel non-invasive cancer treatment that utilizes ultrasound to activate sonosensitizers and generate reactive oxygen species (ROS) to damage tumor cells. Nanocarriers-assisted delivery of sonosensitizers has gained considerable attention because it can significantly improve the physicochemical properties and anticancer activities of sonosensitizers. Extracellular vesicles (EVs), a class of naturally occurring nanoparticles secreted by cells, were extensively employed as biocompatible nanocarriers for drug delivery as an alternative to synthetic nanocarriers. Combination of SDT with chemotherapy has shown great promise to achieve synergistic therapeutic outcomes for cancer treatment. In this study, stimuli-responsive EVs that can selectively release chemotherapeutic agents and sonosensitizers into cancer cells were developed for safe and efficient chemo-sonodynamic cancer therapy. The engineered stimuli-responsive EVs facilitated the release of chemodrugs and sonosensitizers in response to acidic pH in the endo/lysosomes or redox potentials in the cytoplasm. *In vivo* studies using tumor-bearing mouse models demonstrated that the stimuli-responsive EVs preferential accumulated in tumors and exhibited efficient anticancer activity without significant systemic toxicity. These findings demonstrate that stimuli-responsive EVs are promising platforms for safe and efficient chemo-sonodynamic combination cancer therapy.

5:00 PM SB01.03.16
ZnL_2-BPs Integrated Bone Scaffold under Sequential Photothermal Mediation—A Win-Win Strategy Delivering Antibacterial Therapy and Fostering Osteogenesis Thereafter Yuzheng Wu and Paul K. Chu; City University of Hong Kong, Hong Kong

Implant-related infections are serious complications after bone surgery and can compromise the intended functions of artificial implants, leading to surgical failure and even amputation in severe cases. Various strategies have been proposed to endow bone implants with desirable antibacterial properties, but unfortunately, most of them inevitably suffer from some side effects detrimental to normal tissues. In this study, a multifunctional bone implant is designed to work in conjunction with sequential photothermal mediation, which can deliver antibacterial therapy (<50 °C) in the early stage and foster bone regeneration (40–42 °C) subsequently. Black phosphorus nanosheets (BPs) are coordinated with zinc sulfonate ligand (ZnL_2), and the ZnL_2-BPs are integrated into the surface of hydroxylapatite (HA) scaffold to produce ZnL_2-BPs@HAP. In this design, BPs produce the photothermal effects and ZnL_2 increases the thermal sensitivity of peri-implant bacteria by inducing envelope stress. The biosafety of the antibacterial photothermal treatment is improved due to the mild temperature, and furthermore, the gradual release of Zn^{2+} and PO_4^{3-} from the scaffold facilitates osteogenesis in the subsequent stage of bone healing. This strategy not only broadens the biomedical applications of photothermal treatment but also provides insights into the design of multifunctional biomaterials in other fields.

5:00 PM SB01.03.18
Mechano-Responsive Hydrogel for Direct Stem Cell Manufacturing to Therapy Andy Tay; National University of Singapore, Singapore

Bone marrow-derived mesenchymal stem cell (MSC) is one of the most actively studied cell types due to its regenerative potential and immunomodulatory properties. Conventional cell expansion methods using 2D tissue culture plates and 2.5D microcarriers in bioreactors can generate large cell numbers, but they compromise stem cell potency and lack mechanical preconditioning to prepare MSC for physiological loading expected *in vivo*. To overcome these challenges, in this work, we describe a 3D dynamic hydrogel using magneto-stimulation for direct MSC manufacturing to therapy. With our technology, we found that dynamic mechanical stimulation (DMS) enhanced matrix-integrin β1 interactions which induced MSCs spreading and proliferation. In addition, DMS could modulate MSC biofunctions including directing MSC differentiation into specific lineages and boosting paracrine activities (e.g., growth factor secretion) through YAP nuclear localization and *FAK-ERK* pathway. With our magnetic hydrogel, complex procedures from MSC manufacturing to final clinical use, can be integrated into one single platform, and we believe this 'all-in-one' technology could offer a paradigm shift to existing standards in MSC therapy.

5:00 PM SB01.03.19
Parallel, Scalable and Customizable Production of Gel-Encapsulated Cells for Advanced Biomanufacturing and Therapeutics Stephen A. Morin and Ruiguo Yang; University of Nebraska – Lincoln, United States

Gel-encapsulated cells are at the heart of several emergent biotechnologies including cell-based therapeutics and bioprinting; however existing techniques such as microfluidics and batch emulsification cannot provide scalability and tunability simultaneously. An advanced manufacturing scheme to produce gel-encapsulated cells that is both scalable and universally compatible with encapsulants of different chemistry, mechanics, volumes, and/or shapes, and cargos that may include a range of cell lines or different molecular and biomolecular agents is needed. We report a universal strategy that enables the biomanufacturing of packageable and deployable bio-suspensions of gel-encapsulated cells and molecular/biomolecular cargos capable of meeting the demands of cell-based therapeutics and tissue printing. At the heart of our approach is an elastomeric chemical template that enables the simultaneous collection/assembly of spray-deposited liquid pre-polymer/cellular suspensions into photocrosslinkable microdroplets which can readily access liter-scale volumes of microgel product (10^{11} microgels/hour). The procedure we report enables the manufacture of application-specific, customized bio-suspensions for next-generation therapies and tissue printing/engineering systems that promise to make personalized cell therapeutics and tissue regeneration/organ replacement procedures a reality.

5:00 PM SB01.03.20
Insights into Growth Regulation by Connecting Simulations of Plant-Growth to the Plant Gall Life Cycle Richard W. van Nieuwenhoven and Ille C. Gebeshuber; TU Wien, Institute of Applied Physics, Austria

In Nature, plants must cover all their necessities from locally available resources. They can extract their main structural building elements, such as carbon, from thin air. Many non-plant organisms have found ways to manipulate plant growth to their advantage. Gall wasps, for example, can reprogram plants to grow tailored breeding chambers using biochemical substances. Plant growth simulation algorithms have proven to be successful in modeling plant development. This study will investigate a minimum distortion in these established algorithms to simulate the effect of the mechanism used by gall wasps. Connecting the simulation results with detailed observations of galls in Nature is expected to help us understand the effects of the control mechanism exerted by gall wasps. Future research can bridge these findings with advances in biochemical research of gall growth to gain deeper insight into plant growth regulation. Utilizing such natural resource control strategies could solve many of humanity's sustainability problems.

5:00 PM SB01.03.21
Optimizing the Scale-Up Production of the Biocementing Bacterium Sporosarcina pasteurii Adriana E. Joson[1,2], Michael Carter[1,2], Joshua Mancini[1,2], Karen A. Holley[1,2], Matthew J. Tuttle[1,2], Rhett Martineau[1], Chia-Suei Hung[1] and Maneesh Gupta[1]; [1]AFRL, United States; [2]UES, Inc., United States

Cement is one of the most consumed materials globally, second only to water. The production and maintenance of cement is unsustainable, costly, and a major contributor to greenhouse gas emissions. As urbanization and cement consumption continue to increase, the need to identify a sustainable, comparable, and environmentally friendly alternative becomes increasingly evident. Biocement is a sustainable biomaterial with properties similar to traditional cement. This technology relies on the CaCO3 production resulting from the growth and enzymatic activity of Sporosarcina pasteurii, a bacterium known for its capability of microbially induced calcite precipitation (MICP). The process exploits urease enzymes to catalyze a reaction that produces the ideal basic environment for this alkaliphile to thrive and drive CaCO3 formation. While the process of biocementation is still in its genesis, optimization of biocementation begins with optimizing production of the bacteria responsible for this technology. Here, we propose the optimization of large scale industrial growth through the use of 10 liter bioreactors to serve as a transitional step. By implementing and modifying specific growth parameters, we are able to monitor specific idiosyncrasies of S. pasteurii to produce the largest biomass yields in the shortest time possible, all while maintaining cementation (MICP) efficacy. To curb toxic ammonia production, we decreased the urea concentration that was recommended in previous literature, resulting in a 90% reduction of the produced ammonia with nominal effects to growth rate or cementation efficacy. Even in the absence of urea, bacterial growth is robust, so long as the environment is basic (9.5 pH), with the only detriment being an increase in lag time. With these basic parameters in mind, we were able to evaluate growth in alternative media. These low cost production techniques will further provide the building blocks for this contemporary technology and pave the way for a green and economically feasible alternative construction material.

5:00 PM SB01.03.22
Utilizing Poly Glutamic Acid for Enhancement of *Sporosarcina Pasteurii* Induced Biocementation Karen A. Holley[1,2], Joshua Mancini[1,2], Matthew J. Tuttle[1,2], Brandon M. Bradow[1,2], Rhett Martineau[1], Michael Carter[1,2], Chia-Suei Hung[1], Maneesh Gupta[1] and Laura Lang[1,2]; [1]Air Force Research Laboratory, United States; [2]UES Inc., United States

Biocementation is a process that utilizes microorganisms to bind soil particles together, leading to the formation of a more stable and cohesive soil structure through a cement-like matrix. *Sporosarcina pasteurii* is a bacterium we use for our cementation at the Air Force Research Laboratory. S. pasteurii has the ability to produce calcium carbonate, which helps to bind the particles together, resulting in increased strength and stability. The use of biocementation has several advantages over traditional stabilization methods, including reduced energy and material inputs, improved sustainability, and increased durability. This works demonstrates that poly glutamic acid can be added to the biocementation solution to facilitate an increase in precipitation of calcium carbonate. This increase leads to more stable sand columns and will allow us to decrease the amount of urea and calcium that is used in the biocementation solution, further decreasing the material inputs of biocemented structures.

5:00 PM SB01.03.23
High-Throughput, Multiscale Testing and Evaluation of Living Cemented Materials Brandon M. Bradow[1,2], Rhett Martineau[1], Laura Lang[1,2], Matthew J. Tuttle[1,2], Joshua Mancini[1,2], Michael Carter[1,2], Karen A. Holley[1,2], Adriana E. Joson[1,2] and Maneesh Gupta[1]; [1]Air Force Research Laboratory, United States; [2]UES, Inc., United States

Microbially-induced calcite precipitation (MICP) has been recognized as an alternative to traditional cements; reversibly and quickly achieving cementation at room temperature with a lesser degree of CO_2 emissions. Low-carbon materials created using this technology may be useful for erecting impromptu structures, development of sites for humanitarian relief, or any other application requiring rapid, unintrusive ground improvement. However, improving and scaling up the biocementation process requires the development of faster-paced iterative testing devices for assessing methods production. In this study, we investigated variously scaled apparatus, which allows for gradually upscaled testing and increasing resolution with respect to evaluation of materials. These devices generally take the form of walled openings with a liquid-permeable mesh in the lower portion, allowing percolation of bacterial suspension solutions and cementation solutions. To increase throughput of experimentation, we used a pipetting robot to apply solutions between 176 microliter to 8 milliliter scale. This allowed for various methods and solutions to be tested simultaneously with numerous replicates. Experimental manipulation included the growth environment of the bacteria, growth media, and soil conditions. Using this process, it is possible to alter formulations to target specific traits and features of biocement. In our results, we found that strength is largely proportional to the amount of Ca^{2+} administered to the system, in addition to preconditions such as urea availability during growth, growth media type, and soil moisture content. Some conditions thought to not be viable for cementation are now considered viable, such as bacterial cultures grown without urea. Not only is this method viable, but it has comparable strength values to the average 60-80 PSI (unconfined compressive strength, UCS) achieved with conditions considered average per our results with a standard treatment. Using these methods, our standard treatment has improved by 160% from an average of 50 PSI to an average of 80 PSI, with strengths of 300 PSI being recorded outside of standard conditions. Our automated method allows testing of high-impact questions at a low-stakes opportunity cost by removing the restrictions imposed by time and material commitment.

5:00 PM SB01.03.24
Tuning Properties of Iridescent Biofilms for Material Applications Kennedy Brown[1], Claretta J. Sullivan[1], Chia-Suei Hung[1], Nicholas Posey[2], Matthew Dickerson[2], Patrick Dennis[1] and Nancy Kelley-Loughnane[1]; [1]AFRL/RXE, United States; [2]AFRL/RXN, United States

Nature employs hierarchical assembly as a successful strategy for enhancing the physical properties of its materials. Scientists study these natural materials, including morpho butterfly wings and mollusk nacreous shells, in an effort to replicate their properties in functional materials. Though mechanistic insights from these studies have led to significant progress, translating nature's design principles into scalable platforms for manufacturing hierarchical materials remains a bottleneck. We previously demonstrated the potential of iridescent *Cellulophaga lytica* biofilms to circumvent this issue with facile growth and scalability. In particular, their ability to self-assemble into hierarchically ordered communities in ambient conditions make them attractive candidates for templating ordered materials at industrial scales. Bacteria evolved strategies for precisely controlling morphology and dimensions on scales that are difficult to achieve in industrial manufacturing. In the current study, we demonstrate how biofilm functionality can be tuned by altering the morphology, dimensions and chemistry of its constituent bacteria. This study further strengthens the case for using these biofilms as platforms for sustainably manufacturing photonic materials and ordered templates.

5:00 PM SB01.03.25
Engineered Consortia for Enhanced Function of Iridescent *Cellulophaga lytica* Biofilms as a Living Sensing Material Claretta J. Sullivan, Kennedy Brown, Patrick Dennis and Nancy Kelley-Loughnane; AFRL/RXE, United States

Gliding bacteria such as *C. lytica* form intensely iridescent biofilms by packing themselves into polycrystalline domains. We have shown that these biofilms respond to environmental cues including salinity and temperature by dynamically changing the color reflected. As such, the biofilms offer a visible readout of its sensing status. In the current study, our goal was to develop these iridescent biofilms into living, sensing materials where *C. lytica* serves as a colorimetric reporter. Toward that end, we added genetically tractable *E. coli* to *C. lytica* biofilms, making a functional consortia in which each organism has a distinct role. Initial results address the challenges of incorporating *E. coli* into the biofilms without disturbing the iridescence generated by *C. lytica*. In addition, efforts to increase the cooperation between the two organisms will be presented. The engineered consortia made up of a non-canonical color-generating organism and a genetically tractable one could be a strategy for making living sensors suitable to a variety of environments.

SESSION SB01.04: Session IV
Session Chairs: Marie-Eve Aubin-Tam and Maneesh Gupta
Friday Morning, April 14, 2023
Moscone West, Level 2, Room 2012

8:15 AM *SB01.04.01
Biologically Fabricated Materials from Engineered Microbes Neel S. Joshi; Northeastern University, United States

The intersection between synthetic biology and materials science is an underexplored area with great potential to positively affect our daily lives, with applications ranging from manufacturing to medicine. My group is interested in harnessing the biosynthetic potential of microbes, not only as factories for the production of raw materials, but as fabrication plants that can orchestrate the assembly of complex functional materials. We call this approach "biologically fabricated materials", a process whose goal is to genetically program microbes to assemble materials from biomolecular building blocks without the need for time consuming and expensive purification protocols or specialized equipment. Accordingly, we have developed Biofilm Integrated Nanofiber Display (BIND), which relies on the biologically directed assembly of biofilm matrix proteins of the curli system in *E. coli*. We demonstrate that bacterial cells can be programmed to synthesize a range of functional materials with straightforward genetic engineering techniques. The resulting materials are highly customizable and easy to fabricate, and we are investigating their use for practical uses ranging from bioremediation and biodegradable bioplastics to engineered therapeutic probiotics.

8:45 AM *SB01.04.02
Manipulating Growth and Mechanical Properties of Plants with Genetic Engineering Meredith N. Silberstein, Bex Pendrak, Isabella Burda, Si Chen and Adrienne H. Roeder; Cornell University, United States

In plant developmental biology, a growing field of interest is how the growth and mechanical properties of various plant tissues and organs are influenced by mutations, with the understanding that these closely couple and have strong implications for plant function. In the engineered living materials field, this same fundamental knowledge can be used to program structures of desired properties. Plant tissue growth is an organic process that produces non-uniform tissues with varying cellular compositions. It is therefore of interest the understand the distribution of constituents, constituent properties, and the aggregate macroscale properties.

In this talk, we will present a study of the mechanical properties of *Arabidopsis thaliana*. *A. thaliana* is a model organism frequently used by plant biologists because of its simple structures, fully sequenced genome, and susceptibility to genetic modifications. Wild-type and two different mutations of *A. thaliana* at various developmental stages were tested to investigate the role of plant age and mutations on the tissue-scale material properties. To characterize leaves specifically, rectangular specimens were cut from the center of leaves, avoiding the midvein which has been shown to significantly affect tensile properties of leaf tissues. The samples were mounted on paper frames to stabilize the material, with a similar technique to that used in the tensile testing of fibers. Speckle patterns were applied to enable the use of the Digital Image Correlation (DIC) technique, which tracks strains across the surface of the samples. Samples were deformed under uniaxial tension at a constant strain rate until failure. They were then analyzed in terms of elastic modulus, Poisson's ratio, ultimate strength, failure progression, and homogeneity of the strain field. We will also present results on the cell size, shape, and growth patterns underlying the tissues in these mutants to help form structure-function relationships in this genetically modified material system.

9:15 AM SB01.04.03
Tuning the Mechanical Behavior of Extracellular Matrix Composite Scaffolds for 3D-Bioprinting Grace Hu[1], Zeqing Jin[2], Austin J. Graham[3,4], Zev Gartner[1,3,4] and Grace Gu[1,2]; [1]University of California, Berkeley & San Francisco, United States; [2]University of California, Berkeley, United States; [3]University of California, San Francisco, United States; [4]Chan Zuckerberg Biohub, United States

3D-bioprinting facilitates the construction of scaffolds with complex geometries and at high precision. Design and process parameters for 3D-bioprinted materials must be carefully considered and characterized for each specific application.[1] Given the critical mechanical and physiological roles of type I collagen and laminin within the native extracellular matrix (ECM), we investigate how the printability and stiffness of composites of type I collagen and laminin is controlled through various printing process parameters. Numerical simulations are first implemented to characterize the swelling behavior of collagen, which are then compared to experimental testing. With an eye towards translation and ease-of-use, we utilize the commercially-available CellInk BioX bioprinter to control infill density, concentration, nozzle diameter, and heating duration throughout printing, observing vastly different mechanical properties in the resultant hydrogels.

Building from this work, we also seek to establish a reliable framework for 4D-bioprinting, in which the structure undergoes programmable mechanical and biochemical transformations over time. To this end, we computationally analyze and experimentally validate origami-inspired tissue folding mechanisms. Mouse embryonic fibroblasts (MEFs) are employed due to their contractile behavior that can be predictably modeled using finite element methods.[2] Collagen-Matrigel composites are prepared to investigate how MEF clusters contract the surrounding matrix as a function of material stiffness and mechanical cell state. The MEFs exhibit excellent cell viability, proliferation, and ability to dependably remodel the matrix over 24 hours. Ultimately, these results inform strategies for 4D tissue printing for biofabrication, developmental models, and regenerative medicine.

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9:30 AM SB01.04.04

The Development of 3D Printable Living Microreactors for the Detoxification of Organophosphates Adam W. Perriman[1,2,2], Mark Shannon[1] and George Klemperer[1]; [1]University of Bristol, United Kingdom; [2]The Australian National University, Australia

Engineered Living Materials (ELMs) present an exciting opportunity to integrate and scale outputs from synthetic biology. However, ELM fabrication and performance are somewhat limited by the need for both matrix cytocompatibility and fabricability. Idealy, the living component should interface with and modulate the bulk structure of a material. Accordingly, we present the rational design and testing of living composites where expression of an artificial oxidoreductase by E. coli suspended in an ionogel bioink drives redox-mediated formation of a self-healing interpenetrating double network. Moreover, we demonstrate that this new class of ELMs can be 3D bioprinted to produce perfusable bacterial microreactors that actively detoxify organophosphates.

9:45 AM BREAK

10:15 AM SB01.04.05

Spatially Organized Photosynthetic Living Materials Jeong-Joo Oh, Satya Ammu, Vivian Vriend, Roland Kieffer, Kunal Masania and Marie-Eve Aubin-Tam; Delft University of Technology, Netherlands

Engineered living materials (ELMs) are emerging class of functional materials, often fabricated by incorporating living cells within an inert polymer matrix to form desired functions. Unraveling the formation, spatial localization, and behavior of cellular populations within an artificial niche is a prerequisite for predicting and intensifying the functions of living materials. This study focuses on the growth and spatial distribution of eukaryotic microalgae *Chlamydomonas reinhardtii* within hydrogel networks for the strategic fabrication of living materials with intensified CO_2 capture. Existing unicellular microalgae within scaffolds form multicellular algal aggregates, called palmelloid, around the surface of bioprints, which play a crucial role in forming the functional surfaces of materials. With increasing depth of the matrix, the number and volume of cellular clusters decrease due to photon attenuation and limited air transfer. By tailoring material thickness and increasing the exposure of palmelloid to its circumjacent environments, the CO_2 capturing performance of bioprints can be enhanced. Interestingly, material designs to regulate photosynthetic activity show similarities to the strategies for intensifying photosynthetic activity inspired by plant leaves. Our results imply that the spatial control of cell population can control the function of ELMs and can be exploited for biomimetic structural research for leaf mimicry.

10:30 AM SB01.04.06

Plasmonic Stimulation of Gold Nanorods for the Photothermal Control of Engineered Living Materials Selim Basaran[1], Sourik Dey[1], Shrikrishnan Sankaran[1] and Tobias Kraus[1,2]; [1]INM–Leibniz Institute for New Materials, Germany; [2]Universität des Saarlandes, Germany

Composites of living cells in polymer gel matrices are called "Living Materials"[1]. They are useful for the controlled release of drugs that are produced by the cells while protecting them and their environment. Here, we demonstrate an optically triggered Living Material based on thermoresponsive bacteria. A "core" of a pluronic hydrogel with engineered *Escherichia coli* was enclosed in "shell" of a composite hydrogel that contained gold nanorods (AuNR) that were 41 nm long and 10 nm in diameter. The absorption spectrum of the AuNR coincides with the transparent window of human tissues. The plasmonic rods absorb laser light, heat the shell, and activate the bacteria, inducing the production of mCherry proteins or darobactin. Living materials were prepared in structured microslides that enabled both quantitative studies of spatial and temporal temperature variation and protein expression.

First, we characterized the thermoplasmonic composite and determined its overall photothermal conversion efficiency and the resulting thermal response with a AuNR concentration equivalent to an optical density of $OD_{808\text{ nm}} = 4$. Infrared thermography and embedded thermocouples were combined to obtain temperature distributions at a sampling rate of 0.2 Hz and an accuracy of 0.1 K. Illumination with a collimated laser spot of 5 mm diameter at 808 nm heated the cylindrical core-shell Living Material from an initial 20°C to a steady-state temperature of 40°C in air in 300 seconds. The IR camera indicated a lateral temperature gradient from center to the border with a maximum temperature difference of 4.7°C.

The genetically engineered *E. coli* contained in the core were activated by heating and produced the fluorescent protein mCherry. In a second set of experiment, we quantified its production as a function of laser power, time, and position via *ex situ* fluorescence microscope. The fluorescence intensity correlated with the temperature distribution measured above. The maximal protein expression rate for the living material with this *E. Coli* strain was found to be between 39-44°C, consistent with reference experiments in suspensions. Protein production at 0.6 W/m^2 was maximal at the center of the illuminated area and declined at its borders, where temperature dropped. Increasing laser power first led to an increase of fluorescence intensity at the borders. A uniform fluorescence intensity was reached across the illuminated area at 0.7 W/m^2. Protein expression continued for at least 4 h, with a linear increase of fluorescence that indicated sustained expression activity of the bacteria. Further increasing power density reduced the fluorescence intensity at the center. The decline occurred when the center temperature exceeded 45°C, the maximum viable temperature for the bacteria.

In a third set of experiments, we compared the results obtained for the model compound mCherry to the antibiotic darobactin that was produced by a different strain of engineered *E. Coli*. After photothermal triggering, darobactin was expressed, diffused through the gel, and into surrounding media, where we detected its presence via ESI-MS as a function of laser irradiation time. The results will be discussed in view of possible applications in therapies for chronical inflammations, e.g. in periodontitis.

Acknowledgement:
We thank Shardul Bhusari for providing the hydrogel.

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10:45 AM SB01.04.07
Membrane Targeted Azobenzene Drives Optical Modulation of Bacterial Membrane Potential Giuseppe M. Paternò[1,2], Tailise Carlina de Souza-Guerreiro[3], Gaia Bondelli[2], Iago Grobas[4], Guglielmo Lanzani[2,1] and Munehiro Asally[3]; [1]Politecnico di Milano, Department of Physics, Italy; [2]Istituto Italiano di Tecnologia, Italy; [3]University of Warwick, United Kingdom; [4]University of Oxford, United Kingdom

The possibility to control living matter with exogenous stimuli can have tremendous impact on synthetic biology, medicine and materials science, among others. For instance achieving control over cells behaviour remains a challenge at the interface between living and non-living matter,[1] and would enable the development of new bio-mimetic and bio-enabled materials able to perform tasks.[2] Within this context, bacteria have arisen as "active and actively-controllable materials", exhibiting neuro-like behaviour, extended bioelectric signalling[3,4] and tunable assembly properties.[5] In the last decade, it has been observed that the regulatory element of such an active behaviour is the electrical potential across the membrane, which governs bacteria electrophysiology, metabolisms and bioenergetics.[6] Light can be a powerful tool in these regards, as one can control the membrane potential and, thus, cell function and behaviour remotely and with relatively high spatiotemporal precision.
Here, I will show that a membrane-targeted azobenzene can be used to photo-modulate precisely the membrane potential in cells of the Gram-positive bacterium *Bacillus subtilis*. We found that upon exposure to blue- green light, the isomerization reaction in the bacteria membrane induces hyperpolarisation of the potential ($\Delta V = 20$ mV), within a bio-mimetic mechanism reproducing the initial fate of retinal. Apart from being promising results in the view to photocontrol bacterial motion and assembly behavior in consortia, this approach also highlights the role of previously uncharacterized ion channels in bacteria electrophysiology.[7]

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SESSION SB01.05: Session V
Session Chairs: Marie-Eve Aubin-Tam and Maneesh Gupta
Friday Afternoon, April 14, 2023
Moscone West, Level 2, Room 2012

1:45 PM SB01.05.01
Development and Strategies to Improve Cellular Uptake of an Artificial Membraneless Organelle-Based Bioreactor Manisha Abesekara and Ying Chau; Hong Kong University of Science and Technology, Hong Kong

Liquid-liquid phase separated microcompartments inspired by membraneless organelles is a promising tool in developing bioreactors. They have liquid-like interior, sequestrate biomolecules, exchange materials with external environment and confine biochemical reactions. Adapting the sticker-spacer model of intrinsically disordered proteins, artificial membraneless organelles (aMLOs) were developed using a polymer-oligopeptide hybrid material consists of a dextran backbone and two oligopeptides. The capacity of aMLO to perform biochemical reactions was evaluated by a CRISPR reaction within the microcompartment. For the translation of CRISPR technology for therapeutic use, the core challenge is the development of an effective and safe delivery approaches. The CRISPR reactive complex loaded micron-size bioreactors in cytosol of target cell would be a noninvasive delivery approach with high effectivity. Cas9, sgRNA and target oligo-duplex were enriched within aMLOs with 720-fold, 865-fold and 835-fold increased concentrations, respectively. Consequently, the CRISPR cleavage reaction was achieved within the aMLOs under physiological conditions.
Additionally, strategies of cytosolic delivery of aMLOs were studied. To tap membrane fusion pathway, aMLOs were wrapped with macrophage cell membranes. The wrapping did not change the native enrichment/exclusion functions of the aMLOs but improved the stability from ~9 hours to up to 3 days. Wrapped aMLOs found to be internalized by source cells with intact cargo-molecules. Cellular uptake was further improved by sonoporation with low frequency (40 kHz) ultrasound of mechanical index (MI) and peak pressure of 0.4 and 75 kPa, respectively. Low frequency ultrasound can increase activity of mechanosensitive channels and induce pore formation at membrane protein-lipid interface to improve uptake. In the sonoporation experiment, above 80% cells were viable under continuous ultrasound treatment up to 5 min. Overall, results imply the possibility of developing deliverable bioreactors made of aMLOs and strategies to improve its cellular uptake.

2:00 PM SB01.05.03
Optimization of the Laser-Induced Forward Transfer Process for the Printing of Living Cells Adrien Casanova[1], Lucas Duvert[1], Ahmed Al-Kattan[1], Stefano Testa[2], Frédérique Magdinier[2] and Anne-Patricia Alloncle[1]; [1]Aix-Marseille University, CNRS, LP3 UMR 7341, Campus de Luminy, Case 917, France; [2]Aix-Marseille University, INSERM, MMG, Marseille Medical Genetics, France

Printing techniques applied to biology have begun to develop since the 2000s and hold great promise in a near future. They are based on interdisciplinary approaches and use a combination of cells, chemistry, engineering and sophisticated protocols to create artificial tissues.
In that scope, it has been more than a decade since Laser-Induced Forward Transfer (LIFT) is studied in lab scale for its ability to print biomaterials and more specifically living cells [1], [2]. This method uses a short laser pulse to transfer tiny amounts of material from a thin film donor to a receptor substrate. Under appropriate conditions, the pulse induces the formation of a jet propagating perpendicularly to the donor substrate. The targeted material is then deposited as a droplet on the collector. Due to its nozzle free non-contact direct writing technique, it is considered as a suitable method to print three dimensional cellular structures with a very high spatial resolution. Combined with stem cells technology this innovative printing process opens new perspectives for the creation of complex bio-models strongly mimicking the *in-vivo* environment with numerous applications ranging from regenerative

medicine to pharmaceutic study and drugs screening. However, the optimization of its performance and its use with living cells require a deep understanding of the ejection dynamic depending on several laser parameters (laser fluence, repetition rate, laser spot size, laser wavelength, pulse duration, absorption mechanism…) and of the effects of living cells on the bio-ink printability. At LP3 (Marseille-France) and in close collaboration with MMG (Marseille-France), we took advantages of our expertise in LIFT process [3] to master the printing by LIFT of living cells in good condition (high spatial resolution, high printing resolution and high cellular viability after printing) [4].
Here, we will present the LIFT process and its optimization allowing to master the bio-ink deposition in order to create reliable ordered patterns of bio-ink micro-droplets containing stem cells with a high spatial resolution. By changing the film concentration in cells and the laser pulse energy, we can control the droplet size and the number of cells in each droplet (from tens of cells down to the single cell level). Then, we will present a complete viability study of the printed cells after transfer to prove the ability of this process to create relevant bio-models.

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2:15 PM SB01.05.04
Smart Sampling Capsule for Small Intestinal Bacteria Overgrowth Detection Sina Nejati, Aleena Masaeng and Rahim Rahimi; Purdue, United States

Small intestinal bacterial overgrowth (SIBO) is the condition when the bacteria in the upper gastrointestinal tract grow excessively beyond 10^5 colony forming units (CFU)/mL. The high population of bacteria then leads to malabsorption, indigestion, constipation, and a decrease in the efficiency of the immune system. Currently available techniques for the diagnosis of SIBO rely on jejunal aspiration and breath tests for measuring the hydrogen and methane produced through the bacterial metabolism of carbohydrates. However, these approaches commonly suffer from invasiveness, high expense, and poor accuracy by yielding false-positive results. Here, to sidestep the issues associated with discomfort to the patient, contamination, and unreliable results, we designed and developed a new 3D-printed sampling device to site-selectively collect small intestinal bacteria. The capsule's pH-responsive enteric coating served as an actuation mechanism to open the device in the region of the small intestine to facilitate bacteria collection while maintaining its integrity in the highly acidic environment of the stomach. A water-soluble glue was used to maintain the compression of a biocompatible polyetheretherketone (PEEK) spring, which was then inserted inside the capsule. When the enteric coating disintegrated and the GI tract fluid collected, the water-soluble glue was dissolved, causing the spring to expand. Upon expansion, the bonded flexible disc on top of the spring effectively sealed the capsule preventing contamination from the lower GI tract. Once the device has been discharged, the device could be readily opened to collect the small intestinal bacteria and quantify the CFU/mL. To achieve the least amount of deformation after the expansion of the spring, various materials were tested under compression for different time points and the length variation was recorded. Additionally, a series of systematic force profile studies was performed with different glue thicknesses to identify the exerted force for proper sealing of the device as well as understand the duration of the sampling. To demonstrate the non-selective sampling capability of the device, different dye concentrations as well as two bacterial strains including Escherichia coli and Pseudomonas aeruginosa with different concentrations were investigated. The results showed an excellent matching concentration between the collected sample and the sampling environment. The targeted bacterial sampling performance and spring-assisted sealing mechanism were validated using both realistic in vitro GI tract models with bacteria cultures and ex vivo with dissected porcine small intestines. Here, it is envisioned that such smart sampling capsule technology will offer new ways to gather specific bacteria from the small intestine to identify the potential for SIBO disease more accurately.

2:30 PM *SB01.05.05
Engineering Microbial Communities in Biofilms Meghna Thakur[1,2], Lina J. Bird[1], Brian J. Eddie[1], Isabel R. Baker[1], Anthony P. Malanoski[1] and Sarah Glaven[1]; [1]U.S. Naval Research Laboratory, United States; [2]George Mason University, United States

Engineering living bacteria within biofilms has remained a challenge owing to difficulty in their cultivation under laboratory conditions due to reliance on syntrophic partners. In order to develop these bacteria for technological use, tools to genetically manipulate them directly, without the need for standard laboratory isolation and cultivation, are required. Here we describe our efforts toward *in situ* genome editing of autotrophic bacteria in an electrode biofilm. We first demonstrate a CRISPR-based genome editing tool called INTEGRATE in a biofilm-forming marine bacteria, *Marinobacter atlanticus* in pure culture. Next, we tracked the introduction of a fluorescent marker protein superfolder GFP (sfGFP) into *M. atlanticus* biofilm cells via conjugation with a fluorescent donor *E. coli* strain using confocal microscopy. Utilizing a fluorescent *M. atlanticus* biofilm, the genomic integration of sfGFP in the cells could be monitored in real-time. Lastly, we targeted an electroautotroph *Candidatus* Tenderia electrophaga that exists in a consortia of ca. 20 other species, and can only grow from CO_2 fixation and electron uptake from an electrode, and showed, for the first time, successful genome integration of a fluorescent marker protein in this uncultivated electroautotroph. This work represents the first step towards *in situ* genome editing of microbial communities that form electroactive biofilms as an approach towards developing living catalytic materials.

3:00 PM BREAK

3:30 PM SB01.05.06
The Mechanical Theory of Nonequilibrium Coexistence Ahmad Omar; University of California, Berkeley, United States

Nonequilibrium phase transitions are routinely observed in both natural and synthetic systems. The ubiquity of these transitions highlights the conspicuous absence of a general theory of phase coexistence that is broadly applicable to both nonequilibrium and equilibrium systems. In this talk, we present a general mechanical theory for phase separation rooted in ideas explored nearly a half-century ago in the study of inhomogeneous fluids. The core idea is that the mechanical forces within the interface separating two coexisting phases uniquely determine coexistence criteria, regardless of whether a system is in equilibrium or not. We demonstrate the power and utility of this theory by applying it to active Brownian particles, predicting, from first principles, a quantitative phase diagram for motility-induced phase separation in both two and three dimensions. Finally, we extend and apply this mechanical perspective of phase coexistence to nonequilibrium order-disorder transitions and systems comprised of particles with nonreciprocal interactions.

3:45 PM SB01.05.07
Augmenting Adoptive T Cell Therapy in Solid Malignancies via Cell Nanoengineering and Photoacoustics Jinhwan Kim, Kelsey Kubelick, Anamik Jhunjhunwala, Jeungyoon Lee and Stanislav Emelianov; Georgia Institute of Technology, United States

Cancer immunotherapy using adoptive T cell transfer has shown remarkable success in many hematologic malignancies, however, this has not reliably translated to solid tumors. There are two main reasons that hinder T cell therapy translation in solid malignancies: 1) inability to visualize and track the infused T cells within tissues, and 2) limited delivery of T cells into deep-seated tumors that are not adjacent to vasculature. To address these two points, we introduce an approach, termed “cell nanoengineering”, based on a synergistic combination of adoptive T cells and functional nanoparticles coupled with

an imaging system to track the delivery and therapy *in vivo*. Specifically, we modify T cell surfaces with light-absorbing, anticancer chemotherapeutic drug-loaded functional nanoparticles that can penetrate deeper into a 3D solid tumor, and introduce a real-time ultrasound-guided photoacoustic (US/PA) imaging system. This combined approach enables the tracking of nanoengineered adoptive T cells with excellent spatial resolution at great imaging depths to improve understanding of infused T cell trafficking, followed by selective drug release into the entire 3D tumor microenvironment for combinatorial cancer chemo-immunotherapy in solid malignancies.
As a PA contrast agent and drug loading vehicle, mesoporous silica-coated, miniaturized gold nanorods (mSiO$_2$-AuNRs) with an aspect ratio of 6 (λ_{max} = 1064 nm) were synthesized. As an anticancer drug, 5-fluorouracil (5FU) or doxorubicin molecules were loaded in the mesoporous silica layer. For T cell nanoengineering, maleimide-modified mSiO$_2$-AuNRs were conjugated to the free thiol groups on the surface of T cells. To test the biological impact of T cell nanoengineering, T cell functions (i.e., viability, target cell killing) were tested at different nanoparticle concentrations: control cells and nanoengineered T cells at optical densities (ODs) of 1, 5, 10, and 20. Nanoengineered T cells at OD=1 and 5 showed negligible toxicity. At OD=10 and 20 significant T cell death was induced, and these nanoengineering conditions were eliminated from further analysis. Furthermore, T cell killing of matched B16-OVA cells at various ratios was maintained following cell nanoengineering, and no significant difference was observed in control vs. nanoengineered T cells. The addition of chemotherapeutic drugs (i.e., 5FU or doxorubicin) enhanced the target cell killing *in vitro* due to combinatorial chemo-immunotherapy. Furthermore, the loading of chemotherapeutic drugs selectively affected B16-OVA and not T cells at various drug amounts.
In vivo US/PA tracking, tumor regression study, and survival monitoring were carried out in ovalbumin (OVA)-expressing tumor-bearing C57BL/6 mice after intravenous injection of nanoengineered and matched OT1 murine primary T cells or the same amount of drug-loaded mSiO$_2$-AuNRs without T cells, followed by US/PA imaging (40 MHz, 680–970 nm and 1064 nm, Vevo LAZR, Visualsonics Inc.). Multiwavelength PA imaging successfully visualized nanoengineered T cells or nanoparticles delivered into solid tumor region. Nanoengineered T cells showed 3-fold higher PA signal (i.e., successful delivery) than the mSiO$_2$-AuNRs in the solid tumor, indicating the natural homing ability of matched T cells can be harnessed to improve the delivery of combination therapeutics. It followed that mice treated with nanoengineered T cells showed the best tumor regression and survival compared to other controls: T cell only or drug-loaded mSiO$_2$-AuNRs only.
Our results indicate that nanoengineered T cells can be successfully detected within the range of pre-clinical injection doses with high sensitivity for *in vivo* US/PA tracking. Also, the ability of T cells to home to the tumor site enables better delivery of nanoparticles into solid tumors, thus achieving greater tumor regression and enhanced survival.

4:00 PM SB01.05.09
Cell Encapsulation and Functionality in Engineered Living Microfibers by Uniaxial Electrospinning Daniel Verrico[1], Catherine Reyes[2], Fang Qian[2] and Gary Wnek[1]; [1]Case Western Reserve University, United States; [2]Lawrence Livermore National Laboratory, United States

The ability to print living materials in architected geometries enables superior control over cell functionality that will surely enhance the future of biofuel, pharmaceutical, and biocatalyst production. Bulk living materials – or biocompatible hydrogels with encapsulated microbes – may face the challenge of slow mass transfer that limits their production capacity. Cell functionality can be greatly improved when living materials are fabricated in precise geometries such as lattices & scaffolds, which also favor biocatalysis. Here, we present a novel uniaxial electrospinning approach to developing microfibrous poly(ethylene glycol) (PEG) constructs for single cell-level encapsulation and bioprocess intensification. This approach allows PEG microfibers to be generated from an aqueous solution of poly(ethylene glycol) diacrylate (PEGDA), which cannot be conventionally electrospun on its own. By adding a sufficient amount of salt, surfactant, and high molecular weight poly(ethylene oxide) (PEO) to the solution; we can obtain micron sized PEG/PEO fibers loaded with viable yeast cells and having an average fiber diameter of 0.8 µm. Upon photo-curing with a water-soluble initiator, the PEO can be washed away to produce swellable PEG microfibers with encapsulated microbes. Since yeast can be genetically modified to produce a variety of other valuable products, like biofuels or pharmaceuticals, this material could find use as a biocatalyst in industrial processes or as a platform for designing bioinspired materials with other lifelike functions.

SESSION SB01.06: Virtual Session I
Session Chairs: Maneesh Gupta and Taylor Ware
Tuesday Morning, April 25, 2023
SB01-virtual

8:00 AM *SB01.06.01
Functionalization of Bacteria by Surface Modification Jinyao Liu; Shanghai Jiao Tong University, China

The gut microbiota has been demonstrated to be an important regulator in human health. Disorders in the gut ecosystem have been implicated in various diseases, such as inflammatory bowel disease, diabetes, Alzheimer's disease, and cancers. Although fecal microbiota transplantation has demonstrated effective to positively modulate the gut microbiome, the implementation has been largely restricted by invasive operation and indeterminate composition, which inevitably result in low patient compliance and severe safety issues. Oral delivery of probiotic species to the gut microflora is an alternative to address these limitations, unfortunately, environmental complexity and a continuous flow within the gastrointestinal tract result in low oral bioavailability and limited intestinal colonization. Synthetic bioengineering is the most commonly used and feasible strategy to modify bacteria to tackle these challenges. However, the number of bacterial strains that can be genetically engineered is limited so far. Furthermore, many biomacromolecules especially eukaryotic proteins cannot be highly expressed and folded preciously and functionally by bacteria resulting from inefficient post-translational modifications, codon usage issues, and the formation of inclusion bodies that are not functional. Most importantly, engineered bacteria confront with potential risk of gene contamination via horizontal gene transfer, particularly with respect to in vivo applications. The focus of my research group is the use of biomaterials to modify or restructure the surface of bacteria to introduce exogenous functions that are naturally unachievable, which can increase bacterial survival and colonization in vivo following oral administration.
For example, probiotics individually coated with a self-assembled lipid membrane exhibit significantly improved survival against environmental assaults (e.g., gastric acid, bile acid, antibiotics, etc.) and almost unchanged viability and bioactivity, demonstrating enhanced efficacies in oral delivery and treatment of intestinal mucositis. Moreover, probiotics wrapped with a yeast membrane-derived biomaterial can be delivered into lymphoid follicles after oral ingestion and promote robust mucosal immune responses and the production of secretory immunoglobulin A, which can prevent and treat gut barrier impairment. In addition, in-situ co-deposition with dopamine can generate a hybrid multifunctional coating, which can provide a dual protection and targeting ability to modified bacteria for locally modulating the gut microbiota around the inflamed tissue and enhancing the treatment of colitis. Also, oncolytic bacteria camouflaged with a cell membrane-derived biomaterial show a low inflammatory response, slow elimination by macrophages, increased accumulation in tumor tissue, and almost unchanged inherent bioactivities, which generate greatly enhanced antitumor efficacy under a safe dosage. Briefly, the main focus of my research is the development of functional coatings to modify bacteria, which can be endowed with various exogenous functions and applied as editable bacterial therapeutics for intervening gut microbiome imbalance and the associated diseases.

8:30 AM SB01.06.02
Evaluation of Photochemical Activity of Algae and Grass-Chloroplasts when Encapsulated into Hierarchical Silica- Monoliths Cynthia Cervantes and Alicia Sommer; Yachay Tech University, Ecuador

The photosynthetic activity of plants and microalgae can be widely exploited to produce biomaterials with varied properties such as the absorption of CO_2 and the removal of metals such as Cu and Ni in wastewater. In this study, microalgae species Chlorella Vulgaris and chloroplasts extracted from Pennisetum Clandestinum turfgrass residues were immobilized into silica monoliths with hierarchical porosity by the high internal phase emulsion (HIPE) method. Optical and fluorescence microscopy as well as UV-Vis, diffuse reflectance and fluorescence spectroscopy were used to monitor the preservation of photosynthetic activity in the monoliths. The results demonstrate that the monoliths synthesized are capable of maintaining their photosynthetic activity and producing O_2 even after 90 days of encapsulation.

8:45 AM SB01.06.04
The Biomechanics of Ultra-Stretchable Nerves Rakesh Das, Amir Ayali, Moshe Guershon, Amjd Ibraheem, Eran Perlson and Bat-El Pinchasik; Tel Aviv University, Israel

When digging in the ground during egg laying the female locust extends her abdomen to 2-3 times of its original length. How the abdominal nervous system accommodates such extreme elongation remains unknown. We characterized and quantified the system's biomechanical response using controlled ex vivo elongation and force measurements. The microstructure of the nerves was studied using histology and high-resolution confocal microscopy. Although the nervous system of sexually mature females demonstrated fully reversible hyper-extensibility of up to 275%, the elongation observed in premature females and males was much more limited. The unique extension dynamics of the different groups were captured by their very different force-displacement curves. Confocal microscopy suggested that elongation is not owing to undulations of the nervous system structure. Thus, the exceptional resistance to deformation and rupture presents the female locust abdominal nervous system as a valuable model for understanding the functionality and pathology related to nerve extension and reversible elongation.

9:00 AM *SB01.06.05
Material Design Criteria for Living Therapeutic Devices Aránzazu del Campo; INM-Leibniz Institute for New Materials, Germany

Engineered Living Materials, where active biofactories are contained in diffusive matrices, open new opportunities to design therapeutic wearable devices and implants for comfortable treatment of chronic diseases. In this talk, fundamental design parameters and demonstrated properties of the encapsulating matrix to guarantee functionality and safety of living therapeutic devices will be presented, together with current examples developed in the group.

9:30 AM SB01.06.06
Fabricating Mycelium-Agrowaste 3D Composite Materials for Use in Building Construction Insulation. Kumba B. Bonga, Despina Fragouli and Athanassia Athanassiou; Italian Institute of Technology, Italy

Environmental degradation is occurring at an alarming rate due to the unsustainable activities of the construction industry posing a serious threat to our ecosystem, human health, and economy[1]. Its adverse consequences propel the three planetary crises we are encountering currently: climate change, biodiversity loss, and pollution[2]. The building sector accounts for 39% of gross annual carbon emissions worldwide including emissions created in producing construction materials[3]. The strides toward attaining zero net carbon emissions and a toxic-free environment include mainstreaming sustainability, efficient energy use, and an integrated waste management system. The focus of the building industry is recently directed towards the development of bio-based materials to be used in the construction of eco and health-friendly building structures. Traditional polymeric foams, such as polystyrene and polyurethane, are commonly used for thermal insulation in infrastructure and housing construction[4]. Nonetheless, such materials are non-renewable, and their production and use involve complex manufacturing processes with substantial energy inputs. Furthermore, it has been proved that they leach out several toxins, which can bio-accumulate in fish and wildlife, presenting a well-documented environmental health problem[5]. Recently, new environmental-friendly bio-based insulation materials are introduced which often require less energy to be produced than traditional materials. The development of sustainable biopolymer materials is a vital mitigation strategy to achieve clean and profitable solutions to the threats of plastic pollution by polymeric foams in our environment.This work is focused on the development of self-growing materials based on Mycelium-Coffee silverskin combinations that could replace traditional insulation materials. It involves the development of sustainable biopolymer composites composed of Lignocellulosic Agrowastes (Coffee silverskin), obtained from roasted coffee seeds, and fungal mycelium derived from non-pathogenic fungal strains (*Pleurotus ostreatus*). *Pleurotus ostreatus* is suitable for growth on coffee silverskin as it produces a diversity of extracellular digestive enzymes, which play important role in lignocellulose degradation. Different mixed proportions of the Agrowaste and mycelium were considered to determine the best condition, which supports the growth of *Pleurotus ostreatus* on Coffee silverskin to produce the composite material with low thermal conductivity and density suitable for thermal insulation applications. Studies on the thermal conductivity revealed that the values of the biocomposites were quite low ranging between 0.04 to 0.12 k(W/mK). Other characterization analyses including mechanical characterization tests and humidity sorption capacity, were also conducted to determine the physico-chemical properties of the developed composite material. The results from the material characterization indicated that the Mycelium-Agrowaste composites can be appropriate for use in building insulation and other suitable applications.

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SYMPOSIUM

April 11 - April 14, 2023

Symposium Organizers
Ciro Chiappini, King's College London
Roey Elnathan, Monash University
Wenting Zhao, Nanyang Technological Unviersity
Yunlong Zhao, University of Surrey

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* Invited Paper
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SESSION SB02.01: Fabrication I
Session Chairs: Róisín Owens and Bozhi Tian
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2011

10:30 AM *SB02.01.01
Fabricating Silicon Nanoneedle Arrays for Cellular Manipulation Nicolas Voelcker; Monash University, Australia

The presentation will review nanofabrication technologies combining colloidal or electron beam lithography techniques with wet or dry etching (wet: metal-assisted chemical etching; dry: deep reactive ion etching) to fabricate arrays of silicon-based nanoneedles and nanotubes with adaptable and programmable designs.

11:00 AM SB02.01.02
A Biodegradable Flexible Porous Silicon Nanoneedles Platform for Topical Delivery of Biologicals Cong Wang, Salman Mustfa, Davide Martella, Chenlei Gu, Priya Vashisth and Ciro Chiappini; King's College London, United Kingdom

Vertically aligned porous Si nanoneedles (pSi NNs) arrays have attracted great interest in biomedicine and is capable for intracellular and intratissue delivery of biomolecules. Extensive research has focused on the construction of pSi NNs on rigid and opaque Si carrier, which restricts potential benefits and limits the functionality of the NNs array in clinical systems. The rigidity of NNs arrays makes the application to tissue less effective as they cannot conform to the non-planar tissue surface, resulting in a mechanical mismatch. Also, the opacity of NNs arrays restrict the possibility of tracking dynamic cellular processes at the nanoneedle interface and real-time assessment of cell behaviour. Herein, we report a robust, rapid and precise methodology to generate well-ordered vertical pSi NNs on flexible and transparent substrates with desired flexibility, tuneable optical transparency, good cell and tissue compatibility. These devices are manufactured by first forming porous silicon nanoneedles on Si carriers through metal assisted chemical etching (MACE) and reactive ion etching (RIE), followed by the formation of an underlying porous silicon and a detachment layer by electrochemical etching (EC), to transfer NNs onto recipient substrates. We explored the role of synthesis parameters including MACE, electrochemical etching and RIE conditions in controlling the porosity, transparency, and geometry (length, diameter, density) of pSi NNs to understand the relationships among the structure, property and performance of NNs to achieve the desired scalability, stability and controllability. This method can generate pSi NNs onto different receiving platforms to unlock the potential of nanoneedles on arbitrary substrates, while preserving the original spatial arrangement (i.e., vertical orientation, geometry, density), while providing a mechanically elastic interface that compensates the large mismatch in contact with the biological systems, allowing for the interaction of NNs for intracellular drug delivery. The tuneable transparency enables the direct observation of real-time interactions which are hampered by the opaque carrier. *In vitro* data showed the efficient delivery of biomolecules into living biological cells and tissues, indicating the utility of this flexible pSi NNs platform for therapeutic applications. Comprehensive demonstrations of various recipient substrates (e.g., polydimethylsiloxane, hydrogel, polylactic acid, medical bandages) indicated this proposed method to be readily adaptable for facilitating the fabrication of high-density nanostructures onto diverse substrates, not limit to the flat surface, to shed the lights on the future applications including clinical systems, nanomedicines, drug delivery, tissue engineering and implantable devices.

11:15 AM SB02.01.04
Magnetically Actuated Single-Cell Microgrippers Robin Liu[1], Wangqu Liu[2], Xin Song[1], Ruili Zhang[2], David H. Gracias[2] and Eric Diller[1]; [1]University of Toronto, Canada; [2]Johns Hopkins University, United States

Microtools that can manipulate single cells can be used to probe tissue heterogeneity and investigate cell mechanobiology questions of broad relevance to tissue engineering and the understanding and development of several diseases. Existing tools are either large or manipulated by hand, limiting throughput and scalability. Here, we report the development of single-cell scale microgrippers with precise and reversible magnetic actuation for cellular manipulation and mechanoresponse study. The microgrippers consist of flexible nanoscale thin-film hinges and rigid arms integrated with magnetic materials. With the appropriate use of sacrificial films, the arms of the grippers can be released from the substrate. Pre-stressed hinges power the microgripper and allow it to self-fold into a half-open pyramidal 3D cavity, small enough to encapsulate a single cell. Using an external magnetic field, we show that we can control the arms to exert force precisely on the encapsulated cell. The motion and force output of microgripper arms are predictable by a theoretical model. We discuss studies of microgrippers capturing and exerting forces on micro-objects such as cells and microbeads and show that the arms of the microgripper can be reversibly actuated over hundreds of cycles. Moreover, the lithographic fabrication and small dimensions of microgrippers allow us to fabricate them *en masse* using wafer-scale scalable processes, improving experimental throughput and cost-effectiveness. We envision that these new microtools can be readily integrated with lab-on-a-chip devices and advance single-cell studies.

SESSION SB02.02: Fabrication II
Session Chairs: Bianxiao Cui and Song Li
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2011

1:30 PM *SB02.02.01
3D Mesoscale Functional Frameworks as Interfaces to Organoids John A. Rogers; Northwestern University, United States

Three-dimensional (3D), sub-millimeter-scale tissue constructs derived from human stem cells are of rapidly growing importance in biological and medical research. Despite their great potential for studies of topics with both fundamental and translational interest, such types of miniaturized, fragile 3D living biosystems cannot be examined easily using conventional methods based on planar technologies, such as conventional multi-electrode arrays. An ideal solution would involve complaint, shape-matched device platforms in 3D geometries that can gently envelop the organoids as multifunctional electronic, optoelectronic, microfluidic, thermal, mechanical and biochemical interfaces. This talk summarizes our recent work on a 3D technology platform of this type, where reversible, engineering control over shapes, sizes and complex geometries can be tailored to match organoids of interest and also to support interconnected collections of them. Various aspects of the materials associated with these systems, and their applications to cortical and cardiac spheroids will be discussed.

2:00 PM *SB02.02.02
Bioelectronic Tools to Study the Gut-Brain Axis Róisín Owens; University of Cambridge, United Kingdom

The human gut microbiome has emerged as a key player in the bidirectional communication of the gut-brain axis, affecting various aspects of homeostasis and pathophysiology. Until recently, the majority of studies that seek to explore the mechanisms underlying the microbiome-gut-brain axis relied almost exclusively on animal models, and particularly gnotobiotic mice. Despite the great progress made with these models, various limitations, including ethical considerations and interspecies differences that limit the translatability of data to human systems, pushed researchers to seek for alternatives. Physiologically relevant in vitro human models, as well as advanced tools to study in vivo animal models, are urgently required. In this talk I'll discuss a new generation of electronic tools, based on organic electronic materials, for understanding the gut-brain-microbiome axis. First, I'll discuss our progress towards generating a complete platform of the human microbiota-gut-brain axis with integrated monitoring and sensing capabilities. Bringing together principles of materials science, tissue engineering, 3D cell biology and bioelectronics, we are building advanced models of the GI and the BBB/NVU, with integrated real-time and label-free electronic monitoring, aiming to elucidate the role of microbiota in the gut-brain axis communication. Second, I'll discuss conformable electronic devices we've developed for both ex-situ measurements of GI tissue from rats, as well as in vivo experiments in live rats. These devices allow highly sensitive monitoring of impedance of the tissue (as an indicator of gut health) as well as the enteric nervous system.

2:30 PM *SB02.02.03
Nanostructured Heterojunctions for Biological Modulation Bozhi Tian; University of Chicago, United States

Biointerface devices can facilitate a deeper understanding of biological dynamics and improve the quality of life. My research group integrates nanoscience with biophysics and bioengineering to study semiconductor-based biointerfaces. We have previously identified and quantified the photothermal, photofaradic, and photocapacitive effects of nanostructured semiconductors, which can be used to modulate electrical activities in neurons and cardiomyocytes at the semiconductor-based biointerfaces.

In this talk, I will describe two heterojunction platforms that have recently been developed in our lab for photostimulation of cells and tissues. A heterojunction plays a crucial role in semiconductor-based devices such as diodes, solar cells, photodetectors, and light-emitting diodes. Compared with homojunction semiconductor devices, heterojunction devices can produce minority carriers (for example, through light illumination) that can be used in critical applications such as energy harvesting. There are, however, still several opportunities for the future development of semiconductor-based heterojunctions in biointerface studies. One of our heterojunctions uses porosity-based silicon structures, while the other uses titania/gold multilayered membranes. I will illustrate the photostimulation mechanisms in cells and tissues for both heterojunctions. Finally, I will present future biointerface developments in our lab.

3:00 PM BREAK

SESSION SB02.03: Biophysics I
Session Chairs: Yannick Coffinier and Nicolas Voelcker
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2011

3:30 PM *SB02.03.01
Membrane Curvature Initiated Mechanotransduction in Cells Bianxiao Cui; Stanford University, United States

Membrane curvature in the range of tens to hundreds of nanometers is involved in many essential cellular processes. At the cell-matrix interface, where the cells make physical contact with extracellular matrices, the membrane may be locally deformed by matrix topography or mechanical forces, and this deformation may actively regulate signal transmission through the interface. We explore nanofabrication to engineer vertical nanostructures protruding from a flat surface. These nanostructures deform the plasma membrane to precisely manipulate the location, degree, and sign (positive or negative) of the interface curvature in live cells. We found that these membrane curvatures significantly affect the distribution of curvature-sensitive proteins and modulate mechanotransduction in live cells. These studies show a strong interplay between membrane curvature and mechanotransduction and reveal molecular mechanisms underlying the connection.

4:00 PM SB02.03.02
Dynamically-Driven Osteoblast Attachment and Stress Fibers Formation on 3D Nano-Architected Scaffold-On-Chip Ottman Tertuliano; University of Pennsylvania, United States

The underlying mechanisms leading to bone density loss, which increases bone fracture susceptibility, are not well understood at the cellular level. Decades of cell studies on relatively compliant 2D surfaces and hydrogels have led us to believe mechanical stimulation of bone can reverse bone loss. To date, an understanding of the stimuli that promote adhesion of bone like cells on 3D surfaces remains elusive . Here we employ tunable 3D nano-architected materials as platforms to examine the effects of different dynamic loading conditions on osteoblast-like (SAOS-2) cell proliferation and adhesion. After cyclic compression, stress fibers formation increased across material systems regardless of constant strain or stress. Increasing loading frequency from 0 to 3Hz resulted in a 50 % increase in stress fibers formation, suggesting that osteoblasts might be most sensitive to changes in loading frequency. These findings demonstrate that 3D architected materials offer an innovative platform to study complex cellular behaviors and can contribute to understanding the role that mechanical stimulation plays in cytoskeletal reorganization.

4:15 PM *SB02.03.03
Mechano-Epigenetics for Cell Engineering Song Li; University of California, Los Angeles, United States

Cell reprogramming into induced pluripotent stem cells or into a completely different lineage has wide applications in regenerative medicine, disease modeling and drug screening. Although the roles of transcriptional factors and chemical compounds in cell reprogramming have been widely studied, the effects of biophysical factors are not well understood. We have demonstrated that micro-structured materials can modulate the morphology of cell nuclei and epigenetic state, which in turn enhances cell reprogramming efficiency. In addition, we show that active forces such as a millisecond squeezing of cell nucleus in microfluidic devices can help overcome the epigenetic barrier and promote cell reprogramming. These findings have important implications in mechano-genomics, and may lead to the development of new technologies for cell engineering.

4:45 PM SB02.03.04
Poster Spotlight: Fast and Accurate Noninvasive Monitroing System for Early Detection of Epithelial-Mesenchymal Transition of Cancer Cell
Andrew Choi, Daeeun Shin and Joon Ho Kang; Korea Institute of Science and Technology, Korea (the Republic of)

A cascade of studies has revealed a distinct form of cell morphogenesis during each stage of cancer. In conquering cancer, the analysis of the physical/mechanical properties (stiffness and volume) which govern the migration, proliferation, differentiation, and cellular transition of the cancer cells experiencing morphogenesis has become more than essential. To analyze the aforementioned properties, various approaches based on the utilization of an atomic force microscope, optical stretching, shear stress, and the particle tracking method have been utilized. However, these approaches are mostly applied to fixed cells only and often require expensive staining reagents or equipment. Furthermore, the invasive manner of these approaches inevitably stresses live-cells overtime during the observation; ergo, it limits the monitoring time and the field of observation.

Acknowledging the current drawbacks of the monitoring system of cancer cell morphogenesis and the physical stresses exposed to individual cancer cells during the observation, we designed/fabricated a microfluidic chip containing a unique micro-pillar structure and suggested a noninvasive method of observing the morphology of individual label-free cancer cells in real-time at a resolution of ~ 100 nm scale. A different intensity level of the cell culture medium mixed with FITC-Dextran 4 kDa inside of our microfluidic chip precisely evaluated the morphology (area, volume, height) of the cultured cancer cell. And the isotropic micro-pillar within the fabricated microfluidic chip perfectly separated the “object filled zone” (height = 23 μm) having the lowest intensity level and the “object cleared zone” (height = 0 μm) having a maximum intensity level. The morphogenesis of the cancer cells during the different stages of epithelial-mesenchymal transition (EMT) upon the treatment of transforming growth factor beta (TGF-β) was clearly observed *via* our fabricated microfluidic chip and the volume changes of individual cells were additionally observed through our noninvasive, label-free approach. With the utilization of our monitoring system, we were able to find the dominant physical parameters of morphogenesis for detecting early EMT action. To this end, we herein, with an eagerness to assuage the grief of patients suffering from cancer, suggest a novel method of exploiting microfluidic chips for precisely observing erratic cancer.

4:50 PM SB02.03.05
Poster Spotlight: Electroactive Nanoinjection Platform for Intracellular Delivery and Genetic Editing Ali-Reza Shokouhi[1], Yaping Chen[1], Nicolas Voelcker[1] and Roey Elnathan[2]; [1]Monash Institute of Pharmaceutical Sciences, Australia; [2]Deakin University, Australia

Nanoinjection—the process of intracellular delivery using vertically configured nanostructures—is a physical route that efficiently negotiates the plasma membrane, with minimal perturbation and toxicity to the cells. Despite the implementation of nanoinjection tools and their assisted analogues in diverse cellular manipulations, there are still substantial challenges in harnessing these platforms to gain access into cell interiors with much greater precision without damaging the cell’s intricate structure. Here, we propose a low-voltage, simple, scalable, and reusable electroactive nanoinjection (ENI) platform based on vertically configured conductive nanotubes (NTs) that allows for rapid influx of targeted biomolecular cargos into the intracellular environment, and for successful gene editing. The localization of electric fields at the tight interface between conductive NTs and the cell membrane drastically lowers the voltage required for cargo delivery into the cells, from kilovolts (for bulk electroporation) to only ≤10 V; this enhances the fine control over membrane disruption and mitigates the problem of high cell mortality experienced by conventional electroporation. Through both theoretical simulations and experiments, we demonstrate the capability of the ENI platform to locally perforate GPE-86 mouse fibroblast cells and efficiently inject a diverse range of membrane-impermeable biomolecules with efficacy of ~63% (antibody), ~56% (mRNA), and ~52% (plasmid DNA), with minimal impact on cells’ viability post nanoscale-EP (>90%). We also show gene editing through the delivery of siRNA that targets TRIOBP, yielding gene knockdown efficiency of ~41%. We anticipate that our ENI platform is set to offer a new path to intracellular delivery with broader selection of cargo and cell types, and will open opportunities for advanced *ex vivo* cell engineering and gene editing.

SESSION SB02.04: Poster Session: Nanotechnologies for Cell Manipulation
Session Chairs: Roey Elnathan and Nicolas Voelcker
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SB02.04.01
Endometrial Organoids Generated within Microfluidic Droplets as a High-Throughput Screening Platform to Overcome Female Infertility
Myeong Jae Baek[1], Leekang Jeon[2], Hyo Min Lee[2] and Yun Kee Jo[1,1]; [1]Kyungpook National University, Korea (the Republic of); [2]Pohang University of Science and Technology, Korea (the Republic of)

Endometrial diseases, such as Asherman's syndrome and endometrial cancer, are the main cause of infertility. Numerous therapeutic drugs have been developed to overcome the endometrial disease-derived infertility, which leads to the increasing necessity of highly accurate screening for new drugs. Organoids, *in vitro* three-dimensional self-assembled constructs that mimic the structural and functional features of the corresponding organ, have emerged as a reliable test-bed to evaluate therapeutic performance and safety of drugs. However, conventional dome cultures have faced to the poor reproducibility and maturity of organoids mainly due to non-uniform supply of medium. Here, we propose a homogenous organoid culture platform using microfluidically fabricated microgels to establish a reproducible test bed for screening of female infertility-associated drugs. The endometrial organoids cultured within the highly uniform microgels exhibited the phenotypic and genotypic features specific to endometrial epithelium, as well as high level of homogeneity. Moreover, we confirm the hormone-responsiveness of endometrial organoid, suggesting the reliability to recapitulate functional features of endometrial tissues. In addition, we confirmed hormone-responsive changes of endometrial organoids in thickness, which suggest the reliability to recapitulate functional features of endometrial tissues. Taken together, our endometrial organoids can be a powerful high-throughput screening platform of drugs for female infertility treatment with further expansion to precise personalized medicine.

5:00 PM SB02.04.02
Photoacoustic Modulation of Alzheimer's Beta-Amyloid Aggregates Structure Using MOF-Derived Carbon Nanoparticles Yonghan Jo, Jinhyeong Jang and Chan Beum Park; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Photoacoustic materials release acoustic waves onto the surroundings by converting absorbed photon energy. In an aqueous environment, light-induced acoustic waves form cavitation bubbles by altering the localized pressure to trigger the phase transition of water from liquid into vaporous phase. Herein, this study report the photoacoustic dissociation of beta-amyloid (Aβ) aggregates, a prominent hallmark of Alzheimer's disease, the most pervasive type of dementia, by metal−organic framework-derived carbon (MOFC) nanoparticles. MOFC nanoparticles, which possess defect-rich and entangled graphitic layers, exhibit a near-infrared (NIR) light-responsive photoacoustic characteristic and generate intense photoacoustic cavitation under tissue-penetrable NIR light irradiation. Our analysis exhibits that photoacoustic cavitation induced by MOFC occurs in the water within milliseconds, and is controllable by the dose of NIR light. The photoacoustic cavitation effectively denatures extremely robust β-sheet-dominant neurotoxic Aβ aggregates into nontoxic debris by altering the asymmetric distribution of water molecules around the amino acid residues of Aβ. Furthermore, the cellular metabolic activity test confirmed that photoacoustic cavitation alleviated Aβ-induced neurotoxicity. This work reveals the therapeutic potential of spatiotemporally controllable NIR-driven photoacoustic cavitation as a modulator of the Aβ aggregate structure.

5:00 PM SB02.04.03
Application of a Reduced Graphene Oxide Mask to Cells as an Effective Barrier to Cytotoxins Jeremy S. Marshall[1], Keith Whitener[2], Dhanya Haridas[2], Woo-Kyung Lee[2] and Matthew Thum[2]; [1]Nova Research Inc., United States; [2]Naval Research Laboratory, United States

Toxic exposure damages tissues and cells. Deployment of a physical diffusion barrier on cell surfaces provides a simple method for inhibiting these cytotoxic effects. We have previously shown that thin (< 250 nm) films of thermally reduced graphene oxide (rGO) have low permeability to small molecules, and that these rGO films can be integrated with cells in a biocompatible manner using gelatin as a cell protectant. Here we use rGO films as diffusion masks to inhibit exposure of various mammalian cell types to a number of cytotoxins, in an effort to gauge the cytoprotective effect of the films. In separate trials, rGO-masked cells were exposed to 70% ethanol and 2.5% glutaraldehyde to determine the effectiveness of the rGO mask. We also evaluated the impact of mask thickness as well as the incorporation of other polymers with the mask on overall cytoprotective effectiveness. Applying LIVE/DEAD stain to cells exposed to 70% ethanol revealed clearly defined areas of live- and dead-stained cells corresponding to the areas with and without rGO coverage, respectively. LIVE/DEAD staining of glutaraldehyde-exposed cells indicated a significant amount of cell death occurring in cells underneath the mask. Further examination revealed isolated spots where the gelatin cell protectant was heavily crosslinked as a result of glutaraldehyde exposure. These results suggest that rGO masks can be strongly protective against certain cytotoxins such as ethanol, whereas others such as glutaraldehyde might penetrate the mask along defects.

5:00 PM SB02.04.04
Synthesis of Bismuth Nanoparticles for Adsorption to a Novel Chemotherapy Mary Elizabeth Kane and Molly Roesch; Rochester Institute of Technology, United States

Magnetically steerable nanoparticles as drug carriers have become increasingly popular in recent years. The ability to selectively guide them to afflicted sites allows for the treatment of diseases such as cancer that have been historically difficult to cure due to high healthy cell death rates. The synthesis of bismuth nanoparticles has been explored for this purpose. Bismuth metal is biologically inert and highly diamagnetic; nanoparticles with a 2 - 5 nm diameter could be directed through the body, including across the blood brain barrier, and subsequently used to remove the drug to which it is conjugated. These nanoparticles will be conjugated with D112, a chemotherapeutic dye that displayed a high selectivity ratio as developed by Kodak but was found to be hepatotoxic in mice. The magnetic steerability of the particles could be useful for the treatment of brain cancer and other cancers that are exceedingly difficult to treat. The most promising synthesis system uses a modified polyol method with a propylene glycol and metformin solvent, bismuth hydroxide feedstock, a D112 fragment as the stabilizer, and hydrazine reductant. Hydrazine drives the burst nucleation of the particles, and an additional stabilizer is used to quickly quench the growing nanoparticles in the desired size range. The reaction pH is critical for reduction and is controlled with sodium hydroxide. This system has achieved relatively stable particles about 13.9 nm in diameter according to Dynamic Light Scattering (Photon Correlation) Spectroscopy. Further tests are needed to optimize the stabilizer ratio, pH, and reaction duration to produce a particle dimension at the desired size. The high cancer to healthy cell death selectivity of the dye, directibility and potential translocation properties across a patent blood-brain barrier coupled with X-Ray detectability of the nanoparticles, and the ability to remove both from the body before liver or kidney failure can set new precedents in the field of cancer treatment and beyond.

5:00 PM SB02.04.06
Poster Spotlight: Fast and Accurate Noninvasive Monitroing System for Early Detection of Epithelial-Mesenchymal Transition of Cancer Cell
Andrew Choi, Daeeun Shin and Joon Ho Kang; Korea Institute of Science and Technology, Korea (the Republic of)

A cascade of studies has revealed a distinct form of cell morphogenesis during each stage of cancer. In conquering cancer, the analysis of the physical/mechanical properties (stiffness and volume) which govern the migration, proliferation, differentiation, and cellular transition of the cancer cells experiencing morphogenesis has become more than essential. To analyze the aforementioned properties, various approaches based on the utilization of an atomic force microscope, optical stretching, shear stress, and the particle tracking method have been utilized. However, these approaches are mostly applied to fixed cells only and often require expensive staining reagents or equipment. Furthermore, the invasive manner of these approaches inevitably stresses live-cells overtime during the observation; ergo, it limits the monitoring time and the field of observation.

Acknowledging the current drawbacks of the monitoring system of cancer cell morphogenesis and the physical stresses exposed to individual cancer cells during the observation, we designed/fabricated a microfluidic chip containing a unique micro-pillar structure and suggested a noninvasive method of observing the morphology of individual label-free cancer cells in real-time at a resolution of ~ 100 nm scale. A different intensity level of the cell culture medium mixed with FITC-Dextran 4 kDa inside of our microfluidic chip precisely evaluated the morphology (area, volume, height) of the cultured cancer cell. And the isotropic micro-pillar within the fabricated microfluidic chip perfectly separated the “object filled zone” (height = 23 μm) having the lowest intensity level and the “object cleared zone” (height = 0 μm) having a maximum intensity level. The morphogenesis of the cancer cells during the different stages of epithelial-mesenchymal transition (EMT) upon the treatment of transforming growth factor beta (TGF-β) was clearly observed *via* our fabricated microfluidic chip and the volume changes of individual cells were additionally observed through our noninvasive, label-free approach. With the utilization of our monitoring system, we were able to find the dominant physical parameters of morphogenesis for detecting early EMT action. To this end, we herein, with an eagerness to assuage the grief of patients suffering from cancer, suggest a novel method of exploiting microfluidic chips for precisely observing erratic cancer.

5:00 PM SB02.04.07
Local Electrochemical Generation of Reactive Oxygen Species for Targeting Cancer Cells Eva Miglbauer[1], Oliya S. Abdullaeva[2] and Eric D. Glowacki[1,3]; [1]Linköping University, Sweden; [2]Luleå University of Technology, Sweden; [3]Central European Institute of Technology, Brno University of Technology, Czechia

Cancer is one of the leading death causes worldwide. Therefore the de,velopment and advancement of anti-tumor treatments, which can be applied supplementary to surgery and also minimize the harm to the patient, are of importance.
One approach to achieve this goal is the application of reactive oxygen species (ROS) -mediated cell death. At elevated concentrations ROS can induce damage to cells due to oxidative stress and can further lead to apoptosis. Due to the high reactivity of especially hydroxyl radicals, the molecules' lifetime is rather short resulting in a very small transport distance and consequently to a confined range in the body. ROS-mediated therapies like photodynamic therapy or Fenton nano particle-based systems are already widely investigated. However, they might be either limited by the penetration depth of the light, lack efficiency due to constrained availability of reactants or suffer from particle aggregation.
To address these problems, we introduce implantable electrochemical devices for direct current anti-tumor treatment with local ROS generation. On a metal cathode H_2O_2 is produced via $2e^-$ oxygen reduction reaction which ensures sufficient availability of peroxide with simultaneous oxygen deprivation. Concurrently, a metal serves as a sacrificial counter electrode and dissolves due to oxidation. The released metal ions and H_2O_2 react in a Fenton-like way, leading to formation of hydroxyl radicals.
Here, we present a novel platform for local ROS delivery based on the electrogeneration of H_2O_2 and metal dissolution followed by radical formation and show proof-of-concept on a A375 cell line.

5:00 PM SB02.04.08
Membrane Targeted Nanoactuators for Cellular Photostimulation Matteo Moschetta[1], Arianna Magni[1,2], Valentina Sesti[2,1], Giuseppe M. Paternò[2,1], Fabio Benfenati[1], Chiara Bertarelli[2] and Guglielmo Lanzani[1,2]; [1]Istituto Italiano di Tecnologia, Italy; [2]Politecnico di Milano, Italy

Photostimulation has recently attracted interest for its possible application in the biomedical field. Several approaches have been proposed to perturbate cellular activity using light in a spatiotemporal precise manner. Organic semiconductors (films, nanoparticles) and photochromic molecules (azobenzene and its derivates) have been revealed to be able to perturb the plasma membrane electrical properties under light stimulation. Light absorption by these materials can be converted into an electrical, mechanical, or thermal stimuli leading to a change of membrane electrical properties. In this regard, Ziapin2 an amphiphilic alkyl-substituted 4,4'-diaminoazobene was recently developed. Ziapin2 inserts properly in the cell membrane persisting in a cis configuration. The insertion in the membrane and the consequent formation of Ziapin2 dimers lead to a shrinkage of the membrane and an increase of the membrane capacitance. Light stimulation induces a cis-trans isomerization with a significant perturbation of the cell membrane potentials, able to trigger action potential firing in excitable cells without directly affecting local temperature. Moreover, capacitance increase after Ziapin2 portioning in the membrane induces stable changes in cellular physiology even under dark conditions. We propose to modify Ziapin2 to obtain a push-pull molecule able to overcome such limitations. The new molecule, named PP-2Pyr, reveals be more soluble in water to improve its biocompatibility and clearance. The substitution of the amino group with a nitro group increases the red-shift absorption avoiding the need to use UV light, not suitable for applications in living cells. Here, we report a study of PP-2Pyr biological functions, going through biocompatibility assays and electrophysiological characterization using an immortalized cell line (HEK cells) as cellular model of investigation. In accordance with the theoretical design of the molecule, the absorbance/emission spectra display a significant red-shift in PP-2Pyr absorbance with a peak at 517nm and an emission peak at 600nm. The biological investigation reveals that PP-2Pyr are able to enter properly in cells after few minutes of incubation with no evident cytotoxicity at two different concentrations (5 and 10μM) until 5 days after the exposure. In addition, after molecule internalization cells exposed to an acute light stimulation lasting 30s do not display evidence of a significant phototoxicity. We also demonstrated that in cells loaded with the compound, millisecond pulses of visible light induce a transient and defined depolarization of the membrane potential followed by a delayed and slight hyperpolarization. The amplitude of the membrane depolarization is dependent of both the light power density and the molecule concentration. Despite further studies of the push-pull photophysical features and biological behavior are in progress, data so far available indicate PP-2Pyr as a promising tool for photo-excitation of cells for both in vitro and in vivo applications.

5:00 PM SB02.04.09
Poster Spotlight: Electroactive Nanoinjection Platform for Intracellular Delivery and Genetic Editing Ali-Reza Shokouhi[1], Yaping Chen[1], Nicolas Voelcker[1] and Roey Elnathan[2]; [1]Monash Institute of Pharmaceutical Sciences, Australia; [2]Deakin University, Australia

Nanoinjection—the process of intracellular delivery using vertically configured nanostructures—is a physical route that efficiently negotiates the plasma membrane, with minimal perturbation and toxicity to the cells. Despite the implementation of nanoinjection tools and their assisted analogues in diverse cellular manipulations, there are still substantial challenges in harnessing these platforms to gain access into cell interiors with much greater precision without damaging the cell’s intricate structure. Here, we propose a low-voltage, simple, scalable, and reusable electroactive nanoinjection (ENI) platform based on vertically configured conductive nanotubes (NTs) that allows for rapid influx of targeted biomolecular cargos into the intracellular environment, and for successful gene editing. The localization of electric fields at the tight interface between conductive NTs and the cell membrane drastically lowers the voltage required for cargo delivery into the cells, from kilovolts (for bulk electroporation) to only ≤10 V; this enhances the fine control over membrane disruption and mitigates the problem of high cell mortality experienced by conventional electroporation. Through both theoretical simulations and experiments, we demonstrate the capability of the ENI platform to locally perforate GPE-86 mouse fibroblast cells and efficiently inject a diverse range of membrane-impermeable biomolecules with efficacy of ~63% (antibody), ~56% (mRNA), and ~52% (plasmid DNA), with minimal impact on cells’ viability post nanoscale-EP (>90%). We also show gene editing through the delivery of siRNA that targets TRIOBP, yielding gene knockdown efficiency of ~41%. We anticipate that our ENI platform is set to offer a new path to intracellular delivery with broader selection of cargo and cell types, and will open opportunities for advanced *ex vivo* cell engineering and gene editing.

SESSION SB02.05: Biophysics II
Session Chairs: Masaru Rao and Andy Tay
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2011

9:00 AM SB02.05.02
Generating Human iPSC-Derived Neurons on Nanowire Arrays—What is the Impact of Nanowire Length, Diameter and Array Pitch on the Cells? Malte Siegmund[1], Jann Harberts[1], Carina Hedrich[1], Wonjong Kim[2], Anna Fontcuberta i Morral[2], Robert Zierold[1] and Robert H. Blick[1,3]; [1]Universität Hamburg, Germany; [2]EPFL (École polytechnique fédérale de Lausanne), Switzerland; [3]University of Wisconsin-Madison, United States Minor Outlying Islands

Nanowire (NW) arrays interfaced with biological cells have been demonstrated to be potent tools for advanced applications such as sensing, stimulation, or drug delivery. Many implementations, however, have so far only been studied with rather robust basic cell models. Here, the generation of human induced pluripotent stem cell (iPSC)-derived neurons was presented on various types of NW arrays despite the sensitive nature of such cells.[1] Specifically, ordered NW arrays featuring combinations of three NW lengths (1, 3, and 5 µm), three array pitches (1, 3, and 5 µm), and two NW diameters (thin/thick pairs, 270–600 nm/590–1070 nm) were utilized in our study. The geometrical characteristics of the different NW arrays majorly influenced the interaction between cell and substrate. Overall, three interaction regimes were found, namely, fakir-like where the cells only are in contact with the very NW tips, encapsulating where the NWs heavily deformed the cell membrane and the nucleus, and intermediate regimes in between. In general, the induced topographical stress on the cells increased with the NW length. The specific settling regimes of the neurons were predominantly governed by the array pitch. Despite the substantial differences in the cellular arrangement, the cultures showed equal proportions of neuronal marker-positive cells (MAP2, NeuN, TH) after 8–9 days of terminal differentiation on the NW arrays (14–15 days in total) compared to planar controls. In addition, the generated neurons [2] were functional with similar kinetics of the action potentials highlighting the equivalence of the NW arrays for neuronal differentiation and rendering them suitable for advanced applications. The herein presented work expands our previous studies on human iPSC-derived neurons grown on (non-)ordered (spiky) NW arrays.[3],[4] In the future, stem cell research and regenerative medicine might substantially benefit from further functionalized NW arrays enabling the well-established mechanisms such as NW-mediated *in vitro* gene editing or intracellular delivery of biomolecules to further control and/or to enhance neuronal differentiation.

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9:15 AM *SB02.05.03
Micro and Nanomechanical Cues in Driving Collective Cell Migration Chwee Teck Lim; National University of Singapore, Singapore

Cells migrating in sheets or large cohorts tend to behave very differently from cells migrating individually, especially under different geometrical features and physical constraints at the micro and nanoscales. Such distinctive behavior of cells migrating in a collective manner underlies several important biological processes such as developmental processes, wound closure, maintenance of intestinal epithelium and cancer metastasis. As such, they can also provide important insights towards better tissue repair, regenerative medicine and even cancer therapy. Here, we characterize the kinematic behavior of epithelial cell cohorts migrating under well defined geometrical and physical confinements in both two- and three-dimensions and at the micro and nanoscales. We also explore the differences in collective cell migration between normal and cancer cells.

9:45 AM SB02.05.04
Mimicking the Cell Signaling Environment with Spatially-Encoded DNA Hydrogels Namrata Ramani, C. Adrian Figg, Alex Anderson, Peter Winegar, EunBi Oh and Chad Mirkin; Northwestern University, United States

Extracellular matrix (ECM) biochemical and biophysical cues play a key role in cellular processes, including cellular proliferation, differentiation, migration, and apoptosis. Yet understanding the specific role among the hundreds of biochemical cues is incredibly complex. Synthetic hydrogels offer a route to recapitulate the ECM through incorporation of user-defined biochemical cues in biologically relevant physical environments. Patterning biomolecules in hydrogels offers a route to visualizing and measuring the role of how spatially organized cue presentation can modulate cell behavior. However, the number of orthogonal bioconjugation chemistries limits the ability to probe the role of many biochemical cues at once. To this end, we have developed a technique for spatially encoding PEG hydrogels with oligonucleotides using thiol-yne photochemistry, where the sequence specificity of DNA enables chemical control over individual patterned domains. Herein we demonstrate that these hydrogels can be rapidly photo-patterned using mask-free digital photolithography with high resolution DNA features (1.5 mm) over centimeter-scale areas, with control over DNA density and feature depth. Moreover, we exploit the sequence dependent properties of DNA to reversibly tether DNA strands, localize protein-DNA conjugates, and bind unmodified proteins with DNA aptamers. Importantly, we observe that localized cell signaling protein-DNA conjugates can selectively activate cells on patterned domains. This work highlights that this approach is capable of isolating biochemical cues allowing one to observe spatially confined cell signaling processes, which may lead to a better understanding, and control, over the complex signaling environments that determine cell fate.

10:00 AM BREAK

10:30 AM *SB02.05.05
Photoacoustic Interface for High Precision Neural Stimulation Chen Yang; Boston University, United States

Neuromodulation at high precision poses great significance in advancing fundamental knowledge in the field of neuroscience and offering novel clinical treatments. Here we reported our research on developing the photoacoustic neural interface based on highly efficient photoacoustic materials and applying them in neural stimulation in vitro and in vivo. Specifically, four different platform technologies with either implantable and noninvasive potentials will be discussed, including fiber based photoacoustic emitters, nanocomposite based photoacoustic films, photoacoustic nanotransducers and optic-generated focus ultrasound (OFUS) based on photoacoustic lenses. Our technologies employ the photoacoustic process, in which pulsed light is delivered into an absorbing layer, generating a localized acoustic wave at ultrasonic frequency. High spatial resolution of sub-millimeter up to single neuron and sub-cellular structures, such as axons and dendrites, have been achieved. Single acoustic pulse of sub-microsecond converted from a single laser pulse of 3 ns is shown as the shortest acoustic stimuli so far for successful neuron activation. Direct photoacoustic stimulation of brain target, electrophysiology recording and behavior responses have been demonstrated in vivo. Specifically, in OFUS, a curved photoacoustic film forms a concave ultrasound lens to achieve the ultrasound focus with a size of 70 micron and a pressure of 21 MPa at the focus transcranially, opening up new opportunities for high precision non-invasive neural stimulation. New insights on the cellar mechanism was obtained using the sonogenetic method. Our work demonstrated that photoacoustic stimulation is a high precision and non-genetic neural stimulation offering various neural interfaces with a non-invasive potential.

11:00 AM *SB02.05.06
Nanoscale Spatio-Mechanical Regulation of the Immune Response in Cytotoxic Lymphocytes Mark Schvartzman; Ben-Gurion University of the Negev, Israel

Cytotoxic lymphocytes – the sentinels of our immune system – differentiate between pathogens and healthy cells by sensing biochemical cues delivered by the ligands expressed on the surface of target cells. Yet, it is becoming progressively clear that lymphocytes also sense physical environmental cues, such as ligand arrangement, mechanical stiffness, and topography. To shed light on this sensing mechanism, we explored the role of the ligand arrangement in the immune function of Natural Killer (NK) cells using nanoengineered stimulating platforms based on patterned arrays of ligands. The first generation of such platforms was based on arrays of nanoimprinted metallic nanodots functionalized with activating ligands. This platform allowed us to discover the minimal spatial requirement of ~ one ligand per sq. micron needed to activate NK cells[1]. The next, more advanced generation of arrays came to examine how the segregation between activating and inhibitory ligands affects the inhibition of activating signaling in NK cells. The platform was based on ordered arrays of nanodots of two metals selectively functionalized with activating and inhibitory ligands, whose segregation was systematically tuned between 0 nm to 40 nm[2]. Surprisingly, we found that inhibition efficiency increased with the spacing between the ligands within the probed range and rationalized this finding by physical modeling of the ligand-receptor binding kinetics.

We also studied the role of environmental elasticity and topography in the function of cytotoxic lymphocytes. Here, we engineered a stimulating platform based on ligand functionalized nanowires. The nanowires deliver chemical, nano-topographical, and mechanical cues, whose combination produces an enhanced immune response of NK cells [3]. While patterned in microdomains, these nanowires spatially guide the cytotoxic activity of NK cells [4]. To separately reveal the effect of each cue, we recently stimulated NK cells and CD8+ T cells on nanowires with varied length and bending moduli and found that these physical parameters of nanowires significantly affect the signaling and the immune function of the lymphocytes [5],[6]. Overall, our work provides an important insight into the way the physical cues regulate the function of NK cells and T cells.

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11:30 AM *SB02.05.07
Cellular Recording in Space and Time via Genetically Encoded Protein "Ticker Tapes" Dingchang Lin; Johns Hopkins University, United States

A longstanding goal in biology is to map the dynamics of cell signaling throughout a tissue or organism. Such maps could reveal mechanisms of spatial and temporal patterning, for example in brain activity, embryonic development, or disease progression. Fluorescent protein-based markers are a powerful tool for mapping gene expression. However, optical imaging of fluorescent reporters faces a tradeoff between temporal and spatial information. Imaging in fixed tissue can report organ-wide patterns of gene expression but typically at only one or, at most, two timepoints. Time-lapse in vivo microscopy can report longitudinal gene expression dynamics but only in a small optically accessible region, limited by light-scatter and optical instrumentation, and in vivo imaging typically requires surgery and/or immobilization of the animal. Theoretical analyses have explored the possibility of encoding organ-wide dynamics in DNA or RNA sequences, but, despite progress, such ideas have not yet been realized. Tools to record the dynamics of large numbers of cells, without constraints from in vivo imaging, could transform our ability to study ensemble dynamics in the nervous system and in other tissues. In this talk, I will share with the audience our recent progress in filling this technological gap via engineering a protein-nanostructure-based recording scheme that can store the history of cellular activities locally within individual cells for retrieval at a much later time. As proof of concept, the history of neural activation was written into growing protein assemblies in live neurons at an unprecedented temporal resolution better than 30 min. The genetically encodable nature of the tool also unlocks the capability to record from a large population of cells simultaneously. In all, this tool offers a tenable solution toward organ-wide cellular level activity mapping in space and time, which is hitherto not achievable.

SESSION SB02.06: Drug Delivery
Session Chairs: Mark Schvartzman and Chen Yang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2011

1:30 PM *SB02.06.01
Nanostructures for Probing and Transfecting Living Cells Christelle Prinz; Lund University, Sweden

Interacting with cells in a minimally invasive manner is key to performing longitudinal studies in biomedicine. Nanotubes and nanostraws are increasingly used to transfect cells with better efficiencies and cell viabilities compared to existing transfection methods (liposomes, viral vectors and electroporation) . Here, a review of our work using nanowires and nanostraws for biosensing and transfection will be presented.

2:00 PM SB02.06.02
mRNA Delivery by Laser-Induced Poration Using Porous Silicon Nanoparticles Chantelle Spiteri, Valeria Caprettini, Martti Kaasalainen and Ciro Chiappini; King's College London, United Kingdom

A diversity of physical, chemical and viral methods have been developed to transport membrane-impermeable payloads into the cells leading to great progress in stem cell research, regenerative medicine and therapeutic applications. However, most of these techniques are for bulk poration rather than single-cell resolution; therefore, understanding individual cells remains a challenging platform to explore for tissue engineering and modelling human development *in vitro***.** One of the physical techniques investigated for spatial and temporal control over intracellular delivery is optoporation. Optoporation is a light-mediated technique whereby a high-intensity laser pulse induces transient pores and hence increases the cell membrane permeability allowing exogenous cargo molecules to diffuse and access the cell. Moreover, nanomaterials are used to enhance the coupling of the focused light leading to greater optoporation efficiency and also preserving the cell's viability by reducing the laser energies required for cell membrane permeabilization. Yet, the commonly used nanomaterials for optoporation such as gold and carbon-based nanoparticles are not biodegradable and can be genotoxic limiting their applicability in advanced therapies and modelling.

To overcome these challenges, we fabricated biodegradable and biocompatible mesoporous silicon nanoparticles of approximately 300 nm through electrochemical etching. Assessing the toxicity of the nanoparticles revealed that a 24-hour interaction between MCF-7 breast cancer cells and nanoparticles of concentrations up to 150 µg/mL showed no significant impact on cell death or proliferation. Coupling the nanoparticles with a femtosecond laser at 800 nm resulted in a 40% delivery efficiency of propidium iodide into the targeted cells within a 2D single-cell layer system. This patterned delivery of propidium iodide was also achieved in individual cells making up the 3D cancerous spheroid model. The short-term viability (30 minutes) and subsequently the long-term viability post-optoporation is demonstrated in the 2D system through calcein-AM retention and the transfection and expression of eGFP mRNA respectively. Altogether, we demonstrate that porous silicon nanoparticles coupled with the femtosecond laser in the NIR region attain spatial-selective delivery and expression of the genetic material. Our nano-sensitised optoporation paves the way toward patterned mRNA delivery in a 3D cell system which holds promising potential for biomedical research and cell-based engineering applications.

2:15 PM *SB02.06.03
Biodegradable Silicon Nanoneedles for Ocular Drug Delivery Chi Hwan Lee[1], Dong Rip Kim[2] and Woohyun Park[1]; [1]Purdue Univ, United States; [2]Hanyang University, Korea (the Republic of)

Ocular drug delivery remains a grand challenge due to the complex structure of the eye. Here, we introduce a unique platform of ocular drug delivery through the integration of silicon nanoneedles (Si NNs) with a tear-soluble contact lens. The Si NNs can penetrate into the cornea in a minimally invasive manner and then undergo gradual degradation over the course of months, enabling painless and long-term sustained delivery of ocular drugs. The tear-soluble contact lens can fit a variety of corneal sizes and then quickly dissolve in tear fluid within a minute, enabling an initial burst release of anti-inflammatory drugs. We demonstrated the utility of this platform in effectively treating a chronic ocular disease, such as corneal neovascularization (CNV), in a rabbit model without showing a notable side effect over current standard therapies. This platform could also be useful in treating other chronic ocular diseases.

2:45 PM SB02.06.04
Efficient Non-Viral CAR-T Cell Generation via Silicon-Nanotube-Mediated Transfection Yaping Chen; Monash University, Australia

The advances in engineered nano–bio cellular interfaces—driven by vertically configured nanostructure arrays—have fostered unprecedented progress in modulating and regulating cellular processes at the nanoscale. In particular, nanoinjection has been developed to realize delivery of diverse bioactive payloads into a wide range of cells and tissues both *in vitro* and *in vivo*. Nevertheless, progress has been slow in relation to nanoinjecting primary T lymphocytes, which are central players during adaptive immune responses and hold great clinical potential in fighting diseases including cancer. In particular, chimeric antigen receptor (CAR)-T therapy holds great promise in treating cancer and other diseases; but the current viral-based method raises a significant cost and safety hurdle. In this study, we show for the first time successful CAR transfection into primary T cells via vertically aligned silicon nanotube (SiNT) arrays. By co-culturing with target lymphoma Raji cells, we prove that transfected CAR-T cells can suppress Raji cell growth, indicated by significant increase in effector:target (E:T) ratio (by up to 30.7-fold). SiNT-generated CAR-T cells using non-activated (N_SiNT) T cells perform comparable or even higher lymphoma suppression compared with pre-activated (A_SiNT) T cells, indicating that SiNT-mediated transfection can bypass the requirement of antigen stimulation and preserve higher immune potency. N_SiNT CAR-T cells produce significantly higher amounts of cytotoxic agents, demonstrating stronger inhibition on Raji cells' luciferase expression, compared to their A_SiNT counterparts or those generated by electroporation, particularly with a larger E:T ratio (4:1) and a longer co-culture period (72 h). The results demonstrate the capacity of SiNT-mediated transfection of generating effective anti-lymphoma CAR-T cells. Considering the growing potential of cell-based therapies, we expect that a non-viral nanoinjection platform such as ours will facilitate the full realization of their therapeutic promise.

3:00 PM BREAK

3:30 PM *SB02.06.05
High Aspect-Ratio Nanostructures for Genetic Engineering Andy Tay; National University of Singapore, Singapore

Background: Chimeric antigen receptor T cell (CAR-T) therapy is a treatment using genetically reprogrammed T cells for cancer immunotherapy. However, it is challenging to transfect T cells with high efficiency while preserving critical biological polyfunctionalities. Viruses and bulk electroporation offer low transfection efficiency, induce aberrant cytokine productions, and delay cell proliferation, leading to less efficacious and more costly treatments. Emerging methods such as nanoparticles suffer from poorly controllable intracellular release of cargo while microfluidics run into high operating costs from use of biomolecule concentrates in continuous flow.

Methods: Here, we describe a high aspect-ratio nanostructure-based method named magnetic nano-electro-injection (MagNEI) platform for T cell immuno-engineering. During MagNEI transfection, localized electric fields transiently open membrane pores of cells magnetically stabilized onto hollow nanochannels. The electric fields then electrophoretically inject DNA into T cells. Once DNA enters the cells, magnetic forces are applied *via* FDA-approved Dynabeads to preferentially transport them into the nuclei.

Results: MagNEI provided up to 90/80/50% delivery efficiency for high molecular weight proteins, mRNA, and DNA. The long-term, stable expression of DNA plasmids was 3-4 folds better than gold standard AAVs and Lonza bulk electroporation. While viruses and Lonza bulk electroporation adversely reduced T cell proliferation by 30% and T cell migration by 80%, MagNEI did not. MagNEI also did not cause significant increase in IL-6 cytokine productions or changes in gene expression relative to untreated control T cells.

Conclusions: Our results demonstrate the technical and biological superiority of MagNEI as a transfection method. We envision that the use of MagNEI platform can overcome transfection difficulties for genetic engineering of primary immune cells to advance CAR-T therapy.

4:00 PM SB02.06.06
Magnetically-Induced Brownian Motion of Iron Oxide Nanocages in Cells and Their Application for Efficient siRNA Delivery Min A. Kang[1], Justin Fang[1], Aloka Paragodaarachchi[1], Keita Kodama[2], Yuko Ichiyanagi[2] and Hiroshi Matsui[1,3]; [1]Hunter College-CUNY, United States; [2]Yokohama National University, Japan; [3]Cornell University, United States

While nanoparticle carriers have been used widely to deliver therapeutic RNAs for gene therapy, overcoming endosomal escape to enhance transfection efficiency remains a major challenge. Most RNA carriers are trapped in endosomes, fused with lysosomes, and degraded before they can be released into the cytoplasm, which is the major reason of low transfection efficiency.
Lipids have been the golden standard for transfection reagents, and it has been reported that lipid nanoparticles could alter intracellular transport along cytoskeleton and avoid lysosomal degradation due to their random Brownian movement. Thus, we developed the concept that efficient endosomal escape of nanoparticle carriers and the improvement of efficiency of therapeutic reagent delivery could be achieved if their Brownian motion and diffusion could be externally optimized to release them to cytoplasm.
Superparamagnetic iron oxide nanoparticles (SPIONs) can undergo two types of magnetic relaxations in alternating magnetic fields (AMFs). At a certain range of frequencies of AMFs along with specific sizes of SPIONs, the phase difference of the oscillating magnetic moment with respect to the field direction of AMF can be dissipated by either Néel relaxation or Brownian relaxation. Here, we investigated whether superparamagnetic cage-shaped iron oxide nanoparticles (IO-nanocages), previously demonstrated to carry payloads inside the cavity for therapeutic molecular delivery, can be controlled to undergo magnetically-induced Brownian motion, dependent on size at the conventional AMF frequency of 335 kHz. The combination of SQUID (superconducting quantum interference device) measurement and computational simulation of the magnetic relaxation time for superparamagnetic IO-nanocages reveals their size-sensitivity to these two relaxation modes.
The motivation for this application is to trigger endosomal escape by externally-driven Brownian motion of nanoparticles and deliver siRNAs to cytoplasm efficiently. Superconducting quantum interference device (SQUID) measurements reveal the size-sensitivity of Brownian relaxation, and magnetically-driven Brownian motion of IO-nanocages improved siRNA delivery efficiency in cells by reducing luciferase expression to 51% while endosomal membranes were observed to be compromised to release IO-nanocages to cytoplasm in the presence of AMF. This magnetic delivery system was also applied to deliver anti-cancer therapeutic siRNAs, silencing mGluR5 expression in human and mouse osteosarcoma cell lines, and the proliferation of both human and mouse osteosarcoma cells decreased significantly to 20% with the silencing efficiency via magnetic delivery of IO-nanocages. This outcome suggests that this magnetic delivery method can be further used in future clinical applications in cancer therapy, and we are also exploring the applications of IO-nanocages to intracellular mechano-responsive applications such as mechanotransduction with magnetic fields.

4:15 PM *SB02.06.07
Deterministic Mechanoporation for Intracellular Delivery Masaru P. Rao; University of California, Riverside, United States

Microfluidic intracellular delivery approaches based on plasma membrane poration have shown promise for addressing the limitations of conventional cellular engineering techniques in a wide range of applications in biology and medicine. However, the inherent stochasticity of the poration process in many of these approaches often results in a tradeoff between delivery efficiency and cellular viability, thus potentially limiting their utility. Herein, we present a novel microfluidic device concept that mitigates this trade-off by providing opportunity for deterministic mechanoporation (DMP) of cells en masse. This is achieved by the impingement of each cell upon a single needle-like penetrator during aspiration-based capture, followed by diffusive influx of exogenous cargo through the resulting membrane pore, once the cells are released by reversal of flow. Massive parallelization enables high throughput operation, while single-site poration allows for delivery of small and large-molecule cargos in difficult-to-transfect cells with efficiencies and viabilities that exceed both conventional and emerging transfection techniques. As such, DMP shows promise for advancing cellular engineering practice in general and engineered cell product manufacturing in particular.

4:45 PM SB02.06.08
Nanoneedle-Mediated Gene Editing in Epidermolysis Bullosa Fibroblasts Ciro Chiappini, Salman Mustfa, Marija Dimitrievska, Cong Wang, John A. McGrath and Joanna Jackow; King's College London, United Kingdom

Gene therapy can address the unmet clinical need for non-invasive treatments in dystrophic epidermolysis bullosa(DEB), a rare skin disease associated with trauma-induced erosions and blisters, which progress to chronic wounds and cancer. All forms of DEB, whether autosomal dominant(DDEB) or recessive(RDEB), result from mutations in the *COL7A1* gene, which encodes type VII collagen(C7). For RDEB, a small number of early phase gene therapy trials has been reported[1,2] while DDEB treatments are limited. In DDEB, glycine substitutions within the C7 triple helix compromises C7 assembly through dominant-negative interference.

Base editing is a highly effective approach to restore functionality of the mutated allele. The targeted nature of this approach is well suited for gene therapy for RDEB, if supported by an effective delivery strategy. Nanoneedles are a “bed of nail” substrate that interface tightly with cells and the superficial layers of tissues to directly transfer payloads with minimal perturbation of cell function[3]. Intracellular delivery using nanoneedles, known as nanoinjection, yields efficient transfection for a broad range of nucleic acids including RNAs in primary, hard to transfect cells[4] and to the exposed layers of tissues[5]. Nanoinjection is highly biocompatible, with minimal cell toxicity and perturbation of cell function, making it an ideal candidate for efficient base editing in DEB cells[6].

Here we develop nanoinjection for base editing of DEB fibroblasts. Nanoinjection to RDEB fibroblasts is highly efficienct without observable toxicity, providing significant improvement over cationic lipid transfection. We edited fibroblasts form an RDEB patient harbouring the compound heterozygous mutation for c.5047C>T (p.Arg1683*) and c.7344+4G>A (IVS95+4G>A). Our nanoinjection approach of adenine base editing (ABE) targeted the c.5047C>T mutation using conical nanoneedles (5µm height, 600nm base, 20nm tip, 2µm spacing).
The fibroblast cultured on nanoneedles showed retained morphology, high viability and proliferative capacity indicative of good cytocompatibility. We compared the ABE7.10 and ABE8e editors (mRNA + gRNA) targeting the c.5047C>T mutation loaded at different ratios and concentrations of mRNAs and gRNA on nanoneedles, using lipofection as control. Nanoneedles interfaced with the cells delivered the ABEs directly to the intracellular space. At 48h, the optimal editing efficiency for ABE7.10 by nanoinjection was 17%, as compared to 6% by lipofection. When using ABE8e nanoinjection, editing efficiency increased to 46%, resulting in 82% total of the wild-type G allele as compared to 65% for lipofection. The edited cells were expanded to assess C7 production DEJ assembly in organotypic skin models *in vitro*.

SESSION SB02.07: Biosensing
Session Chairs: Andrew Holle and Peng Shi
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2011

8:30 AM *SB02.07.01
FluidFM Technology—Pushing Boundaries in Single Cell Omics and Genome Engineering Pascal Behr; Cytosurge AG, Switzerland

Pascal holds a doctoral degree from ETH Zurich in the field of biomedical engineering. He co-founded the Swiss deep tech company Cytosurge and holds the role of CEO in the company. Cytosurge is developing FluidFM technology, combining atomic force microscopy principles with innovative micro fluidics. The company provides state of the art solutions in the areas of genome engineering and time resolved single cell omics.

9:00 AM SB02.07.02
Engineering a Nanobiopsy Platform for Non-Destructive Biosensing in Tissue Chenlei Gu[1,2], Davide Martella[1], Cong Wang[1] and Ciro Chiappini[1,2]; [1]King's College London, United Kingdom; [2]London Centre for Nanotechnology, United Kingdom

Nowadays, a broad range of molecular assays, e.g., lipids, nucleic acids, and proteins, designed for cell/tissue samples have been established for basic biology and diagnostics. However, most such assays are destructive, and thus limited in following the dynamics of the underlying processes. Hence, the challenge remains, of monitoring molecular dynamics within live systems over time.

Nanoneedles are arrays of vertical, high-aspect-ratio nanostructures, and thanks to the development of microfabrication technology, both the geometry, structure and flexibility of nanoneedles can be well-controlled and fine-tuned at nanoscale resolution, which serves as versatile platforms for transmembrane delivery and intracellular interrogation. Facilitated by nanobiopsy, which is a non-destructive, controllable and label-free method for capturing and retaining intracellular molecules after interfacing the tissue samples, nanoneedles thus can probe individual biomarkers or small biomarker panels. Moreover, through the repeated sampling of the same cell or regions of tissue, nanoneedles also can provide information on the temporal evolution of their different molecular profiles.

My project aims to develop a pipeline for the non-destructive and longitudinal molecular sampling of living systems using nanoneedles. We have fabricated types of nanoneedles with both opaque and a tunable transparency substrate, explored methodologies for functionalizing nanoneedles for cell access and molecular retention, established the automatic nanobiopsy platform to interface the nanoneedles with tissues in situ, and strategies to retrieve the immobilized intracellular molecules for ex-situ analysis without impacting the tissue. We have tested the nanobiopsy platform in frozen tissue and extended the approach to generate molecular replicas from fixed and fresh live tissues. We have developed staining assays to assess the lipophilic components and nucleic acids in the tissue replicas, and identified the optimal conditions for capturing molecules from the mouse brain.

9:15 AM *SB02.07.03
Longitudinal Single Cell Analysis Enabled by Nanopipettes Paolo Actis, Fabio Marcuccio, Chalmers Chau and Lucy Stead; University Of Leeds, United Kingdom

Physiological and pathological processes within the human body are controlled by complex cell-cell interactions within the context of a dynamic microenvironment. The ability to dynamically measure phenotypes (i.e. gene expression, protein activities, ion fluctuations, signaling) at the single cell level is key to understanding cellular behaviour in a complex environment.
I will present the integration of nanopipettes with scanning probe microscopy techniques to enable the extraction of genetic material from living cells. I will discuss the longitudinal profiling of brain cancer cells to characterize the transcriptional reprogramming at the single cell level after chemotherapy and radiotherapy.

9:45 AM SB02.07.04
NV-Centers Nanodiamonds to Study Oxidative Stress in the Male Germ Line Arturo Elias Llumbet[1,2], Aldona Mzyk[1], Claudia Reyes San Martín[1], Thamir Hamoh[1] and Romana Schirhagl[1]; [1]UMC Groningen, Netherlands; [2]University of Chile, Chile

Nanodiamonds with structural Nitrogen-Vacancy (NV) defects can translate magnetic noise in their surroundings into easily detectable fluorescent signals. This makes them ideal sensors for short-lived free radicals produced in biological systems. Free radicals are a crucial group of Reactive Oxygen Species (ROS) whose quantification offers pivotal insights into oxidative stress-related conditions such as cancer, aging, drug response, and infertility. We use NV-centers nanodiamonds for the magnetometric detection of free radicals at a single-cell level with subcellular resolution. We have successfully applied diamond magnetometry in all the conditions mentioned above. Now, we are focused on the connection between oxidative stress, aging, and male infertility. Various socioeconomic factors have contributed to the established trend in western countries of delaying fatherhood, which is linked to reproductive problems such as subfertility, congenital anomalies, and neuropsychiatric disorders in the offspring. Studies conducted on sperm samples offer a perspective limited to the outcome of age- and oxidative stress-related mechanisms that affect spermatogenesis, completely ignoring what happens to the precursor germ cells of spermatozoa. Germ cells reside inside the seminiferous tubules of the testicles and experience complex differentiation processes that are sensitive to free radicals and other ROS. Using the D-Galactose mouse model of accelerated aging, we studied free radical production in different types of germ cells and also in Sertoli cells, the nurse cells for spermatogenesis. We think that the single-cell reporting capacity of diamond magnetometry applied for the first time to the complex scenario of the male germ line is attractive for the field of Reproductive Medicine and highlights the versatility of nanodiamonds as nanoscale biosensors.

10:00 AM BREAK

SESSION SB02.08: Bioelectronics I
Session Chairs: Paolo Actis and Pascal Behr
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2011

10:30 AM *SB02.08.01
“Brain” on a Chip—Toward a Precision Neuroelectronic Interfaces Hongkun Park; Harvard Univ, United States

Deciphering the brain's functional connectome requires new experimental tools that are sensitive enough to quantify the strength of individual synaptic connections yet also highly scalable to simultaneously measure and control a large number of mammalian neurons with single-cell resolution. In this presentation, I will describe our efforts to combine the advances in nanoscience and semiconductor technology to develop new electronic interfaces that can perform high-fidelity recording and stimulation of thousands of networked mammalian neurons in parallel. The same interface can also be used for multi-parametric functional imaging of other living cells and tissues, enabling fully electronic high-throughput live-cell assays for phenotypic screening. This technology should benefit a broad range of functional interrogations of cell networks and may lead to improved brain-machine interfaces.

11:00 AM SB02.08.02
Seeing the Sound—A Non-Invasive Acoustic Neural Interface Facilitated by Mechanoluminescent Nanomaterials Xiang Wu, Fan Yang and Guosong Hong; Stanford University, United States

Understanding the complex neural circuitry and its correlation to specific behaviors requires spatially and temporally precise modulation of neuron subtypes in certain brain regions. For decades, neural stimulation has predominantly been achieved by traditional electrical stimulation electrodes. More recently, optogenetics, which utilizes visible light to achieve neural modulation by genetically expressing microbial opsins in mammalian cells, has gained great popularity due to its rapid and precise control of neural activities. However, owing to the limited tissue penetration of visible light, invasive craniotomy and intracranial implantation of tethered optical fibers are usually required for *in vivo* optogenetic modulation.

Here, we report a new method termed ‘sono-optogenetics’, which provides non-invasive optogenetic neuromodulation in the brain without any scalp incision, craniotomy, or brain implant. Sono-optogenetics delivers nanoscopic light sources—mechanoluminescent nanoparticles—via the endogenous blood circulation, and provides millisecond-timescale switching of 470 nm light emission for optogenetic neuromodulation via brain-penetrant focused ultrasound. Furthermore, the mechanoluminescent nanoparticles could be recharged by an external photoexcitation light in superficial blood vessels during circulation, enabling repetitive through-scalp optogenetic stimulation and inducing behavioral responses in live mice. Unlike the conventional ‘outside-in’ approaches of optogenetics with fiber implantation, our method, which combines non-invasive ultrasound excitation and intravenous delivery of mechanoluminescent nanoparticles, provides an ‘inside-out’ approach to deliver nanoscopic light emitters via the intrinsic circulatory system and switch them on and off at any time and location of interest in the brain. **This work was published in PNAS (Wu, X. et al. Sono-optogenetics facilitated by a circulation-delivered rechargeable light source for minimally invasive optogenetics. *Proc. Natl Acad. Sci. USA* 116, 26332–26342 (2019)) and was awarded the Science and PINS Prize for Neuromodulation in 2020.**

To further optimize this acoustic neural interface and extend its utility, we developed a biomineral-inspired suppressed dissolution approach to synthesize multicolor mechanoluminescent nanoparticles with diameters down to 20 nm and bright emissions that cover the entire visible spectrum, including $Sr_2MgSi_2O_7$:Eu, Dy (470 nm), ZnS:Cu, Al (534 nm), ZnS:Mn (578 nm), and $CaTiO_3$:Pr (610 nm). We were able to, for the first time, visualize the ultrasound-mediated localized light emission produced by the nanoscopic light source in the vascular systems of multiple mouse organs, including kidney, liver, and brain. Specifically, upon non-invasive transcranial focused ultrasound stimulation, the mechanolumiescence generated inside the brain was sufficient to activate channelrhodopsin-2 (ChR2)-expressing neurons in live mice. **This work was recently published in JACS (Yang, F. and Wu, X. et al. Palette of rechargeable mechanoluminescent fluids produced by a biomineral-inspired suppressed dissolution approach. *J. Am. Chem. Soc.* 144, 18406–18418 (2022)).**

In summary, sono-optogenetics not only represents a non-invasive acoustic neural interface for neuromodulation, but also provides a unique tool of generating localized visible light inside highly scattering biological tissues for many optical biotechniques, such as fluorescence imaging, light-controlled gene-editing, and photodynamic therapy.

11:15 AM *SB02.08.03
Pushing Limits of Neural Electrodes for Intracortical Recording and Stimulation Chong Xie; Rice University, United States

I will present our efforts in ultraflexible neural electrods and recent progress in scaling-up their channel count and density. I will also discuss using these electrodes for recording and stimulation in animal models.

11:45 AM SB02.08.04
Achieving Cell Optostimulation with Membrane-Targeted Molecules Arianna Magni[1,2], Matteo Moschetta[1], Giuseppe M. Paternò[2,1], Chiara Bertarelli[2,1], Luca Beverina[3], Fabio Benfenati[1] and Guglielmo Lanzani[1,2]; [1]Istituto Italiano di Tecnologia, Italy; [2]Politecnico di Milano, Italy; [3]Università degli Studi di Milano-Bicocca, Italy

In the last years, different non-genetic approaches have been proposed to obtain the light-driven modulation of cellular activity. A variety of different photoactive materials can be exploited as photo transducers, converting the light stimulus into a mechanical, thermal, electrical, or chemical stimulus that can be recognized by cells and tissues.

We are interested in using small organic molecules as photoswitches. Molecules have been designed and synthesized to satisfy the following requirements: (i) absorb light in the visible or near-infrared window of the spectrum; (ii) spontaneously and efficiently partition into the lipid bilayers owing to their amphiphilicity, (iii) exhibit low toxicity in dark condition and preferentially also under illumination.

The observation and the evaluation of the photoinduced effects of the different molecules on both HEK-293 cells, primary neurons, and bacteria strains, together with the photophysical characterization of the aforementioned molecules, lead to the identification of different light-driven mechanisms that allow us to control and manipulate the cell activity.

The photoinduced effects observed on cells are found to be related, for instance, to (i) the thinning or thickening of the membrane due to conformational changes in the molecules, (ii) the increase of the membrane permeabilization, and the formation of pore-like structures likely due to the lipid peroxidation following the photosensitization of singlet oxygen within the cell membrane, (iii) the rearrangement of the charges adsorbed to the membrane due to variations in the molecular dipole moment.

SESSION SB02.09: Roundtable Panel Discussion
Session Chairs: Ciro Chiappini and Wenting Zhao
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2011

1:30 PM ROUNDTABLE DISCUSSION

2:30 PM BREAK

SESSION SB02.10: Emerging Applications
Session Chair: Chong Xie
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2011

3:30 PM *SB02.10.02
Mechanical Memory in Cells Migrating Through Nanostructured Confining Microenvironments Andrew Holle[1,2]; [1]Mechanobiology Institute, Singapore; [2]National University of Singapore, Singapore

The mechanical architecture of extracellular matrix (ECM) presents variable levels of stiffness and confinement to nearly all the cells in the body. Migrating cells are exposed to this confinement during diverse biological processes such as embryonic development, cancer metastasis, and immune cell homing, all of which involve cellular relocation from one mechanical niche to another. During this process, cells are also exposed to nanoscale cues in the form of matrix topography, which can be aligned, orthogonal, or random to the direction of migration. While many studies have explored the cellular response to externally-applied compression, it remains unclear why cells actively decide to enter highly confined spaces. We propose that cells retain mechanical memory of their microenvironmental stiffness, and that this memory plays an active role in their migratory potential. Multiple cell types that show non-permanent responses to substrate stiffness (e.g. cancer cells, fibroblasts) were cultured on soft (1 kPa) or stiff (34 kPa) polyacrylamide hydrogel substrates or glass. Cells were exposed to either 3 or 7 days of mechanical dosing prior to transfer to glass coverslips or into microchannel chips. Microchannel chips were fabricated via a two-step photolithography process that results in microchannels with heights of 10 µm, lengths of 150 µm, and widths between 3 and 10 µm. Nanostructuring of microchannel imprints on silicon wafers was performed to provide parallel, orthogonal, or random nanoscale cues. Cells were then assayed for their ability to spread and migrate on 2D surfaces, as well as interact with and enter confinement in diverse microchannel environments. Mechanically-dosed MDA-MB-231 cancer cells did not show any changes in cell or nuclear morphology after dosing on soft, stiff, or glass substrates. Migration speed and the ability to enter confinement also was unaffected by mechanical dosing. On the other hand, HFF-1 fibroblasts were able to retain a significant mechanical memory of their dosing. HFF cells were found to spread on glass significantly slower when they had been preconditioned on 1 kPa substrates compared to either 34 kPa substrates or glass. This effect was primarily in the initial spreading phase, as cells reached equivalent levels of spread area after four hours. Fibroblasts dosed on soft substrates were also found to migrate significantly faster than those on stiff or glass substrates. Interestingly, the amount of time cells were dosed enhanced this difference in migration speed. While dosing did not affect the overall number of cells interacting with confining microchannels, fibroblasts dosed on soft substrates were able to permeate through both moderate (10 µm) and extreme (3 µm) confinement faster than cells dosed on stiff or glass substrates. As a wide variety of cells must navigate diverse microenvironments, our results suggest that the stiffness of the 'home' niche may convey important mechanical advantages to cells migrating through confining interstitial spaces in vivo, and that this can influence subsequent migration on or through nanostructured surfaces. Future work on the precise cellular transcriptome and machinery found in dosed fibroblasts but not dosed cancer cells will likely reveal clinically relevant information for targeting metastasizing cancer cells.

4:00 PM SB02.10.03
Tunable Superhydrophobic Microwell Array Devices for High-Throughput Culture of 3D Cancer Models Maria Lopez Cavestany[1], Kalana Jayawardana[1], Olivia Wright[1], Noah Reckhorn[1], Tin Nguyen[1], Alberto Esteban Linares[1], Dmitry Koktysh[1], Daryl Briggs[2], Charles P. Collier[2], Dale Hensley[2], Deyu Li[1] and Michael King[1]; [1]Vanderbilt University, United States; [2]Oak Ridge National Laboratory, United States

3D cancer models offer higher physiological relevance than 2D cancer models as they are able to recapitulate tumor architecture with higher fidelity. Products to produce cancer spheroids, such as the Aggrewell800, are available commercially but rely on user coating with an anti-adherence solution, have difficulty forming tight spheroids in some cell lines, and provide only two microwell sizes. Cancer cells are known to cluster in circulation, conferring higher shear and treatment resistance, in addition to increased metastatic potential compared to single cells. Current methods in the literature to produce *in vitro* models of circulating tumor cell clusters or microemboli (CTM) are inconsistent and lack the ability to control cluster size. The goal of our study was to utilize microfabrication techniques to design a chip with tunable microwell array and a superhydrophobic surface at the bottom to achieve a device that can produce a range of 3D cancer models. Two different superhydrophobic array devices (SHArD) have been implemented to reliably culture a spheroid model (SHArD-S) and a CTM model (SHArD-C) *in vitro.*

Superhydrophobic surfaces were fabricated by spin coating a ZnO nanoparticle solution in MQ water onto a 3" Si wafer. Wafers were annealed and then baked at 90C for 4 hr while submerged in a zinc nitrate hexahydrate and HMTA bath to grow nanorods. ZnO nanorod thin film was characterized via SEM to be highly uniform and reproducible. The nanorods were randomly oriented on the wafer surface and had an average length of 500µm. Width ranged from 40nm to 100nm, corresponding to the size of the initial nanoparticle powder. Ultrathick SU8 lithography was performed for the SHArD-S to obtain a microwell wall height of about 400µm with an aspect ratio of 3. Lines were spaced 800µm apart resulting in square sections of 650x650µm^2. For the SHArD-C, the adhesion promoter OmniCoat was spin coated onto the wafer surface. SU8 lithography was done to create a 75µm thick grid, resulting in 100 x 100µm^2 microwells. The final step for both devices was to deposit a layer of non-adherent polymer via C_4F_8 plasma polymerization in an Oxford PlasmaPro100. Coating was confirmed to be homogenous and maintain surface nanoroughness via SEM and water contact angle (WCA) measurements. The static WCA of the nanorods coated with the non-adherent polymer was 167°. The dynamic WCA were 165.2° and 168.6° for the advancing WCA and receding WCA, respectively. Microfabrication processes and characterization were carried out at the VINSE cleanroom and the CNMS cleanroom at Oak Ridge National Laboratories.

For spheroid formation, the colorectal cancer cell line HCT116 was plated for 4 days with in the microwells at 2.5k, 5k, and 7.5k cells per microwell in the SHArD-S and the Aggrewell800 for comparison. Spheroids were observed via confocal microscopy by staining with DAPI to quantify compactness. Spheroids cultured in the SHArD-S were significantly less round and more compact than those cultured in the Aggrewell800, more closely resembling tumors in the body. Additionally, spheroids were exposed to physiologically relevant fluid shear stress (FSS) of 188 s^{-1} using a cone-and-plate viscometer to assess cell:cell adhesion stability. Spheroids grown in the Aggrewell 800 plates displayed a large decrease in cross-sectional area after FSS, while those grown in the SHArD-S showed no significant change in cross-sectional area. For CTM formation, HCT116 cells were plated for 48hrs in the SHArD-C at 3, 5, and 7 cells per microwell. Brightfield microscopy showed that CTM size was easily controlled by varying plating density of the cells within each microwell. CTMs grown in the SHArD-C did not disaggregate when exposed to FSS in a cone-and-plate viscometer. We thus provide a novel method to reliably produce highly tunable 3D cancer models from cancer CTMs to cancer spheroids, allowing one to simulate cell:cell interactions throughout the metastatic cascade.

SESSION SB02.11: Bioelectronics II
Session Chairs: Roey Elnathan and Yunlong Zhao
Friday Morning, April 14, 2023
Moscone West, Level 2, Room 2011

8:30 AM *SB02.11.01
Three-Dimensional Transistor Arrays for Cellular Recording Sheng Xu; University of California, San Diego, United States

Recording cellular electrical activities is critical for understanding pathologies and better therapeutic outcomes. This field is currently limited by the tools available for recording the cells. Existing techniques are either lack of accuracy or unable to scale up to record multiple cells simultaneously. In this presentation, I will show a vertically aligned needle-shaped field effect transistor array. I will go through its fabrication strategies, discuss the electrical characterizations, and demonstrate its use in interfacing cultured cells and organoids. Using the transistor array, we were able to directly record signal transport within one cell and among a cellular network, with high spatial and temporal resolutions. Those results hold implications for a wide range of fundamental studies and clinical applications.

9:00 AM SB02.11.02
Direct Recording of Action Potentials of Cardiomyocytes Through Solution Processed Planar Electrolyte-Gated Field-Effect Transistors Mario Caironi[1], Adrica Kyndiah[1], Michele Dipalo[1], Alireza Molazemhosseini[1], Fabrizio A. Viola[1], Francesco Modena[1], Giuseppina Iachetta[1], Nicolas F. Zorn[2], Felix J. Berger[2], Jana Zaumseil[2] and Francesco De Angelis[1]; [1]Istituto Italiano di Tecnologia, Italy; [2]Universität Heidelberg, Germany

Minimally invasive recording of intracellular action potentials in electrogenic cells is in high demand. Most of present electrical probing tools are either invasive or require complex manufacturing processes. With the aim of enabling a cost-effective, non-invasive probing platform based on devices that can be easily fabricated and processed from solution with large-area printing techniques, we propose planar Electrolyte Gated Field-Effect Transistors (EGFETs) based on solution-processed carbon nanotubes. Remarkably, despite the planar geometry of the device, we could demonstrate the spontaneous recording of intracellular action potentials of human induced pluripotent stem cells derived cardiomyocytes. The simplicity of the device combined with the high signal to noise ratio opens up new opportunities for low-cost, reliable, and flexible biosensors and arrays for high quality parallel recording of cellular action potentials.

9:15 AM *SB02.11.03
Non-Genetic "Optogenetics"—Silicon-Based Biointerfaces for Optical Modulation Menahem Y. Rotenberg; Technion, Israel

I will present recent developments in the field of semiconducting materials for optical biomodulation with resolutions scaling from cellular and sub-cellular level to tissues and organs.

9:45 AM SB02.11.04
Probing Retinal Electrophysiological Activities with Graphene Electrodes-Based Microfluidic Perforated Microelectrode Arrays Alberto Esteban Linares[1], Xiaosi Zhang[1], Hannah Lee[2], Michael L. Risner[2], Sharon M. Weiss[1,1], Yaqiong Xu[1,1], Edward Levine[2,1] and Deyu Li[1]; [1]Vanderbilt University, United States; [2]Vanderbilt University Medical Center, United States

Microelectrode arrays (MEAs) have revolutionized electrophysiological studies of the central nervous system (CNS) by simultaneously recording electrical activities from a population of neurons. Studying retina, a key component of the CNS, with traditional MEAs is challenging due to the strong curvature of the tissue, which prevents intimate contacts between the retina and electrodes, resulting in poor signal-to-noise ratios (SNR). Perforated MEAs (pMEAs) alleviate this issue by patterning the electrode array on a perforated flexible polyimide substrate placed on a fluidic chamber. Negative pressure can be applied from underneath the substrate to gently pull the retina towards the electrode layer to increase the contacts between the tissue and electrodes, therefore improving the SNR. In addition, it has been demonstrated that pMEAs enhance oxygenation of the bottom cell layer of the tissue as more fresh media perfuse through the tissue, allowing for long-term culture.
The large chamber height (1-2 mm) underneath the polyimide layer in commercial or reported custom-made pMEAs renders in-situ high-resolution optical imaging impossible. In addition, the chemical environment in pMEAs is traditionally regulated by bath perfusion, which limits the control of the microenvironment and hinders the possibility of local chemical stimulation. Developing platforms that combine these capabilities could be highly beneficial to unlock crucial information of retinal neuronal circuitry, understand response to different drug stimulations, and develop therapeutic strategies for retinal diseases.
In this work we report on microfluidic pMEAs (μpMEAs) that combine the capability of locally delivering chemical stimulations and high-resolution optical imaging through transparent graphene electrodes to study the response of retinal ganglion cells (RGCs) to different chemical probes. We demonstrate the potential of μpMEAs by measuring different RGC responses to locally delivered high K^+ stimulation through a restricted delivery channel. Results show correlated response from RGCs detected by electrodes located on and off the delivery channel. This coherent response was demonstrated to be mediated by intracellular communications through gap junctions that connect neighboring RGCs. Importantly, transparent graphene probes allowed for high-resolution confocal imaging of neuronal processes on top of the sensing electrodes. We expect that the μpMEA platform could enable novel retinal electrophysiological assays.

10:00 AM BREAK

10:30 AM *SB02.11.05
Dimensionality and Dynamicity Matters in Bioelectronic Interfaces Francesca Santoro; Forschungszentrum Jülich/RWTH Aachen University, Germany

The interface between biological cells and non-biological materials has profound influences on cellular activities, chronic tissue responses, and ultimately the success of medical implants and bioelectronic devices. For instance, electroactive materials in contact with cells can have very different composition, surface topography and dimensionality. Dimensionality defines the possibility to have planar (2D), pseudo-3D (planar with nano-micropatterned surface)[1] and 3D conductive materials (i.e. scaffolds) in bioelectronics devices. Their success for both *in vivo* and *in vitro* applications lies in the effective coupling/adhesion of cells/tissues with the devices' surfaces. It is known how a large cleft between the cellular membrane and the electrode surface massively affects the quality of the recorded signals or ultimately the stimulation efficiency of a device. In fact, the shapes of these newly designed electrode recalls those features of neuronal cells to ultimately induce biomimetic recognition. Furthermore, conductive materials that exhibit dynamic properties might better recapitulate the native environment of tissue. However, engineering such new platforms still require materials synthesis, integration into microfabricated platforms and stable cell interfacing. Here, we propose a new class of conductive materials which resemble the biomimetic architecture of neurite and dendritic spines and also can undergo dynamic reshaping. The cell response can be monitoring and eventually is adapting to the substrate changes over time. These new electrodes can pave the way to adaptive microdevices of use in bioelectronic application such as electrophysiology and sensing.

11:00 AM SB02.11.06
Conductive Thiophene-Based Fibers Synthesized by Living Cells as Novel Bioelectronic Materials Ludovico Aloisio[1,2], Guglielmo Lanzani[3], Giuseppe M. Games Paternò[4], Francesca Di Maria[4] and Matteo Moschetta[1]; [1]Istituto Italiano di Tecnologia, Italy; [2]Politecnico di Milano, Italy; [3]Politecnico di Milano / Istituto Italiano di Tecnologia, Italy; [4]Institute of Organic Synthesis and Photoreactivity (ISOF)-CNR, Italy

In recent years, it has been observed that living cells can be employed as active synthesis platforms for the assembly of intrinsically biocompatible bioelectronic materials. This process, which lies at the interface between living and non-living matter, is of fundamental interest since self-assembly *in vivo* could allow to circumvent brain-blood barrier and deliver large aggregates or even devices to the brain. Within this context, thiophene-based compounds represent workhorse materials for organic bioelectronics, owing to their biocompatibility and to the possibility to afford both electronic and ionic conduction.
Here, we report about the cell-mediated assembly of semiconductive nanofibers based on dithienothiophene-S,S-dioxide (DTTO) derivatives. We found that fibers originate inside cells and grow also "through" them, reaching and piercing the plasma membrane in one cell to penetrate the adjacent cell, without killing them. We extensively characterized the photophysics of DTTO molecules during the various steps of fibers production through steady state and time-resolved spectroscopy. We report the presence of DTTO aggregates inside the fibers, which represent the conductive domains of the nanostructured material and describe the interaction between DTTO molecules and the protein scaffold. By complementing the spectroscopic data with XRD characterization and electrical conductivity measurements, we discovered an extended polymorphism of DTTO in solid state. Our results suggest that the aggregation occurring in living cells is somehow unique of the biotic phase, and it involves at least part of the cell machinery. As fibers show electrical conductivity, they represent a way to directly stimulate cells or to induce artificial gap-junctions between cells, possibly affecting signal propagation as occurring in cardio-myocytes or in general to affect cell population behavior.
Further studies on the fibers' production process are in progress, with the aim to open the way to a wide range of new protein-based materials for bioelectronics and cell photostimulation.

11:15 AM SB02.11.08
3D Generation of Bio-Suited Advanced Atomic Force Microscopy Probes—Broader Venues for AFM Biological Applications Ayoub Glia[1], Muhammedin Deliorman[1] and Mohammad A. Qasaimeh[2]; [1]New York University Abu Dhabi, United Arab Emirates; [2]New York University, United States

Fabrication of Atomic Force Microscopy tips still commonly relies on 2D micromachining of brittle silicon-based materials, thus imposing limitations on the design of the 3D tip structures, and their functionality in a range of bio-suited applications. In our previous work, we deployed two photon polymerization technique for generating biocompatible polymer-based AFM tips (3DTIPs) with great flexibility in design and function. We have demonstrated that, when compared with conventional silicon tips, the 3DTIPs prove effective in obtaining high-resolution, high-speed AFM images with common AFM modes and under ambient and liquid conditions. In particular, the 3DTIPs provide wide tuning range and high dynamic mode scanning speeds due to their extremely low Hamaker constant and reduced quality factor, two important features for advancing AFM imaging. We have also demonstrated that, 3DTIPs are useful for biological experiments that require soft tip-sample interaction with minimal bio-contamination on the tips. In this work, to further advance the 3DTIPs technology, our focus is directed toward biological applications that are deemed impossible or challenging using the conventional silicon tips. For instance, the flexibility of tip designs in 3D facilitates generation of 3DTIPs with horizontally aligned probes. With these probes, various applications can then be exploited in a creative and useful way, such as laterally "moving" cells to a fixing structure, performing sideway cell indentation, and with high aspect ratio tips, cell puncturing/lysing. Furthermore, the softer nature, low Hamaker constant, and superior high-speed imaging capabilities of 3DTIPs give rise to other novel 3D tip designs that suite better for prolonged and "gentle" molecular-level probing of cell viscoelastic and adhesion properties, mapping cell membrane carbohydrates, and real-time quantification/sequencing of DNA at varying spatiotemporal resolutions. The vision of this work is to expand AFM functionality from a mere sensing/imaging tool, to one with manipulation capacities at the nanoscale. This is achieved by developing, in 3D, unique AFM probe designs capable of precise manipulation of bio-samples, from whole cells down to biomolecules. In sum, we foresee those multifunctional capabilities of the 3DTIPs could outperform conventional silicon tips in several biological applications, and open doors for novel functionalities.

11:30 AM CLOSING REMARKS - SYMPOSIUM AWARDS

SYMPOSIUM

April 11 - April 26, 2023

Symposium Organizers
Yei Hwan Jung, Hanyang University
Kyungjin Kim, University of Connecticut
Young T. Kim, Virginia Tech
Lokendra Pal, North Carolina State University

* Invited Paper
\+ Distinguished Invited

SESSION SB03.01: Thin-Film Processing and Characterization I
Session Chairs: Necmi Biyikli and Kyungjin Kim
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2014

10:30 AM *SB03.01.01
Atomic Layer Deposition of Inorganic Charge Transport Layers for Metal Halide Perovskite Photovoltaics Mariadriana Creatore; Eindhoven University of Technology, Netherlands

In the past decade, major progress has taken place in the field of metal halide perovskite photovoltaics (PV), as witnessed by the recently achieved conversion efficiency of 25.7% [1] and the concrete opportunities to go beyond the thermodynamic conversion efficiency limit of single junction PV by means of perovskite/ crystalline silicon tandem PV. Among the most recent efforts towards further development of perovskite PV and subsequent commercialization, strategies ranging from perovskite surface passivation and compositional engineering to thin film encapsulation, contribute to suppress the perovskite absorber and device instability to moisture ingress. In parallel, research efforts are presently dedicated to the replacement of organic charge transport layers (CTLs) such as poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA), [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) or C60, by inorganic CTLs, in order to address other challenges towards device large area processing and commercialization, such as thermal and mechanical device stability, as well as device efficiency yield.
In this contribution, our recent research on atomic layer deposited (ALD) selective CTLs for metal halide perovskite PV [2] is reviewed by addressing two case studies, namely, SnO_2 thin films, selective towards electron transport, and NiO thin films, selective towards hole transport. ALD is selected as deposition technology because of its merit of ultimate control over film thickness and conformality.
ALD SnO_2 [3], based on cycles of tetrakis(dimethylamido)-tin and H_2O as precursor and co-reactant, respectively, is the state-of-the art in both p-i-n perovskite single junction as well as tandem perovskite/crystalline silicon and perovskite/CIGS PV. Its presence is key to the device thermal and mechanical stability, to prevent humidity ingress in the device and suppress damage to the fullerene (PCBM or C60) during the sputtering of the transparent front contact.
ALD NiO [4], based on cycles of bis(methylcyclopentadienyl)nickel and H_2O as precursor and co-reactant, respectively, is found to impart stability to the perovskite device under acceleration test at 85°C, with 80% retention of the initial conversion efficiency after 300 hours at 1 sun illumination. Moreover, when NiO thin (7 nm) films are combined with the state-of-the art hole transport layer in p-i-n devices, i.e., the phosphonic acid-based self-assembled monolayer (SAM), the photovoltaic device exhibits higher thermal stability in comparison to the SAM only-based device. Furthermore, the SAM homogeneity and surface coverage on NiO improve, as witnessed by transmission electron microscopy (TEM) and conductive atomic force microscopy. This result is explained in terms of chemisorption reactions between SAM phosphonic acid groups and NiO hydroxyl groups. The SAM homogeneity on NiO leads to higher shunt resistance in the device with respect to the one with SAM directly processed on ITO. Moreover, the combination of NiO and SAM results in a narrower distribution of device performance reaching more than 20% efficient champion device.

[1] Green *et al*., Prog Photovolt Res Appl. 30, 687 (2022)
[2] Zardetto *et al*., Sustainable Energy & Fuels 1, 30 (2017)
[3] Bracesco *et al*., J. Vac. Sci. Technol. A, 38(6), 063206-1 (2020)
[4] Phung *et al*., ACS Applied Materials and Interfaces. 14(1,), 2166 (2022)

11:00 AM SB03.01.02
Correlation between Defect Type, Doping Level and Schottky Barrier in Hexagonal WS_2 Jungchun Kim[1], Gwang Hwi An[2], Dong Geun Park[1], Donghyun Kim[1], Seoyeon Choi[1], Kiseok Heo[1], Sanghyeok Kim[1], Inkyu Yoon[1], Hyun S. Lee[2] and Jae Woo Lee[1]; [1]Korea University, Korea (the Republic of); [2]Chungbuk National University, Korea (the Republic of)

One of the representative two-dimensional (2D) materials, transition metal dichalcogenides (TMDs) have been widely studied for next generation device application. To realize the high-performance device application of 2D TMDs, it is necessary to understand not only the metal/channel interface related to SBH and contact resistance (R_C) but also properties of channel material. Previous studies approach channel material doping and defect engineering at interface. However, it has not been reported how the defect types and doping concentration of TMDs control the device characteristics on same material.
We investigated the various characteristic analyses depending on two different defects region in a single flake of hexagonal WS_2 FETs. Through photoluminescence (PL) intensity mapping and Raman frequency mapping, it was confirmed that the sulfur vacancy (SV) and the tungsten vacancy (WV) had distinct regions in a single hexagonal WS_2.
Various electrical characteristics on the SV FET and the WV FET at 300 K were compared. In the I_d-V_g characteristics, the SV FET had lower threshold voltage (V_{th}) and approximately 6 times larger I_d at V_g =60 V than those of the WV FET. On/off ratio of the SV FET had 5 times larger than that of the WV FET. Difference in current was originated from conductivity of each defect region. Using each channel conductivity to extract doping concentration (n) of the SV and WV FETs, they had values of $1.29*10^{19}$ cm^{-3}, and $1.44*10^{18}$ cm^{-3}, respectively. Difference in the doping concentration may affect the effective SBH between the SV and WV FETs.
Through the low frequency noise characteristics, the magnitude of the power spectral density (PSD) of the SV FET was approximately 5 times higher than that of WV FET. Normalized PSD of the SV and WV FETs was well fitted by carrier number fluctuation with a correlated carrier mobility fluctuation (CNF+CMF) model. The trap density (N_t) and Coulomb scattering coefficient (α) of the SV and WV FETs were extracted by CNF+CMF model. The N_t of the SV and WV FET was similar with the values of $3.2*10^{20}$ cm^{-3}eV^{-1} and $4.0*10^{20}$ cm^{-3}eV^{-1}, respectively. However, the α related to Coulomb scattering impurity densities of the SV FET ($7.7*10^7$ VsC^{-1}) had 4 times higher than that of WV FET ($2.0*10^7$ VsC^{-1}). Because of the reduced channel dimensionality, α for the SV and WV FETs was determined by the carrier density n. Therefore, the SV FET with higher doping concentration had larger α than that of WV FET.
Temperature dependent activation energy (E_a) and SB characteristics for the SV and WV FETs were analyzed according to temperature (300 K – 420 K). In the Arrhenius plot for on current, the trend of E_a for SV and WV FETs was different from 360 K. In high temperature (360 K – 420 K), the E_a of the SV and WV FET was similar as 53 meV and 57 meV, respectively. Before 360 K, the E_a of WV FET had 115 meV, twice that of high temperature region, while the SV FET had a similar 71 meV. In other words, the SV FET was operated without a change in the carrier transport mechanism at the metal-channel interface. However, in the WV FET, the main carrier transport mechanism was changed at 360 K. The SV FET with a higher doping concentration

became sharper and narrower SBH than the WV FET. The current of the SV FET flowed well through tunneling at all temperatures. In contrast, most of current was dominant on the external energy because of relatively thicker and higher SBH in the WV FET.
In this study, we compared the various characteristics on SV FET and WV FET in a hexagonal WS_2 FET. Since the SV and the WV have different doping concentration within single material, it is highly look forward to studying the various electronic device application using hexagonal WS_2.

11:15 AM SB03.01.03
Elucidating the Surface Adsorption and Substitution Reaction Mechanism of a Heteroleptic $CpZr(NMe_2)_3$ Precursor in Atomic Layer Deposition
Choi Aerim and Il-Kwon Oh; Ajou University, Korea (the Republic of)

With the miniaturization of electronic devices, high-k dielectric materials replacing SiO_2 are being intensively studied to improve leakage current characteristics. Understanding the surface reactions and chemistry of precursor molecules during atomic layer deposition (ALD) has played an essential role. Chemical precursors and reactants contribute significantly to ALD thin film properties. So far, various Zr precursors for ZrO_2 thin films have been studied for the ALD process. Among them, the widely used precursor type is the heteroleptic precursor because the structure can improve the vapor pressure and tune the Lewis acidity of the precursor. However, the surface reaction of heteroleptic precursor molecules requires more attention to understand because the reaction pathway is different for each ligand exchange reaction.
In this study, we used a commercially used $CpZr(N(CH_3)_2)_3$ precursor for the high-k layer of dynamic random access memory (DRAM) by providing low impurities and good conformability with other reactants in H_2O and O_2 plasma. The surface reaction mechanism regarding the ZrO_2 growth and its dependence on impurity incorporation has been elucidated based on the results of quantum chemistry calculations. In addition, chemical composition, surface roughness and microstructural analysis by electron microscopy and X-ray techniques were introduced. The correlation between experimental observations and theoretical calculations was studied using density functional theory (DFT) ; 1) 1st half reaction in a cycle : When $CpZr(N(CH_3)_2)_3$ precursor reacting with OH groups on the substrate surface, it is highly likely to react with 2 $-N(CH_3)_2$ out of 4 ligands, 2) 2nd half reaction in a cycle: showed that the reaction pathway of Zr–Cp ligand exchange ligands is less favorable than that of $Zr–N(CH_3)_2$. In addition, defects and impurities appearing because the reaction between Cp ligands and H_2O molecules is less effective than alkylamide ligands degrade device performance. In contrast, we used O_2 plasma to dramatically remove all ligands, improving the leakage current and dielectric properties of ZrO_2 thin films. We believe that these findings on the surface reaction of heteroleptic ALD precursors will be helpful for future miniature semiconductor devices.

11:30 AM SB03.01.04
Broad-Range Tuning of Plasma Polymer Composition and Stability Using Plasma-Assisted Vapour Thermal Deposition Zdenek Krtous[1,2], Jaroslav Kousal[1], Pavel Solar[1], Jan Hanus[1], Lenka Hanykova[1], Ivan Krakovsky[1] and Suren Ali-Ogly[1]; [1]Charles University, Czechia; [2]Polytechnique Montréal, Canada

The Plasma-Assisted Vapour Thermal Deposition (PAVTD) is a plasma polymerization technique utilizing a classical polymer in powder or granular form ("precursor") which is heated and evaporated (and/or thermally fragmented) in the crucible under low pressure. The released fragments (effective a "monomer" produced in-situ) of an unusually high mass for PECVD/plasma polymerization (5-100 monomeric units) are then repolymerized in the RF plasma. The high molar mass of the monomer leads to an interesting competition between the fragmentation ("top-down" process) and repolymerization ("bottom-up" process). Influence of these processes on the chemical composition and structure i.e. density of crosslinking can be controlled by the intensity of the RF plasma, effectively bridging the gap between classical polymers and PECVD films [1]. The possibility to tailor the macromolecular structure of these films leads to the ability to control the water solubility of the films from the films washable in the range of seconds up to insoluble films [2]. Such films can be used as barrier layers for drug delivery systems.
Currently, the PAVTD method has several drawbacks compared with PECVD. Since the capacity of the crucible is limited, the deposition must be done as a batch process. The thermal release of the precursor fragments is highly temperature-sensitive. The resulting fluctuations in deposition rate make retaining good reproducibility of the process rather tricky. To overcome these technical limitations, a continuous process inspired by the Fused Deposition Modelling (FDM) 3D printing technology is investigated. The polymer precursor is continously fed into a crucible in a filament form, that is readily available for various polymeric materials like polylactic acid (PLA) or polyvinyl acohol (PVA). In comparison with a batch PAVTD, improved control of the release of material from the crucible leads to significantly better deposition rate stability even at order of magnitude higher deposition rates (over 1 nm/s).
The ability of PAVTD to tune the resulting film properties (similarity to original polymer or solubility) will be demonstrated both for batch and contiunous version of the process.

Acknowledgments
This contribution is supported by the grant GA22-21007S of the Czech Science Foundation.

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SESSION SB03.02: Thin-Film Processing and Characterization II
Session Chairs: Necmi Biyikli and Kyungjin Kim
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2014

1:30 PM SB03.02.01
Open-Air Spray-Plasma Deposition of Low Water Vapor Transmission Rate Multilayer Moisture Barrier Characterized Using Calibrated Infrared Imaging Ziyi Pan and Reinhold H. Dauskardt; Stanford University, United States

Emerging optoelectronic devices often require moisture barriers to prevent water ingress. While a variety of methods exist to limit moisture ingress including glass/glass encapsulation and multilayer films produced in vacuum environments, they present disadvantages in terms of rigidity, weight, cost and method of application. A rapid, conformal, and low-cost barrier coating method that can be applied in open-air for moisture barrier protection presents an attractive opportunity. A compounding aspect of barrier evaluation is the need for a both accurate and high throughput methodology. Existing calcium test and permeation methods for evaluating the water vapor transmission rate through moisture barriers while accurate surfer from low-throughput and the need for complex fabrication process or vacuum permeation chambers.

In this work, we show the development of multilayer moisture barrier deposited in the open-air and demonstrate a rapid testing methodology to measure the barrier efficacy. A scalable, open-air plasma process has been developed to deposit alternating layers of inorganic SiO_2 thin film and conformal organosilicate film barriers to prevent moisture ingress. The inorganic layer effectively blocks moisture ingress and the organsilicate layer decouples any pinhole defects in the inorganic layer. For moisture barrier efficacy evaluation, we developed a new testing methodology for water vapor transmission rate (WVTR) testing relying on infrared imaging at water absorption bands. The technique uses calibration of image intensity with moisture content in the polymer substrate and determination of water content that permeated inside the barrier substrate from images taken at different times.

A multilayer alternating barrier films with 900nm achieved WVTR on the order of 10^{-4} g/m^2/day at an accelerated aging condition of 38°C and 90% R.H., with transparencies ranging from 99% to 78% depending on the number of layers.[1,2] An infrared imaging system was developed to measure the performance of ultrahigh moisture barriers to a lower limit of detection of 5 *10^{-5} g/m^2/day, on par with commercial permeation instrumentation.[3] The ability of the rapid deposition of high efficacy multilayer moisture barrier in open-air as well as the non-destructive and in-situ evaluation of its efficacy enabling device resistance to humid environments is crucial towards realizing longer operating lifetimes.

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1:45 PM SB03.02.02

Modelling the Key Reaction Steps for Plasma-Enhanced and Thermal Atomic Layer Deposition of Cobalt Thin Film for the Next Generation Interconnect Ji Liu and Michael Nolan; Tyndall National Institute, Ireland

Cobalt (Co) is a potential material in semiconductor industry due to attractive electrical, mechanism and physical properties. The replacement of Cu with Co as conductive contacts or interconnects in integrated circuit (IC) devices serves as an illustrative example and is an ongoing process driven by large IC device manufacturers. Atomic layer deposition (ALD) is widely used in microelectronics and semiconductor industry to deposit thin films as part of device fabrication in nano- or subnano-dimensions. The key advantages of ALD are the conformality and precise thickness control at the atomic scale, which are difficult for physical or traditional chemical vapor deposition methods. Two types of ALD are usually applied, which are plasma-enhanced ALD (PE-ALD) and thermal ALD. In this study, we present our recent studies on modelling the chemistry and reaction mechanism of (1) PE-ALD of Co thin film[1] using $CoCp_2$ and N-plasma (NH_3 or mixture of N_2 and H_2), and (2) thermal ALD of Co[2] using $CoCl_2$(TMEDA) (TMEDA = N,N,N′,N′-tetramethylethylenediamine) and $Zn(DMP)_2$ (DMP = N,N-3-(dimethylamino)propyl).
For the PE-ALD of Co, we first addressed the surface reaction mechanism at the metal precursor pulse and plasma half-cycle on NH_x-terminated Co (001) and (100) surfaces, which corresponds to the steady growth region. The (001) surface of both metals, with a hexagonal structure, is the most stable and the (100) surface with a zigzag structure is less stable but has high reactivity. These two surfaces allow the study of the influence of the surface facet. We studied the surface saturation coverages of NH and NH_2 and the results are then analyzed with ab initio thermodynamics by calculating the Gibbs free energy. Both the ultra-high vacuum (UHV) condition and standard ALD operating condition are used to elucidate the effect of pressure and temperature on the termination of metal surfaces.
At the metal precursor step, the adsorption and reactions of metal precursor $CoCp_2$ on NH_x terminated metal surfaces were investigated with the inclusion of van der Waals corrections. The plausible reaction pathways include: precursor adsorption, hydrogen transfer, CpH formation and CpH desorption. The direct Cp dissociation mechanism is not considered on these NH_x-terminated metal surfaces due to experimentally observed minimal C impurities at the deposited metal thin films, which indicates that most of the Cp ligand is removed completely. The barrier for proton transfer was calculated using climbing image nudged elastic band (CI-NEB) method. Our results show that (100) surface has higher activity than (001) surface. Our study highlights the role of surface facets on the growth mechanism.
For the thermal ALD, our experimental collaborators found out that the deposited Co thin film is metallic and Zn-free. The self-limiting behavior for $CoCl_2$(TMEDA) at 155°C and a fixed $Zn(DMP)_2$ pulse length of 5s were observed after 6s with a GPC of 0.3Å. Our DFT calculations indicate that the reactions proceed via initial ligand exchange of DMP and Cl on Co(111) surface with $CoCl_2$ termination and Zn is removed via ZnCl(DMP) formation and desorption, resulting $Co(DMP)_2$ termination on the surface. The two DMP ligands are removed via C-C bond formation in a straightforward way. Our simulation results are in consistency with experimental findings and this work offers a facile ALD method to deposit Co metal thin film.
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2:00 PM SB03.02.03

Optical and Electrical Stability of Single-Layer Indium Oxide Thin-Film Transistors Fabricated Using Atomic Layer Deposition with a Novel Indium Precursor (SBIP-03) Ju-Hun Lee[1,2], Seung-Youl Kang[1], ChangBong Yeon[3], Jong-Heon Yang[1], Jaesun Jung[3], Chi-Sun Hwang[1] and Jaehyun Moon[1,2]; [1]Electronics and Telecommunications Research Institute, Korea (the Republic of); [2]University of Science and Technology (UST), Korea (the Republic of); [3]Soulbrain Co.,Ltd, Korea (the Republic of)

Indium oxide (IO) thin-film transistors have been attracting attention due to their high-mobility electrical properties. For this reason, it has been widely studied as a promising channel material for next-generation display backplanes. However, driving TFTs are frequently exposed to harsh environments such as backlight and continuous electrical stress, which can hamper circuit operation. These tough conditions affect not only the performance degradation of TFTs but also the reduction in lifespan. In conjunction with exploring compositionally simplified oxide semiconductors, we examined the stability issues of TFTs having 5 nm thin indium oxide channel. Technical reports on TFTs stability having single layer binary oxide as a channel are rather lacking. In this work, we present a novel liquid precursor of (N, N-di-tert-butylacetimidamido)dimethyl indium, SBIP-03) for atomic layer deposition. The optical stability was examined using three primary colors Red (λ = 633 nm), Green (λ = 520 nm), and Blue (λ = 463 nm) under various exposure times. Also, the electrical stability characteristics were evaluated under negative bias stress (NBS) and positive bias stress (PBS) conditions for the channel length from 5 to 160 µm in the stress time range of 0 to 1000 s. Devices showed stable operation under red and green exposure. Under blue light exposure, the transfer curve was observed to shift – 0.2 V. Stable transfer and output characteristics were obtained regardless of NBS, PBS, and channel length.
Acknowledgment
This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government(MSIT) (NRF-2020M3H4A3081897).

2:15 PM SB03.02.04

Quantitative Analysis of Interfacial Defects in Oxide Films and Electrical Devices Using Nonlinear Optics Hyunmin Hong, Min Jung Kim, Dong-Joon Yi, Dong Yeob Shin, Kwangsik Jeong and Kwun-bum Chung; Dongguk University, Seoul, Korea, Korea (the Republic of)

Transparent oxide-based thin-film transistors (TFTs) have attracted much attention due to their excellent electrical and optical characteristics. In particular, amorphous indium gallium zinc oxide (a-IGZO) TFTs have shown a better threshold voltage (V_{TH}) and field-effect mobility (μ_{FE}) due to the lack of grain boundaries, making this type of transistor a very promising alternative to an amorphous silicon TFT (a-Si TFT). In fabricating the a-IGZO-based TFTs, IGZO is deposited widely using magnetron sputtering. This technique generally provides such benefits as high deposition rates and has low processing temperatures. Therefore, IGZO has great potential to replace the existing silicon-based semiconductors and organic-based semiconductors that are employed as an active layer of the TFT backplane in the flat panel display. However, despite these merits, magnetron sputtering occasionally results in lower TFT performances due to the increase in surface morphology roughness.

The interfacial charge trapping, scattering, and rough surfaces cause a decrease in the saturation mobility (μ_{sat}), on/off current ratio (I_{ON}/I_{OFF}), and stability. An additional supply of O_2 during deposition or annealing in an appropriate environment can provide the oxygen content needed to compensate for oxygen vacancies (V_O) in the film. Although some studies have already reported the effect of oxygen vacancies on the electrical properties of IGZO thin films, the effective mechanism has hardly been clearly presented for this phenomenon.

In this study, we investigated the device properties and defect states in Indium gallium zinc oxide (IGZO) as a function of the oxygen flow ratio and annealing temperature during deposition. To investigate the defects at the interface, light was incident without deformation or destruction of the device using an fs-laser, and the defect density was quantitatively analyzed through the intensity of nonlinear light. In addition, the correlation between the intensity of the nonlinear signal and the device characteristics was analyzed and consistency was verified using the existing qualitative/quantitative defect analysis method.

2:30 PM BREAK

3:00 PM *SB03.02.05

Linking Mechanical Damage to *In Situ* Electrical Resistance in Metallic Thin Films Under Cyclic Loading Megan J. Cordill; Erich Schmid Institute, Austria

With the increasing demand for flexible displays and wearable sensors, the mechanical limitations of these systems need to be systematically investigated and fully understood. Ductile films and lines are an integral part of flexible electronics because they allow current flow between semiconducting islands and other operating features. However, the charge carrying ductile films must be of an optimum thickness and microstructure for suppression of cracking under cyclic tensile loading conditions. Studies of strained films on polymer substrates tend to emphasize only the electrical properties and thickness effects more than the mechanical damage that forms. In-situ measurements of electrical resistance have been used extensively as a failure criterion in cyclically loaded conductive films without regard to the type or amount of mechanical damage. However, not much research has been performed on extracting additional information about the mechanical damage that is contained within electrical resistance data sets. It will be shown that an increase in peak width of the resistance ratio evidences a transition from cracks bridging to through-thickness crack formation for Au and Au/Cr films on Polyimide. Understanding what can be learned from the electrical resistance without the need for additional damage characterizations allows for more insight into the combined electrical and mechanical failure of flexible thin film systems. The new knowledge gained about how the electrical data delivers mechanical damage information will aid in providing specific failure criteria for flexible electronics. Without specific failure criteria the electro-mechanical reliability of flexible material systems cannot be properly evaluated.

3:30 PM SB03.02.06

Through Thickness Film Fracture to Create Substrate Cracks for Chemical Storage of Antimicrobial Peptides Jia-Huei Tien[1], Hector Espejo[2] and David F. Bahr[1]; [1]Purdue University, United States; [2]Western Colorado University, United States

In most applications brittle film cracking on ductile substrates is seen as a nuisance that needs to be eliminated, but under proper conditions these surface structures can be a location for storage or be a carrier for a functional agent, such as lubricants or antimicrobial compounds such as peptides. Pulsed laser induced film growth in metals such as stainless steels and titanium has been used to create networks of cracks which penetrate a few microns into the substrate. To use these surface features in the films to impart additional functionality to a device there must be a balance between having a high enough density of cracks which provide the storage medium, but not so many or so large of cracks to substantially degrade the device's mechanical performance. In this current study we characterize the residual stress in these systems to monitor crack initiation and propagation. Pulse laser irradiation is used to provide high temperature under atmospheric conditions for oxidation reactions on various stainless steels, creating non-stoichiometric oxides that are not formed at slower oxidation conditions. Residual stresses play an important role since the different thermal expansion coefficients between martensite and the oxide layer drives cracking behavior after cooling down to room temperature to provide stress relief. Residual stresses were analyzed using the cos-alpha x-ray diffraction technique, and by varying the incident angle of the x-rays we are able to provide non-destructive measurement of effective residual stress as a function of depth in these materials over the same range as the crack depth. With the thickness of oxidation film in 400nm, subsequential cracking is observed perpendicular to the oxidation layer for 4-8μm at cross-section with the average crack spacing on the order of 20 μm. This density of cracks allows the functional agents to the surface of the material, in this case we used nisin, a polycyclic antibacterial peptide, which is applied to kill gram-positive bacteria and other microorganisms, and will present results on the efficacy of the nisin in controlling Listeria monocytogenes.

3:45 PM *SB03.02.07

Fast and Scalable Open-Air Spray-Plasma Processing of Protective Barrier and Other Functional Coatings Reinhold H. Dauskardt; Stanford University, United States

Open-air spray-plasma processing provides opportunities for versatile scalable and low-cost coating deposition on large and/or complex shapes in air and at low temperature. The generally solvent-free process further allows for the simultaneous functionalization of, and deposition on, substrates in a single step. Recent advances in the use of plasma process gasses (primary and carrier) that include inexpensive N_2 and compressed air together with the possibility of combining plasmas with spray deposition have further expanded the utility of the deposition technique. I will discuss the composition and molecular design of such barrier and multi-functional coatings, new methods for processing using plasma processing in air on plastics, and metrologies to characterize the moisture barrier, adhesive and degradation processes that are important for reliable application over extended operating lifetimes.

Specifically, we review progress using a newly developed and installed open-air plasma system with a 10-cm-wide plasma head and gantry robot system with scan speeds of 1 to 1,000 mm/s allowing for rapid film deposition through both *open-air* spray-plasma and chemical vapor deposition. Importantly, the system includes the capability to co-deposit a wide variety of precursors with precise control over the delivered precursor concentration. We can deposit different multilayer transparent barriers, anti-reflective and hydrophobic coatings at scale. We have successfully achieved alternating organic/inorganic moisture barriers with high transparency and WVTR of ~10^{-4} g/m^2/day. Methods to characterize film adhesion and moisture barrier properties rapidly with an imaging IR system calibrated with calcium and moisture permeation testing is discussed.

The scalable spray-plasma capability provides rapid processing of protective and mechanically robust barriers and other functional films for innovating device technologies that are sensitive to environmental exposures.

SESSION SB03.03: Thin, Flexible Bioelectronic Interfaces

Session Chairs: Yei Hwan Jung and Kyungjin Kim
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2014

9:00 AM *SB03.03.01
Flexible Bio-Integrated Electronics for Unconventional Human-Machine Interfaces Ki Jun Yu; Yonsei University, Korea (the Republic of)

This work focused on semiconductor materials and processing of the bio-integrated devices for unconventional human-machine interfaces. Recent advances in this area include materials, processing devices, integrated systems, and their biomedical applications that are capable of conformal and seamless contacts with the human body. The unconventional approach of building electronic systems opens a new pathway for improving diagnosis and therapeutic effects. Also, electronics in biomedical fields expands a major research field in diverse domains from basic science, and engineering to computer science for practical applications. Here, in this conference, I am introducing a few wearable and implantable bio-integrated electronics based on various novel materials for new device architecture of human-machine interfaces to provide unprecedented functionalities in a biomedical field and society.

9:30 AM SB03.03.02
A Double-Sided Coil Patterned Ultra-Thin Silicon Substate ChangHee Son[1], Sangyeop Lee[2], Placid M. Ferreira[1] and Seok Kim[2]; [1]University of Illinois, United States; [2]Pohang University of Science and Technology, Korea (the Republic of)

Fabrication of devices on ultra-thin silicon(UTS) substrate has significantly advanced as the demand for flexible and compact devices rises. However, the majority of research only focuses on a conventional single-sided fabrication and does not implement a double-sided fabrication due to challenges in fabrication on a UTS substrate. Here we implement a pattern transfer technique that enables transferring the UTS freely between substrates and even flipping the UTS at any step between processes. As an example, we fabricated a double-sided coil patterned UTS substrate(DCUTS) and demonstrated its functionality as an actuator and vibrational energy harvester. A combination of experimental, computational, and theory-based simulation modeling results are presented. The results prove the possibility of adopting this technique in fabricating double-sided, namely, higher density devices or multi-functional devices through two different patternings on the front and back sides.

9:45 AM BREAK

10:15 AM *SB03.03.03
Mechanics Challenges and Considerations for Sub-Micron Thin E-Tattoos Nanshu Lu; The University of Texas at Austin, United States

Compared with conventional wearable devices, skin-conformable ultrathin and ultrasoft e-tattoos offer unique advantages such as low contact impedance comparable with gel electrodes, effective electrical, thermal, optical and/or mass transfer across the skin-tattoo interface, minimal relative motion against the skin during human movement, mechanical imperceptibility, and unobstructive to human touch sensation. We have therefore built a theoretical framework to predict the skin-conformability of e-tattoos based on the tattoo stiffness and thickness, skin roughness, and skin-tattoo interfacial adhesion.[1, 2] The framework was used to guide the thickness design of our graphene e-tattoos (GET).[3, 4] While sub-micron-thin e-tattoos can achieve unprecedented skin conformability, their connection to rigid printed circuit boards (PCB) for data acquisition (DAQ), storage and/or wireless transmission suffer from orders of mismatch in thickness and stiffness. The significant strain concentration at such interfaces makes them notoriously vulnerable and has prevented the mobile and ambulatory use of skin-conformable e-tattoos. We herein propose a simple yet effective solution named “heterogenous serpentine ribbons (HSPR)”,[5] which refers to the strategic overlap between a sub-micron-thin serpentine ribbon and a thicker metallic serpentine ribbon. Compared with heterogeneous strain ribbons (HSTR), HSPR offers a fifty-fold strain reduction and correspondingly, fifty-fold enhancement of stretchability at such interfaces. To demonstrate the capability of HSPR, we have fabricated 300-nm-thin serpentine-shaped GET to form HSPR with 750-nm-thin gold-on-polyimide (Au/PI) serpentine ribbons. While graphene is in contact with the skin, Au is facing up to form the electrical contact with a rigid EDA watch through a soft conductive elastomer. The HSPR construct for GET allows long-term, continuous, unobstructive and ambulatory EDA sensing on human palm during our daily activities as well as during sleep. We believe that the HSPR could be a generic solution to robustly connect any sub-micron-thin e-tattoos to rigid circuits, which could significantly enhance the reliability and usability of ultrathin, skin-conformable e-tattoos.

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10:45 AM SB03.03.04
High-Resolution Pd-Ni Hydrogen Gas Sensor Capable of Detection Ultra- High Purity Hydrogen Seung-Ik Han[1,2], Chiwan Park[1], Le Thai Duy[1], Rubaya Yeasmin[1] and Hyungtak Seo[1,1]; [1]Ajou University, Korea (the Republic of); [2]Ajou university, Korea (the Republic of)

Hydrogen (H_2) has different types of impurities depending on the production method, which determines the purity of hydrogen. For hydrogen to be used as a fuel for a hydrogen fuel cell vehicle, the purity of hydrogen is very important. Low-purity hydrogen containing several impurities adversely affects the catalyst of the fuel cell and greatly reduces the lifespan of the fuel cell system. Gas Chromatography (GC) used in the field is a method of periodically extracting and measuring hydrogen gas, so it is impossible to check in real-time. Therefore, a hydrogen sensor capable of measuring high-purity hydrogen of 90% or more is necessary.

For the hydrogen sensor of the Delta Resistance type, it is important to secure a resolution capable of discriminating the difference in resistance between the measured hydrogen concentrations when measuring the hydrogen concentration. In addition, palladium (Pd) used as a hydrogen detection material has structural instability in a high concentration of hydrogen when used alone.

In this study, a multi-layered alloy catalyst of Pd and Ni was prepared using nickel (Ni) as complementary material to Pd. The core technology of the ultra-high concentration hydrogen sensor is to control the distribution density of the alloyed Pd-Ni catalyst metal layer to secure the hydrogen concentration resolution characteristics. A structurally optimized hydrogen sensor was fabricated by implementing the digit form.

The hydrogen detection layer manufacturing method uses an E-beam evaporator to deposit Pd-Ni, a catalyst metal for H_2 dissociation reaction, on a SiO_2 substrate in the form of a Pd/Ni/Pd sandwich type multilayer thin film. The Pd-Ni sensor was measured at various ultra-high hydrogen concentrations of 90-100% containing impurity gas.

The manufactured hydrogen sensor secured 0.1-1% resolution at high hydrogen concentration and showed excellent performance in detecting hydrogen within 5 seconds. This is thought to be because Ni acted as a co-catalyst in the Pd-Ni double-layer catalyst, resulting in a change in hydrogen adsorption/desorption reaction energy, and the digit structure increased the base resistance.

11:00 AM *SB03.03.05
Ultra-thin, Low-Noise Organic Transistor Integrated Devices for Minimally Invasive Brain Activity Measurement System Tsuyoshi Sekitani; Osaka University, Japan

I will introduce process technologies for high mobility, low noise, and uniform characteristics of organic thin-film transistors that utilize the softness of organic materials, as well as a brain activity measurement system that utilizes these organic nanotechnologies.

In recent years, the flexibility and lightweight properties of organic electronics have attracted attention, and bio-applications, such as wearable applications, have been gaining momentum. In addition to high electrical characteristics, such applications require the simultaneous fulfillment of various properties such as uniformity of characteristics and biocompatibility that allow for large-scale integration. Organic transistors, in particular, have inherently non-uniform characteristics, and this trend will become more apparent over time.

In this study, we have realized organic thin-film transistors with high mobility (μ>1 cm^2/Vs) and low noise on polymer films less than 1 micrometer thick by using photosensitive materials and self-assembled monolayers as gate insulator films [1,2] and have successfully reduced the variation in threshold voltage (V_{th}) less than 4%. This implies a V_{th} variation of 10-70 mV for a drive voltage of 2V. [3].

By highly integrating this organic thin-film transistor with biocompatible materials [4], we have developed an ultra-thin-film measurement device that can minimally invasively measure minute cellular action potentials in living organisms [5-10]. In this presentation, we will introduce a scalp EEG measurement system that measures from outside the skull and a brain measurement system that measures from inside the brain in an extremely minimally invasive manner.

Furthermore, with the aim of expanding the application of ultra-thin film organic devices to a wider range of areas, we are currently conducting research and development of organic electrochemical transistors capable of controlling high currents [11].

These results were obtained in collaboration with Dr. Koki Taguchi, Associate Professor Takafumi Uemura, Associate Professor Teppei Araki, and other members of the SANKEN research group at Osaka University, and Dr. A. Petritz, Dr. B. Stadlober, and other research group members at JOANNEUM RESEARCH, Austria. This work was supported in part by JST Moon Shot Type R&D Project (JPMJMS2012), Grant-in-Aid for Scientific Research (22H00588), and Research Grant (S) from Tateishi Science and Technology Foundation.

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SESSION SB03.04: Reliable and Chronic Neural Interfaces
Session Chairs: Yei Hwan Jung and Kyungjin Kim
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2014

1:30 PM *SB03.04.01
Polymer Implantable Electrode Interfaces to the Nervous System Ellis F. Meng; University of Southern California, United States

Microelectrode array technologies can be adapted to interface with different parts of the nervous system, whether lying on the surface or placed into tissues. While traditionally constructed from rigid materials, emerging polymer technologies compatible with microfabrication offer interfaces possessing greater mechanical flexibility and material transparency. The use of a softer substrate material may alleviate chronic tissue damage and prolong function while material transparency allows use with optical imaging and interface modalities. In addition, the design space enables a variety of form-factors and anatomical targets, including surface, shallow and deep-brain structures, retina, spinal cord, and peripheral nerves. However, access to this technology is limited as is the infrastructure to scale the manufacture and dissemination of polymer interfaces. The Polymer Implantable Electrode (PIE) Foundry is a new resource concept that provides rapid access to custom or generic microelectrode arrays to the research community and borrows from pathways for project space sharing from the integrated circuit manufacturing industry. Progress in advancing this new foundry concept including the dissemination of polymer microelectrode array technologies to neuroscience and neural engineering users will be discussed.

2:00 PM *SB03.04.02
Are We at an Inflection Point—Advanced Thin-Film Encapsulation Concepts Enabling Chronic Implantable Devices in Chronic Human Applications Florian Solzbacher; Univ of Utah, United States

Implantable Brain-Computer Interfaces appear to be heading towards an inflection point: In the past decade the number and frequency of major technological advances and first in human demonstrations of new capabilities have started increasing significantly. Many technical and scientific hurdles have been overcome or at least addressed. The first generations of commercially available products appear to be imminent. They have the potential to become tangible tools to restore lost function and are serious contenders to address a variety of neurological disorders. Much of this has been enabled by breakthroughs in encapsulation approaches leveraging thin film and wafer level approaches for even complex implantable systems. The real-life settings associated with in-home use of these technologies lead to reprioritization of existing--as well as the emergence of novel--practical and fundamental challenges and opportunities. How do we identify and prioritize user, clinician and caretaker needs? What is possible today and what is a realistic technological roadmap that meets those needs?

2:30 PM SB03.04.03
Improved Parylene-Based Barrier Layers Using Low Temperature CVD Technologies Sébastien Buchwalder[1,2], Florian Bourgeois[3], Andreas Hogg[3] and Juergen Burger[1]; [1]Sitem Center for Translational Medicine and Biomedical Entrepreneurship, Switzerland; [2]Graduate School for Cellular and Biomedical Sciences, Switzerland; [3]Coat-X SA, Switzerland

Implantable devices, demanding efficient protection against body fluids as well as maximal miniaturization, require a high degree of biological safety. An ultra-tight encapsulation solution which enables safe long-term implantation close to inflammatory tissue and which has a superior temperature stability for multiple sterilization cycles is highly desirable. In this work, it is shown how these needs can be addressed by an innovative thin film encapsulation technology made of alternating organic and inorganic layers.

Parylene, as organic thin film, is a well-established polymer material, exhibiting excellent electrical insulation and dielectric properties, being often the material of choice for biomedical applications. However, parylene barrier properties are not sufficient to ensure a protection for long-term implantation in the human body of several years. The inorganic materials are dense and hence offer extremely good barrier properties. However, inorganics alone suffer from pinhole and micro-crack defects, which induce a poor long-term hermeticity. On the other hand, the combination of parylene with inorganic thin films provides excellent barrier properties and improves the scratch resistance, limiting the water permeation through potential defects.

This study investigates the barrier performances of inorganic monolayers and parylene multilayers in combination with inorganic films deposited by low temperature chemical vapor deposition (CVD) processes. Parylene VT4 film, deposited by the standard Gorham process (low pressure CVD), was used for its excellent thermal stability and its superior capability to enter into small voids or channels of substrates compared to other parylene types. Silicon-based layers, deposited by plasma-enhanced CVD (PECVD) were examined as single layer, bilayers and combined with parylene film as multilayers. Three precursors and two plasma generation methods (inductively and capacitively coupled plasma) were tested and evaluated for inorganic PECVD layers. Similarly, atomic layer deposition (ALD), including thermal and plasma oxidation methods, was used to compare three metal-oxide layers. Water vapor transmission rate (WVTR) measurements were performed to quantify the barrier performances using electrolytic and diode laser spectroscopy detection methods. The most efficient single layers show a WVTR in the range of 10^{-3} g m^{-2} d^{-1}, at 38°C and 90% relative humidity conditions, while the results of WVTR measurements for parylene-inorganic (1dyad) combinations are in the range of 10^{-4} g m^{-2} d^{-1} at 38°C and 90% R.H. Multilayer stack (more than 1 dyad) will be assessed and WVTR value will be measured for different organic/inorganic layer combinations. Finally, thin film encapsulations will be evaluated on functional active device, (e.g., electronic circuit) immersed in saline solution in order to determine the barrier performances close to real implantable applications.

2:45 PM *SB03.04.04
Investigations on the Longevity of Metal-Polymer Interfaces in Electrode Arrays of Neural Implants Thomas Stieglitz, Jennifer Schulte, Ioana-Georgina Vasilas, Calogero Gueli, Danesh Ahouri Vajari and Paul Cvancara; University of Freiburg, Germany

Neural interfaces need to provide stable and reliable functional interfaces to the target structure in chronic implantations both in neuroscience experiments and especially in human clinical applications. Proper selection of substrate, insulation, and electrode materials is of paramount importance as well as the knowledge how process parameters in device manufacturing influence material longevity. Aspects such as size, thickness, and shape contribute significantly to structural biocompatibility and modulate post-implantation foreign body reaction. Our work focused on polyimide as the substrate and insulating material with integrated thin film metallization as the conductor in our flexible neural interface approach. Platinum, iridium oxide, glassy carbon, and PEDOT serve as interconnect lines and electrode coatings, respectively, depending on the intended electrode size and application. We have investigated different metal-polyimide compounds after in vitro stimulation but also devices after explantation. Optical imaging during electrical stimulation of platinum in vitro showed actuation of thin-films during Implantation as potential origin of adhesion loss. In addition, accelerated aging led to changes in grain structures in these platinum layers. Post explantation analysis of platinum recording arrays from studies up to two years in ferrets proved these initial observations and showed signs of hydrogen embrittlement. In addition, dimpling of arrays into brain tissue, secondary dura and bone growths showed limitations in structural biocompatibility in exemplary cases. Peripheral nerve electrodes from stimulation in human clinical studies over a period of up to six months has demonstrated the stability of iridium oxide sites and the integrity of the metal-polymer multilayer film using silicon carbide as an adhesion promoter. Analysis of explanted fragments, however, showed the necessity to be able to image the device-tissue interface in one stage without separating devices from biological material. The layer composition and tissue contact to the surface might help to better assess the interface compatibility and the influence of surface roughness and coatings on the foreign body reaction and device functionality and longevity. So far, results are encouraging to continue the translational research path from basic studies to the first human clinical trials, which are necessary to prove that new materials, technologies and devices are applicable in clinical applications and can eventually be translated into an approved medical device.

SESSION SB03.05: Thin-Film Barriers
Session Chairs: Kyungjin Kim and Lokendra Pal

Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2014

8:30 AM *SB03.05.01
Combined High Stretchability and Barrier in Hydrogen-Bonded Nanobrick Wall Thin Films Jaime C. Grunlan; Texas A&M University, United States

Hydrogen-bonded multilayer thin films are very stretchable, but their gas barrier properties are modest compared to more traditional ionically-bonded assemblies. In an effort to improve the gas barrier of poly(ethylene oxide) (PEO) – poly(acrylic acid) (PAA) multilayer films, without sacrificing stretchability, montmorillonite (MMT) clay platelets were combined with PAA and alternately deposited with PEO. A ten bilayer PEO/PAA+MMT film (432 nm thick), deposited on a 1 mm PU substrate, resulted in a 54X reduction in oxygen transmission rate after exposure to a 20% strain. This system is the best combination of stretchability and gas barrier ever reported. This same concept can be converted into a single polyelectrolyte complex solution to achieve relatively good barrier in a single step. If there's time, I'll briefly describe how these types of polyelectrolyte thin films can be used to prepare insulation layers with high dielectric breakdown strength.

9:00 AM SB03.05.02
Photocurable Hybrid-Nanocellulose Multilayer Coatings on Biobased Substrates for Food Packaging Applications Aigoul Schreier and Yves Leterrier; EPFL, Switzerland

With waste management concerns, researchers are now focusing on developing recyclable or biodegradable materials in an innovative way. To comply with the food industry requirements, current studies aim to develop materials with high barrier properties to oxygen and water vapor while considering their entire lifecycle. Microfibrillated cellulose (MFC) produced in the form of thin flexible films have attracted an increasing interest in packaging applications due to their excellent grease and oxygen barrier properties. However, the permeability of such materials degrades exponentially with increasing relative humidity (RH) due to disruption of the Hydrogen bonds and swelling of the MFC. The moisture sensitivity of MFC can be reduced through thermomechanical treatments, or by encapsulation with a hydrophobic matrix.
This work aims to develop high diffusion-barrier materials in the form of multilayer coatings composed of MFC and UV-curable organic-inorganic hybrids coated on paper and biobased polymer substrate. Two end of life strategies are considered. The first is based on easy recyclable materials in an already existing paper mill. The second focuses on the development of biodegradable composites within relevant degradable environment.
In the case of a recyclable packaging, MFC is coated as a diluted aqueous suspension and dried to form a dense film. The hybrid interlayers combine a cycloaliphatic epoxy oligomer, 3-glycidoxypropyl trimethylenesilane (GPTS) as a coupling agent and tetraethylorthosilicate (TEOS) to favor interfacial interactions with the hydroxyl-terminated MFC layers. Particular attention is paid to the photo-induced conversion of the hybrid network, to the MFC-hybrid interface and resulting oxygen and water vapor permeability. Multilayers based on pure epoxy and MFC layers on paper led to oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) of 25 cm3/m2/day/bar (23°C, 85%RH) and 14 g/m2/day (23°C, 85%RH), respectively. The achieved water vapor barrier performance is mainly coming from the epoxy. Moreover, epoxy did not properly wet the MFC surface and the interfacial adhesion was low. Adding TEOS and GPTS improved both the wettability and adhesion properties of the resin onto the MFC surface. Indeed, the addition of those two compounds led to the formation of covalent bonds through condensation reactions between the hydrolyzed TEOS and MFC surface. The photopolymerization rate and gel-time of UV-curable resins increased with increasing TEOS and GPTS concentration. A systematic analysis of barrier and adhesion properties is performed to assess the effect of the number of MFC interlayers and the composition of the UV-curable hybrid. The assessment of the recyclability of these multilayer films within a standard paper recycling scheme highlights their capability to be recyclable into Category II grade.
Focus is also given to a fully biodegradable, MFC-based multilayer film alternative using a biobased epoxidized soya bean oil (ESBO) as an organic matrix and a polyhydroxyalkanoate/polylactic acid blend (PHA/PLA) as substrate. Preliminary biodegradability tests confirm the ability of a consortium of bacteria to use each material as a carbon source. The polarity contrast between the precursor (MFC suspension) and the PHA/PLA substrate leads to important delamination issues during film formation. To face this problem, a treatment of the polymer with an organosilane 3-aminopropyl)triethoxysilane (APTES) was performed showing great improvement. Permeability tests are ongoing to further investigate the performances of this new biodegradable MFC multilayer films.

9:15 AM *SB03.05.03
Advanced Renewable Cellulose Nanocrystal and Chitin Nanofiber Barrier Packaging Tequila Harris[1], Kwangjun Jung[1], Yue Ji[1], Tae J. Jeong[1], Carson Meredith[1] and Peter Ciesielski[2]; [1]Georgia Institute of Technology, United States; [2]National Renewable Energy Laboratory, United States

Plastic waste is one of the most prominent materials impacting the environment and human health due to the inability to recycle or the difficulty of recycling and the release of toxins in the form of microplastics. To this end, there is a critical need to develop highly functional bioderived materials for applications such as food packaging, which is the most significant contributor to unrecyclable or difficult-to-recycle plastic waste. Cellulose nanocrystals (CNCs) and chitin nanofibers (ChNFs) are two biologically sourced materials that can be used to create biodegradable and sustainable oxygen and moisture barrier materials that are comparable to widely available barrier layers such as polyethylene terephthalate (PET). In this talk, we will discuss how the functionality of CNC and ChNF barrier thin films can be enhanced through material synthesis and manufacture. Attention will be paid to the process-structure-property relationships of the barrier thin film. Here, we demonstrate the viability of dual layer slot die coating of CNC/ChNF bilayers onto cellulose acetate (CA) substrates when compared to spray coating. It was observed that the dual layer slot die coating on a roll-to-roll system that applies the bilayer in a single pass enables a significantly lower oxygen permeability versus spray coating. It has been found that spray coated bilayer thin films were on average 25% thinner than the dual layer slot die coated bilayer film. However, the thickness-normalized oxygen permeability (OP) of the dual layer slot die coated ChNF/CNC bilayer thin film on CA was 20 times better than that of the spray coated bilayer thin films. OP values for the slot die coated bilayer thin films under optimized drying conditions were as low as 1.2 cm3 µm m(-2) d(-1) kPa, corresponding to an oxygen transmission rate of 0.32 cm3 m(-2) d(-1) at 23 °C and 50% relative humidity. It is also noted that the adhesive properties of the dual layer coating are also improved when the barrier thin film is air dried. Challenges to industrial implementation and approaches to overcome these will also be analyzed.

9:45 AM SB03.05.04
Enhancing the Thermal Stability of the IGZO Transistors by Suppressing the Oxygen Diffusion into Metal Using Self-Assembled Monolayer for Nanoscale Devices Juyoung Yun, Hyuk Park, Seung-Mo Kim, Byoung Hun Lee and Yoonyoung Chung; Pohang University of Science and Technology, Korea (the Republic of)

Amorphous indium-gallium-zinc-oxide (a-IGZO) thin-film transistors (TFTs) are extensively applied in large-area displays, machine learning, and memory devices. Recently, it was reported that the increased electron density caused by the oxygen vacancy reduces the contact resistance between a-IGZO and source/drain (S/D) metal.[1] However, a large amount of oxygen vacancies in the S/D region diffuses into the channel region by thermal stress, which causes performance degradation, such as V_{th} negative shift and loss of switching characteristics, especially in the nanoscale transistor.

To suppress the excessive generation of oxygen vacancies, We introduced the ultra-thin barrier layer (< 1nm), which prevents oxygen diffusion. A self-assembled monolayer (SAM) with various alkyl-chain lengths (C2, C4, C6, C8, C10) was used as a diffusion barrier. We extracted the effective channel length of the IGZO TFT by the transfer line method (TLM) pattern. The device with a thick barrier showed a negligible change of the channel length at 250 degrees thermal stress for 2 hours, indicating that the diffusion of oxygen vacancies was suppressed. Transmission electron microscopy (TEM) images showed reduced interfacial oxide after SAM insertion. Despite inserting a diffusion barrier with excellent insulating properties, the contact resistance was decreased by 72 % compared to the bare device due to the thinned interfacial oxide. As a result, we achieved high thermal stability by inserting a diffusion barrier and, additionally, low contact resistance due to the thinned interfacial oxide, which contributes to the realization of nanoscale devices without any side effects in the channel region.

10:00 AM BREAK

SESSION SB03.06 Functional Biopolymers and Smart Coatings
Session Chairs: Young T. Kim and Lokendra Pal
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2014

1:30 PM *SB03.06.01
PolyCannabinoids—Synthetic Polyesters from Natural Feedstock, Cannabidiol (CBD), Cannabigerol (CBG) and Adipic Acid, as Non-Phenolic Antioxidant Bioplastics Gregory Sotzing; University of Connecticut, United States

Polycannabinoids are a platform technology based upon the polymerization of natural feedstock monomers. Two examples of monomers include cannabidiol, CBD, and cannabigerol, CBG, two of the five main cannabinoids in cannabis. CBD isolate, the pure form of CBD extracted from hemp biomass was used as a diol monomer along with adipoyl chloride, the monomer used for Nylon, to produce a polyester CBD-adipate. Hydrolysis of polyCBD-Adipate occurs under basic condition to produce CBD, insoluble in water, along with the natural chemical adipic acid that dissolves in water. Side-by-side studies with polylactic acid (PLA) show polyCBD-Adipate to be noncytotoxic, and unlike PLA, polyCBD-Adipate shows anti-oxidant activity with ORAC assay. CBD having two rings in its structure is then compared to CBG having one ring. In line with expectations based upon the number of rings, polyCBG-adipate exhibits a glass transition temperature at -33°C whereas polyCBD-Adipate is at 37°C. Copolymerization of CBD, CBG and adipic acid allows for the glass transition to be tuned to any specific temperature within this -33 to 37°C range. The anti-oxidant capability of a bioplastic presents a tremendous opportunity to applications in which materials need to hold up to oxidative stress, potentially protecting species such as drugs and enzymes that are prone to oxidation.

2:00 PM SB03.06.02
Nanomanufacturing of Lignin Biopolymer for High-Performance Wearable Triboelectric Sensors Robert Ccorahua, Shivangi Agarwal and Wenzhuo Wu; Purdue University, United States

Lignin is the second largest biopolymer on earth after cellulose. It represents 40% of the weight of a plant. It is considered the biopolymer with the most difficult processability due to its complexity and dual non-polar and polar nature. Such challenges prevent lignin's limited manufacturability and further applications. Herein, we manufactured lignin films though multiple nanomanufacturing methods by implementing a new environmental-friendly processing method. We further evaluated the parameters of each technique for lignin manufacturing and correlated them with their structure and property as triboelectric films. Moreover, we demonstrated that, compared with other biopolymers, lignin exhibits outstanding triboelectric properties for self-powered wearable devices in human-machine interface applications. Our developed framework opens doors to new technologies that utilize abundant bioderived materials for economically feasible and ecologically friendly manufacturing of functional devices in energy, electronics, and sensor applications.

2:15 PM SB03.06.03
Bioresorbable Shape-Morphing Biomedical Thin-Film Microrobots Wangqu Liu, Arijit Ghosh, Ruili Zhang, Gayatri Pahapale, Zijian Zhong and David H. Gracias; Johns Hopkins University, United States

Shape-morphing microrobots that can adapt to physiological environments and transform their geometry or functionality offer the potential for autonomous deployable, intelligent systems to enable biomedical functions, such as drug delivery and microsurgery. However, safety concerns can limit the wide-scale adoption of such devices. After completing their tasks, there is a risk that such devices can be stuck or retained in the body, which may require additional surgical interventions to be removed. In this work, we report shape-morphing origami microrobots composed of bioresorbable materials such as Fe, MgO, and Mo, offering the possibility for dissolution in the body. We characterize the thin film stresses and deposition parameters to create bilayers that can fold with appropriate angles and dissolve at different times. We demonstrate the creation of foldable microstructures using a novel water-free shadow mask microfabrication process. We believe this study advances water-free thin film microfabrication processes for bioresorbable materials and the devices are an essential step towards the creation of safe, dissolvable shape change microrobots for biomedical applications.

2:30 PM BREAK

3:30 PM SB03.06.04
Delayed Release from Hermetically-Sealed Aqueous Capsules by Modulating the Thin Waxy Shell Eylul Utlu, Leah K. Borden and Srinivasa R. Raghavan; University of Maryland, United States

Biopolymer hydrogel capsules are typically created through physical crosslinking of polymer chains. They are environmentally friendly and non-toxic, making them very useful in different industries. However, hydrogel capsules are often unsuitable for drug delivery since they cannot keep small molecules encapsulated for long times without leaking. In an effort to resolve this problem, our lab has designed capsules with a hydrogel core and a thin shell of paraffin wax around the core. [1] The wax shell keeps hydrophilic solutes hermetically sealed, i.e., there is no leakage for a long period of time (months). The barrier properties of the wax shell arise because it is an extremely hydrophobic material with a melting point well above room temperature (~ 60°C).

While a hermetic seal is useful, there is still a need for solutes encapsulated in the capsule to be released at the appropriate time. For this purpose, we have improved the above capsule design to allow for: (a) a hermetic seal for a period of time; followed by (b) a slow and sustained release of the solute thereafter. The key to our new design is to add a low-melting additive to paraffin wax. Using this design, we can store hydrophilic solutes (such as hormones and therapeutics) in the capsules for multiple days at room temperature without any release (i.e., the solute remains hermetically sealed over this period). After this period, the solute is released at a slow rate out of the capsule. The time delay before solute release can be tuned through several variables, including the concentration as well as the molecular nature of the additive. Since the thin waxy shell is completely biocompatible, this approach could have a potentially significant impact on the delivery of many hydrophilic solutes, including drugs, agrochemicals and cosmetic agents.

[1] J. P. Goertz, K. C. DeMella, Benjamin R. Thompson, Ian M. White and *S. R. Raghavan*
Responsive capsules that enable hermetic encapsulation of contents and their thermally triggered burst release.
Materials Horizons, 6, 1238 (2019)

3:45 PM SB03.06.07
Skin-Covered Hydrogels—A Novel Zero-Order Drug Delivery System Morine Nader[1], Sai Nikhil Subraveti[2] and Srinivasa R. Raghavan[1]; [1]University of Maryland, United States; [2]Princeton University, United States

In most drug delivery devices today, drugs are released out of the device in an immediate or first-order manner, implying that the rate of release is high at the outset and decreases exponentially thereafter. As a result, undesirable side effects are often observed, and moreover, increased dosing frequencies are needed to achieve the necessary therapeutic effect. Zero-order drug delivery devices have the potential to overcome these issues by releasing drugs at a constant rate; thereby maintaining drug concentrations within the therapeutic window for an extended period. Till date, researchers have explored several ways to accomplish zero-order release; however, the majority of these are complex, time-consuming, and difficult to manufacture.

Here, we design a simple way to achieve zero-order release of various water-soluble solutes out of any given hydrogel. Our solution is to create a thin polymeric skin around the hydrogel using an inside-out strategy. We show that uniform polymeric skins with a tunable thickness of 10−100 µm can be easily achieved using our technique. For zero-order release to occur, the skin is made mostly from a hydrophobic monomer, but with small amounts of a hydrophilic monomer. This generates hydrophilic domains in the skin, and we will demonstrate that this combination leads to a zero-order response. Additionally, we show that it is possible to tune the release rate by varying the thickness of the skin and the concentration of the hydrophilic monomer.

SESSION SB03.07: Poster Session
Session Chairs: Yei Hwan Jung and Young T. Kim
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SB03.07.01
Spectroscopic Study of Passivation Effect of Common Polymers on MoS_2 Christine McGinn and Christina A. Hacker; National Institute of Standards and Technology, United States

The unique electronic and optoelectronic properties of two-dimensional transition metal dichalcogenides (2D TMDs) can deteriorate as a result of surface defects and in recent years, several materials have emerged to passivate the surface and mitigate these defects.[1] Hexagonal boron nitride has seen widespread use because it is CMOS compatible, but it has been shown that polymers can have a significant passivating effect on 2D TMDS. [2,3] In addition to facile processing, polymers are typically transparent in the visible range, making them ideal for passivation of optoelectronic 2D TMD devices. A few works have shown an improvement in photodetection by polymer encapsulation. [4] Notably, the addition of ferroelectric polymers led to significant performance improvement in 2D TMD photodetectors, but the passivation effect of the polymer was not studied. [5] Only a few polymers have been studied for passivation, but the degree of passivation has not been quantified or qualified against other polymers. This work uses spectroscopic methods to investigate a representative group of polymers and their relative passivation effects on MoS_2 for improved passivation in 2D TMD devices.

This study consists of spectroscopic measurements of MoS_2 monolayers and three common polymers: parylene N (Pa-N), polymethyl methacrylate (PMMA), and polyvinylidene difluoride trifluoroethylene (PVDF-TrFE). These polymers were chosen as a representative set because they are commonly available and facile to deposit. Parylene is an extremely inert polymer used frequently in organic electronics and biomedical devices for encapsulation. [6] PMMA is a standard electron beam photoresist frequently used to encapsulate 2D TMD devices to prevent degradation. [7] PVDF-TrFE is an electroactive polymer commonly used in organic, flexible, and biomedical devices. [8] Approximately 300 nm of each polymer was deposited onto monolayer MoS_2 on a Si/SiO_2 substrate procured from 2D semiconductors. Spectroscopic measurements including Raman spectroscopy, Fourier Transform Infrared spectroscopy, and photoluminescence spectroscopy were performed on these samples to observe the effect of polymer passivation on the MoS_2 monolayer. FTIR and photoluminescence measurements suggest that Pa-N provides the most passivation of the three polymers tested. The Pa-N coated sample demonstrated the smallest full width half max of the photoluminescence peak and the largest increase in the MoS_2 FTIR signature of the polymers tested, which are both indications of successful passivation. [9] This result is unexpected as it is the most inert of the polymers tested. PMMA and PVDF-TrFE have functional groups containing oxygen and fluorine that would be expected to better fix sulfur vacancies or provide doping. Pa-N also has the lowest dielectric constant of the three so should not provide much dielectric screening. However, the photoluminescence spectrum of PMMA and PVDF-TrFE sample showed marginal to no improvement and the MoS_2 FTIR signature did not improve as much when compared to the Pa-N coated sample. Further studies including electron mobility measurements and depth profiling X-ray photoelectron spectroscopy will be presented to better understand this relationship.

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[8] B. Stadlober et al., *Chemical Society Reviews*, vol. 48, no. 6, pp. 1787–1825, 2019.
[9] W. Wang et al., *ACS Applied Materials & Interfaces*, vol. 12, no. 8, pp. 9563–9571, 2020.

5:00 PM SB03.07.03

Organic/Inorganic Hybrid Nanocluster for Improving Hardness of PC/PMMA Film Soojeong Jeong and Ho Sun Lim; Sookmyung Women's University, Korea (the Republic of)

Conventional glass had been used in transparent parts of displays, cars, and aircraft. These days, many fields are trying to replace glass with polycarbonate(PC) film for less weight, and safe when it is destroyed. Especially, PC film also has flexible properties, it can be used in various shapes. However, PC films are easily scratched because of their low hardness, resulting in poor visibility. In this study, we synthesize organic/inorganic hybrid acrylate polymer using oligosiloxane nanocluster to improve the hardness of PC/PMMA film over pencil hardness of 4H and overcome other issues. Moreover, the hybrid acrylate polymer has low adhesion with PC/PMMA film, we conducted surface modification of the film and controlling the ratio with organic polymer for great adhesion strength of the coating film. These coating materials also demonstrate hydrophobic, bendable and highly transparent properties due to the combination of epoxy siloxane nanoclusters and polyacrylate networks containing perfluoro groups. And finally, the PC/PMMA film with high hardness and flexibility is expected to replace the glass successfully and can be applied in flexible and curved displays.

5:00 PM SB03.07.04
Anomalous Ionic Gating Effect in Degenerate Semiconductors Won Hyung Lee, Junghyup Han, Yong Hyun Cho and Youn Sang Kim; Seoul National University, Korea (the Republic of)

The insulated-gate field effect, a key feature of semiconductor devices used as switches or rectifiers in power electronics, induces the accumulation or depletion of charge carriers to govern the electrical properties of active layers. In particular, as demands for the miniaturization of electronic devices increase, various attempts have been made to achieve higher carrier density and lower operating voltage in field effect transistors (FETs). Notwithstanding, FETs with silicon dioxide (SiO_2), a typical gate dielectric material, require a high gate voltage (>20 V) to form an active channel by accumulating charge carriers between semiconductor/dielectric layers, resulting in high power consumption. To address this, various high-κ materials, including electrolytes, are desirable as the insulated-gate layer due to their high areal capacitance regardless of the dielectric thickness. Interestingly, studies related to ionovoltaic phenomena show that the electric double layer (EDL)-induced electrolytic gating effect enables ultra-high charge carrier accumulation at the semiconductor channel/electrolyte interface compared to the dielectric (*e.g.*, SiO_2) gating effect. However, as elucidating the cause of these interesting phenomena remains a challenging task, numerous studies related to the electrolytic gating effect have focused on practical applications rather than interpretation of the fundamental principle. Indium tin oxide (ITO) is one of the most widely used transparent conducting oxides in optoelectronics because of its electrical conductivity and optical transparency, but its degenerate doping (more like a metal) limits utilization as a semiconductor device. Nevertheless, in the ITO-based channel layer with high initial electron density, hidden non-degenerate semiconductor characteristics can be realized using dramatic electrolytic (ionic) gating effects. In this work, we observe an anomalous ionic gate field effect (gating off) that conversely reduces the conductivity of ITO (*i.e.*, depletion), resulting in a deactivated channel layer. In brief, we newly introduce a groundbreaking gate-off effect opposite to the principle of activating channels by exceeding the threshold voltage, which is the dielectric gating effect commonly used in FETs. Therefore, to implement the same principle as closing an electric faucet by the ionic gating effect, we propose a combination of the degenerate semiconductor (*e.g.*, ITO) and 21 mol of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), a water-in-salt electrolyte with relatively wide operating voltage window. To clarify the causality of ionovoltaic-related anomalous gating effect, we quantitatively analyze an accumulated/depleted electron density in the ITO channel layer through a sophisticated Hall measurement with applied electrolyte-gated voltage, bridging the fundamental correlation between solid-liquid interfaces and semiconductor principles. Hence, although the dielectric gating effect ($I_{on}/I_{off} \sim 1$) cannot dominate the degenerate semiconductor properties due to its high conductivity, the ionic gating effect ($I_{on}/I_{off} \sim 10^3$) operating at low voltage (<2 V) induces EDL formation at the solid-liquid interface, strongly governing the inherent properties of metal-like ITO. The anomalous ionic gating effect observed here has the significance of being able to realize degenerate semiconductors, which have limitations in controlling electrical conductivity, in an on/off state. Furthermore, we believe that this study serves as a stepping stone for revealing the unestablished principle of interfacial phenomena-dependent application devices based on various emerging semiconductor materials such as graphene and other two-dimensional materials besides ITO.

5:00 PM SB03.07.05
Probing Ion-Molecular Interactions at Solid-Liquid Interface Through Ionic Diffusion-Driven Ionovoltaic Transducer Junghyup Han, Won Hyung Lee, Yong Hyun Cho and Youn Sang Kim; Seoul National University, Korea (the Republic of)

Recently, electrolyte-interfacing systems ranging from electrochemical devices such as batteries and capacitors to electronic devices like electrolyte-gated neuromorphic devices have been actively developed, and solid-liquid interactions are one of the fundamental principles in their systems. These interactions also played a critical role in water motion-driven electricity-generating phenomena which originated from ion dynamics at the interface. Specifically, ion adsorption at electrolyte-insulator-semiconductor (EIS) structure accumulates or depletes the charge carrier of the semiconductor by means of coulomb interactions, and then changes its density near the interface, which was demonstrated as ionovoltaic phenomena. However, more details about various specific interactions such as chemical adsorption of ions, ion specificity, and coulombic pairing remain unrevealed issues in academic fields. Herein, an ion–charge carrier interaction at EIS structure is interrogated with an ionovoltaic transducer, controlled by interfacial self-assembled molecules. An electricity-generating mechanism from interfacial ionic diffusion is elucidated in terms of the ion–charge carrier interaction, originating from a dipole potential effect of the self-assembled molecular layer (SAM). While the ion diffuses through the distilled water (DI water) at the EIS structure, the potential difference between the semiconductor under the DI water and the ionic solution evolves. The ionovoltaic signal inversion occurs by applying the surficial molecules with opposite dipoles which are trichloro(1H,1H,2H,2H-perfluoro-n-octyl)silane (PFOTS) and (3-Aminopropyl)triethoxysilane (APTES) and induce cation and anion adsorption, respectively. In addition, this effect is found to be modulated via chemical functionalization of the interfacial molecular layer and transition metal ion complexation therein. The catechol group (CA), which can form a coordination complex with ferric ions (Fe^{3+}) was chemically modified on the APTES-treated device, and the variation of ionovoltaic signal was observed when the device was exposed to the Fe^{3+} solution and CA formed complexation with Fe^{3+}. In the case of Al^{3+} and Cu^{2+} which have a low binding affinity with CA, there was no evident change in generated signal. Those results show the Fe^{3+} concentration dependence and selectivity. With the aid of surface analytic techniques and a liquid-interfacing Hall measurement, electrical behaviors of the device depending on the magnitude of the ion-ligand complexation are interrogated. Specific chemical adsorption of Fe^{3+} on CA affected the interfacial molecular structure and therefore the change in carrier density of the semiconductor was observed, thereby demonstrating the ion–charge carrier interplays spanning at electrolyte–SAM-semiconductor interface. Hence, this system can be applied to study molecular interactions, including chemical and physical influences, occurring at the solid–liquid interfacial region.

SESSION SB03.08: Durable, Functional Thin Films
Session Chairs: Young T. Kim and Lokendra Pal
Friday Morning, April 14, 2023
Moscone West, Level 2, Room 2014

8:30 AM *SB03.08.01
Modification Rigid Type of Biodegradable Polymers with Amorphous PHA and Current Development Sunjong Kim; CJ Biomaterials, Inc., United States

Society has a serious problem of plastic waste management due to littering by mankind. One of the best solutions to this waste problem is composting. There a number of compostable polymers available such as PLA(PolyLactic acid), PBS:Poly(butylene succinate), PBAT:Poly(butylene-adipate terephthalate), etc..
CJ Biomaterials is one of top solution company which can produce PHA's at a commercial level. Amorphous PHA (Phact A1000P) has unique mechanical properties that makes it a good it a good modifier for rigid polymers including compostable resin such as PLA, PBS, scPHA, etc. The addition of amorphous PHA to these already widely used polymers enhance the properties opening new applications and speeds the rate of degradation reducing the cycle time of industrial composting.
Here we focused on modification of PLA which is one of the most common commercialized compostable polymer. However, its rigidity and stiffness were a limitation of possible applications.
Currently, we prepared a bi-orientated film application for a food packaging area. We will share some results of mechanical properties of bi-axially oriented film which mainly had PLA component with PHA as a modifier. When adding 30% of amorphous PHA(aPHA) in a PLA matrix, it showed lower than 40% relative modulus. Additions of 5% of aPHA in PLA in rigid applications gives a 5x increase in Izod impact than reference(neat PLA).
CJ Biomaterials will share its own characteristics of aPHA to expand the use of PLA a flexible packaging.

9:00 AM DISCUSSION TIME

9:15 AM SB03.08.03
Low Thermal Curing Hybrid Sol-Gel Coatings for Scratch and Corrosion Resistance Applications Sudhakara N. Neppalli[1,2,3], Qasim M. Warraich[3], James Kennedy[2] and Brendan Duffy[3]; [1]Trinity College Dublin, Ireland; [2]KASTUS Technologies, Ireland; [3]Technological university dublin, Ireland

Sol-gel surface coatings on metals and metals plated substrates play a crucial role in protecting not only from the harsh environments but also provide wider applications such as hydrophobicity, easy cleaning, anti-microbial, scratch resistance etc. Majority of the sol-gel coatings presently available are designed to cure either at shorter timings at higher temperatures (≥ 100 ^{o}C) or longer timings (≥ 24 hrs.) at lower temperatures (≤ 100 ^{o}C). Limitation of high temperature curable sol-gels are not suitable for plastics and the longer curing conditions are not industrially/economically feasible.
In addressing the issue, we have developed new organic-inorganic hybrid (OIH) sol-gel formulations which is curable at lower temperatures and shorter time intervals. Additional advantage of the developed formulations is that the sol-gels can apply on metal plated plastics such as chrome plated acrylonitrile-butadiene-styrene (c-ABS) and cure at lower temperatures (≤ 80 ^{o}C). Developed sol-gels were applied on aluminium and c-ABS and analysed using dynamic light scattering, UV-Vis spectroscopy, rheometer, filmetrics, nano scratch, neutral salt spray (NSS), pendulum & pencil hardness and optical microscopy. These results shows that particle size distribution is around 2-5 nm and the hardness for the coatings was increased to 6H on c-ABS and 8H on aluminium substrate. NSS test reveals the longer time (800 hrs.) resistance from corrosion.

9:30 AM SB03.08.04
Soft and Stretchable Elastic Films Patterned with Liquid Metal for Energy Harvesting and Electromagnetic Interference Shielding Materials Yuwen Wei[1], Priyanuj Bhuyan[1], Suk Jin Kwon[2], Sihyun Kim[1], Byeongjin Park[2] and Sungjune Park[1]; [1]Jeonbuk National University, Korea (the Republic of); [2]Korea Institute of Materials Science, Korea (the Republic of)

Liquid metal (LM) based soft and stretchable electronics that can be used for multifunctional electronic materials by referring to the human body, such as e-skin, and soft robotics. The development of an e-skin that can be self-powered and can prevent electromagnetic interference (EMI) is essential for the proper function of soft robotics and wearable electronics. Here, we present a design strategy for creating an absorption-dominate flexible and stretchable EMI shielding and energy harvesting, which is composed of a liquid metal grid and elastic polymer. The thin films are sustainable energy sources to power a diverse range of devices by tapping and it also has an impressive EMI shielding function in operation to avoid interference from external electromagnetic signals. The elaborate multilayered film with a thickness of less than 500 µm has a high absorption shielding effectiveness (SE_A) of more than 60 dB as well as a low reflection shielding effectiveness (SE_R) of 1.7 dB over a broadband frequency (50 GHz to 100 GHz). Moreover, the shielding effectiveness in a specific frequency range can be controlled by creating liquid metal mesh patterns with designed geometries. Due to the flexibility and stretchability (more than 1,000%) of the elastic film with liquid metal electrode, the alteration of the mesh patterns can be achieved by stretching the film, thus enabling the adjustment of the EMI shielding interval. Unlike traditional EMI shielding materials, our proposed elastic films can provide high absorption with low reflection and they can be adapted to the resonant frequency by stretching to shield the various frequencies of electromagnetic waves from the device. In addition, the grid structure of LM patterns can enhance structural stability and maintain a high triboelectric performance (120 V) compared to the conventional method of tiling thin layers of LM. This outstanding performance can be demonstrated by activating LEDs and an electronic wristwatch by hand-tapping the films under various deformations (e.g., rollable, foldable, and stretchable). Overall, our findings exhibit potential for developing a novel class of multifunctional soft and stretchable wearable e-skin for energy harvesting and absorption-dominant EMI shielding materials for application in the 5G generation electronics.

SESSION SB03.09: Virtual Session I
Session Chairs: Yei Hwan Jung and Kyungjin Kim
Wednesday Morning, April 26, 2023
SB03-virtual

8:00 AM *SB03.09.01
Flexible Silicon-Nanomembrane-Based Bioelectronic Implants with Ultrathin Biofluid Barrier Materials as Chronic Neural Interfaces Enming Song; Fudan University, China

Flexible engineered systems that establish high-performance, long-lived electrical interfaces to the brain and other tissue parts, at a variety of scales ranging from individual-neuron resolution level to macroscopic area coverage, are of particular interest to the neuroscience and biomedical researches, capable of serving as active implants with the ability to operate in a safe, stable fashion over extended periods of time. Conventional material approaches of state-of-

art, fully-integrated electronic systems, such as deep brain stimulators, pacemakers and cochlear implants, generally feature stiff, thick (millimeter-scale) materials constructed by bulk metal, ceramics and wafers, such as hermetic housings of titanium (Ti) or cofired alumina-glass packages. These resulting systems directly contact or insert into adjacent surface of bio-tissues by passive, rigid electrodes with high modulus, where the materials used for these systems are fundamentally mismatched with the curved, compliant and time-dynamic tissues, with the potential of injury and associated foreign-body response that induces device degradation at biotic/electrode interfaces.
Here, the critical challenge is in the development of active materials and device designs, in a thin-film form, that can serve as stable, intimate sensing and/or actuating interfaces to the targeted biological tissues, simultaneously providing robust biofluid-barrier strategies with multi-decades lifetime. Requirements are for robust defect-free, biocompatible and impermeable biofluid-barrier materials that can be rendered in thin, flexible forms and integrated with targeted electronic platforms. In this context, our work focuses on active, soft electronic materials, ranging from high-performance silicon-nanomembrane (Si-NM)-based bioelectronics, to long-lasting stable implants, to actively multiplexed high-channel-count matrix array for spatiotemporal mapping, to their use as high-resolution neural interfaces with chronic stabilities. To begin with, this report summarizes recent advances in this field of science and engineering, with an emphasis on active and passive constituent materials, design architectures and integration methods that support necessary levels of biocompatibility, electronic functionality and reliability for use *in vivo*. Detailed discussion includes our achievements on recent published work, ranging from (1) microscale fabrication for over 32,000 Si-NM CMOS transistors as flexible interconnected network via transfer-printing technology, serving as electrophysiological recording channels; (2) development of thermally-grown silicon dioxide as ultrathin encapsulation strategy at sub-micron thickness (< 1 µm) with operational stability of projected lifetime over 60 years *in-vivo* in human brain; (3) establishment of implantable, biocompatible electrophysiology mapping techniques for neuromodulation with capabilities of bio-signal sensing/stimulation with a high signal-to-noise ratio (SNR) over 40 dB. As a consequence, our work highlights many thousands of active, high density/resolution device arrays over full-brain-scale areas, with robust, ultrathin encapsulation strategies that can establish long-lived electrical and optical interfaces to neural systems. These achievements will open up future opportunities of new engineering design for neural electronic interfaces of stretchability and biocompatibility for multifunctional electrical/optical neuromodulation for diagnosis/treatment of associated neurological disorders such as epilepsy.

8:30 AM *SB03.09.02
Dry Thin-Film Processing for New Generation Devices—From the Role of Nanoporosity in Barrier Layers to the (Un)Wanted Effect of the Harsh Plasma Environment Alberto Perrotta; National Research Council (CNR), Italy

Functional organic and inorganic thin films offer innovative solutions for a plethora of technological applications: organic and hybrid electronics, smart (bio) devices, membrane technology, photocatalysis, sensors and drug delivery systems. The applicability of such thin films strongly depends on the versatility of the synthetic method in tailoring the chemical-physical properties of the materials. In this perspective, porosity is one of the most (un)wanted properties in thin films fabrication. When the thin films are adopted as permeation barriers, (nano)pores could be detrimental in blocking the targeted species and the fabrication methodologies aim at producing pore-free thin films or being able to “heal” the layer barrier properties.
The research on the porosity and its impact will be presented for organic and inorganic (ultra) thin films obtained via (plasma-based) dry deposition methods such as atomic layer deposition (ALD), plasma enhanced-chemical vapor deposition (PE-CVD), initiated CVD (iCVD) and molecular layer deposition (MLD). The undesired porosity will be investigated specifically in the field of protective coatings applied to flexible electronics. Optical and analytical methods for the characterization of such (intrinsic) porosity will be presented, with an overview on the processing aspects leading to its formation and curing.
On a second aspect, thin film fabrication relying on plasma-based techniques is the method of choice for a growing pool of academic and industrial-based innovation technologies. Plasma enhanced methods allow the production of materials with a considerable lower thermal energy and often with a higher chemical-physical quality. However, materials and devices undergoing plasma-based treatments and thin film deposition have to sustain the harsh plasma environment, often representing the bottle-neck for the applicability of these methodologies. The effect of plasma and plasma polymer deposition on emerging materials for energy harvesting and storage will be investigated. The application of fluorocarbon and S-containing plasma polymers and its effects on the opto-chemical properties, morphology and reliability of halide-based hybrid perovskite materials and devices will be explored, with the final goal of enabling their use in the challenging photocatalysis in aqueous environment. Moreover, plasma processing as a tool to mitigate and passivate surface defects will be also explored for thin film perovskite-based photovoltaic devices. Different plasma chemistries, commonly used in thin film deposition and plasma treatments, i.e., Ar, H_2, N_2, O_2, were applied on the halide perovskite layers, showing the limits of applicability and new opportunities of such a wide used technology on emerging thin film materials. Finally, the effect of plasma processing on bioderived carbon electrodes for a new generation of green electronics for energy storage will be shown.

9:00 AM *SB03.09.03
Hydrogels as Self-Acting Substrates for Generation of Flexible Electronics Lucian Lucia, Sachin Agate and Lokendra Pal; NC State University, United States

We fabricated a hydrogel laminated substrate exhibiting UV light-tunability to induce morphological anisotropy within low swelling zones. Such substrates display remarkable localized depolymerization, resulting in a self-acting patterned swelling phenomenon transverse to the long axial plane. Introduction of aqueous inks therefore biases self-alignment within the post-photocured patterns due to mechanisms such as ink polymer displacement by swelling, physical trapping of high viscosity inks, and hydrophilic selectivity. Our photocuring method can generate patterns smaller than 300 µm and offers an unparalleled platform for surmounting limitations of current printing and ink systems.

9:30 AM SB03.09.04
Anti-Adhesive Bioresorbable Elastomer Coating That Reduce Intraperitoneal Adhesions in Abdominal Repair Procedures Shantanu P. Nikam[1,2], Yen-Hao Hsu[1,2], Jessica Marks[2], David Ruppert[2], Howard Levinson[2] and Matthew Becker[2,2]; [1]The University of Akron, United States; [2]Duke University, United States

Intraperitoneal adhesions (IAs) are a major complication arising from abdominal repair surgeries and affects thousands of patients (>100,000) per year in the US with total treatment cost estimated upward of $1 Billion.
IAs can cause small-bowel obstruction, fistula, infection, chronic pain and inflammation, which often require high-risk re-operation with prolonged hospitalization and sometimes leading to chronically debilitated patients.
Herein, we fabricated a composite mesh using a macroporous monofilament polypropylene mesh and a degradable elastomer coating designed to meet the requirements of this clinical application. The degradable elastomer was synthesized using an organo-base catalyzed thiol-yne addition polymerization. The polymer design affords independent control of degradation rate and mechanical properties. The elastomeric coating was further enhanced by the covalent tethering of antifouling zwitterionic molecules on its surface using ‘Click Chemistry’ which was confirmed by XPS measurements. Quartz crystal microbalance measurements showed the zwitterionic functionalized elastomer further reduced fibrinogen adsorption by 73% *in vitro* when compared to unfunctionalized elastomer controls. Mechanical testing demonstrated the elastomer forms a robust coating on the polypropylene mesh that does not exhibit micro-fractures, cracks or mechanical delamination under cyclic fatigue testing that exceeds peak abdominal loads (50 N/cm). The elastomer exhibited degradation with limited tissue response in a 10-week murine subcutaneous implantation model. We also evaluated the composite mesh in a 12-week study

in a rabbit hernia adhesion model. The zwitterionic composite mesh significantly reduced the extent and tenacity of IAs by 94% and 90% respectively with respect to uncoated polypropylene mesh. The resulting composite mesh device is an excellent candidate to reduce complications related to abdominal repair through suppressed fouling and adhesion formation, reduced tissue inflammation, and appropriate degradation rate.

9:45 AM *SB03.09.05
Exploration of Hemp Hurds Waste for Lignin-Containing Nanocellulose Based-Barrier Films for Sustainable Packaging Preeti Tyagi, Lucian Lucia and Lokendra Pal; NC State University, United States

Over the past two decades, cellulose nanofibers (CNFs) have been explored as a source material for various applications such as reinforcements in polymers, thin films, electronics, hydrogels and food packaging. CNFs are predominately sourced from plant fibers (both wood and non-wood) through several pretreatment and mechanical processes. Production of these nanomaterials is a challenge, mainly because of the cost of feedstock materials. These concerns have given rise to a new category of nanocellulose, lignin-containing cellulose nanofibers (LCNFs), which is cheaper as compared to bleached cellulose nanofibers (BCNFs). Also, LCNFs have been found to be less hydrophilic compared to BCNF, which can be an advantage for many packaging applications.
In this presentation, we will talk about how we used residual hemp (Cannabis sativa) hurds to obtain LCNFs using different pretreatments such as autohydrolysis, carbonate, and kraft pulping. The obtained LCNFs were characterized morphologically, for crystallinity, and chemical characteristics using SEM-EDX, XRD, and ToF-SIMS, respectively. LCNFs films were made and water barrier properties of the same were measured in terms of water contact angle, water vapor permeability (WVP), and water absorption. The results showed that LCNF-based films derived from hemp hurd residual fibers could contribute to a circular economy and sustainability.

SESSION SB03.10: Virtual Session II
Session Chairs: Yei Hwan Jung, Kyungjin Kim and Lokendra Pal
Wednesday Morning, April 26, 2023
SB03-virtual

10:30 AM *SB03.10.01
Robust Encapsulation of Printed Flexible Electronics via Cold Atmospheric Plasma Assisted Silicon Dioxide Coating Rahim Rahimi and Venkat Kasi; Purdue University, United States

Flexible hybrid electronics (FHEs) are emerging devices that bridge the divide between conventional, rigid electronics, and fully printed devices. The FHEs have opened a series of unprecedented application possibilities with broad interest and potential for impact, especially in wearable and implantable healthcare applications. Many such devices are exposed to harsh environmental conditions (e.g., high humidity levels and mechanical stress/strain), requiring them to be encapsulated with insulating polymeric coatings. One important parameter that determines the lifetime and reliability of encapsulated devices is the adhesion between the polymer coating and the printed substrate. In high humidity conditions (e.g., underwater), improper bonding between layers will result in water condensation at the interface between the layers, leading to the failure of the device and electrical shortage. This issue can become more challenging for circuits with complex designs when encapsulant delamination happens in hidden areas that can hardly be noticeable during the initial stage of failure. The bonding between coatings and substrates can be improved by using adhesion-promoting intermediate layers such as SiO_2 deposited through atomic layer deposition (ALD) prior to encapsulating with the polymeric coating. In this process, the hydroxyl groups (-OH) on the glass surface will interact with the silanol groups in the polymer resin coating, resulting in strong Si – O – Si covalent bonds that form between the two materials. Although ALD technology provides precise control of layer thickness at the sub-nanometer scale and is successfully implemented in the packaging of OLED technologies, the process requires complex and time-consuming vacuum-assisted machinery with limitations on the substrate size or dimensions. To address this challenge, we will discuss the novel use of cold atmospheric plasma (CAP) as an alternative to ALD with great potential for scalability and implementation in additive and roll-to-roll manufacturing processes. The CAP deposition process can be used to deposit thin films in a continuous process and directly onto specific locations that are needed. In this process, a plasma head is used to chemically decompose volatile organosilicate precursors and as a source of active species involved in the SiO_2 film deposition.
In this talk, we will review the CAP processing conditions for depositing SiO_2 coatings using Tetraethoxysilane precursor, and it's used as an intermediate barrier layer between the printed circuit and polymeric dielectric layer to improve moisture barrier properties. The processing conditions on the deposited coating's chemical structure, morphology, and electrical properties have been carefully investigated under different CAP processing conditions. This investigation showed the intermediate SiO_2 coating provided a 1000-fold improvement in moisture-resistant barrier properties compared to samples without the intermediate layer. The FHEs prepared with the optimized packaging conditions also show excellent environmental and mechanical stability (even after 1,000 cycles of bending under water). As a proof of concept, the use of the technology was investigated as a reliable packaging approach for robust packaging of printed antennas in automotive applications. It is envisioned that the intermediate SiO_2 coating process can provide a new route in the scalable, more cost-effective, and robust packaging wide range of FHEs for emerging application areas in wearable healthcare, environmental, agricultural, and structural health monitoring applications.

SYMPOSIUM

April 10 - April 26, 2023

Symposium Organizers
Sahika Inal, King Abdullah University of Science and Technology

Wolfgang Knoll, Austrian Institute of Technology
Sabine Szunerits, University Lille, IEMN
Robert Wagner, Danube Private University

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* Invited Paper
\+ Distinguished Invited

SESSION SB04.01: Materials for Bioelectronics
Session Chairs: Sahika Inal and Wolfgang Knoll
Monday Morning, April 10, 2023
Moscone West, Level 3, Room 3004

8:30 AM SB04.01.02
CRISPR Cas13a-Graphene Field-Effect Transistors for Amplification-Free Detection of Nucleic Acids Huijie Li and Yi Zhang; University of Connecticut, United States

Molecular diagnostics, in particular nucleic acid testing, is critical in a wide range of fields relevant to the quality of human life, including a fundamental understanding of physiological processes, pathogen detection, and disease prognosis and diagnosis. Over the past few decades, quantitative polymerase chain reaction (qPCR) has remained as the gold-standard technique for nucleic acid testing. However, qPCR is limited by expensive instruments, the need for well-trained personnel operation, and long sample-to-results time. Recently, the discovery of clustered regularly interspaced short palindromic repeats (CRISPR)-Cas (CRISPR-associated) systems has opened a new path for nucleic acid detection. Leveraging the single-nucleotide target specificity of CRISPR-Cas systems as a result of complementarity between guide RNA and target nucleic acid sequence, scientists have developed a variety of CRISPR-based biosensing strategies for ultrasensitive and highly selective nucleic acid detection. However, the application of current CRISPR-based molecular diagnostics still requires lengthy and complicated target amplifications. In this talk, I will present our recent efforts on the development of a set of CRISPR-based molecular diagnostic platforms without the need for target pre-amplifications by coupling CRISPR assay with bioelectronics of graphene field-effect transistors and other electrochemical biosensors.

8:45 AM SB04.01.03
Satellite-Inspired Ingestible Electronic Platform for Sensing from the Duodenum Yiyuan Yang, Kewang Nan, Fangzhou Xia, Miguel Jimenez and Giovanni Traverso; Massachusetts Institute of Technology, United States

Long term monitoring of gastrointestinal function often requires hospital-based medical interventions which are generally limited to transient optical evaluation as well as short term monitoring of temperature, pH or impedance for generally hours and up to 48 hours. Long term monitoring of both the gastric and duodenal compartments stands to transform our capacity to monitor feeding activity as well as liver and pancreatic function. Here we report the development of a system which combines wireless communication with multi-mode sensing in the form of miniaturized flexible-board electronics with thin film sensors compatible with ingestion. The entire system can be administered either endoscopically or ingested and operate over an extended period. Once active, the device naturally conforms to the GI tract and has the capacity to transiently anchor itself at the level of the pylorus through which integrated sensors can be deployed to support the collection of electrophysiological signals. In vitro and in vivo evaluation support the device’s long-term stability as well as their applicability in measuring local temperature, pressure and impedance in GI tract that serve as important physiological indicators for GI diseases such as inflammation, gastroenteritis, mobility disorders, bloating, ulcers, intestinal ischemia, and bile reflux.

9:00 AM SB04.01.04
Smart Stickers for Non-Invasive Wireless Detection of Early Stage CAUTI Sarath Gopalakrishnan, Muhammad Masud Rana, Michael Anthony Curry Jr, Akshay Krishnakumar and Rahim Rahimi; Purdue University, United States

A urinary catheter is a flexible tube widely used when patients have difficulty urinating naturally and collect urine in a drainage bag. Patients prefer indwelling catheters to avoid multiple insertions of the catheters. However, in many cases, germs like bacteria can enter the body through the catheters and cause an infection in the bladder or kidney called a catheter-associated urinary tract infection (CAUTI). CAUTI affects 0.4 million people every year and causes patient distress, discomfort, pain, and activity restrictions and in some cases can lead to life-threatening conditions. Moreover, CAUTI incurs a medical burden of $340–450 million per year in the US. While many conventional tools such as invasive Cystoscopy, Non-invasive Ultrasound/CT scan have widely used been used for the detection of CAUTI, they are expensive, not real-time, and need manual intervention. A low-cost, non-invasive and contactless automatable sensor is critical in tackling CAUTI.

To address this need, here, we develop a non-invasive smart sticker platform that integrates low-cost smart stickers with a portable reader to detect early-stage UTI through continuous monitoring of urinary frequency and conductivity of urine. Inflammation of the bladder, urethra, or both causes a sensation of the need to urinate thereby increasing the urinary frequency above the healthy range of 5-8 times in 24 hours. UTI causes an increase in the bacterial count and biofilm formation in the flushed-out urine, effectively reducing the conductivity of the patient’s urine at the onset of infection. To capture the urinary frequency through level detection and bacterial infection through conductivity measurements, the smart stickers are designed as two parallel metallic strips manufactured using laser processing of metalized PET tape. This scalable manufacturing technique offers a platform for the rapid production of smart stickers using roll-to-roll processing. Using this platform, a long smart sticker of size 20 cm x 2 cm is manufactured for urine level monitoring to cover the urine bags of volume 2000 mL. Next, to achieve conductivity detection, a short sticker of size 4 cm x 2 cm is manufactured to ensure that the sticker is insensitive to level changes.

The achieve non-invasive measurements, the stickers are attached to the surface of the urine bag and interfaced with a portable reader with the help of a snap-on magnetic connector. The portable reader consists of a signal generator and a scalar reflectometer to form a portable network analyzer. When the urine level increases, the capacitance between the long stickers increases leading to a shift in the resonant frequency. When the conductivity of urine increases, the attenuation between the short stickers increases leading to a reduction in the amplitude of the resonant peak. The readings from the network analyzer are collected by an Arduino module and transmitted using a WiFi module.

A systematic characterization of the smart stickers is performed using artificial urine placed inside the urine bag. The level detector demonstrates a frequency shift from 530 MHz to 234 MHz when the urine level is changed from 500 mL to 2000 mL. Furthermore, the smart stickers provide constant potential voltage over 24 hours of measurement and show an excellent linear sensitivity of 3.1 mV/(mS/cm) from 10 mS/cm to 40 mS/cm in the urine sample. A proof-of-concept analysis is performed to simulate CAUTI by spiking the bacterial CFU in the urine and the readings demonstrated a 10% decrease in the conductivity when CFU levels surpassed the threshold of 10^5 CFU/ml. The smart stickers presented in this work could be the first step towards the development of low-cost and automated noninvasive smart sensor tags for early-stage CAUTI detection.

9:15 AM SB04.01.05
Fully-Printed Multiplexed Wearables for Real-Time Electrochemical Sensing of On-Skin Metabolites Le Yang; Institute of Materials Research and Engineering, Singapore

In an increasingly health-aware population and a move towards remote diagnostics, remote healthcare monitoring, cloud-based med-tech, etc, we tap on the ubiquitous and unlimited reservoir of on-skin biomarkers, including sweat metabolites, in developing a wearable, non-invasive, continuous and real-time sensor – a printed, multiplexed biosensor device. In this talk, we highlight three components of our biosensor. Firstly, we look at the overall framework, of how the device is fabricated by a fully printed process, and what the integrated sensor is capable of measuring.[1-4] Carbon-based electrodes are promising candidates for developing cheap, miniaturized, and disposable biosensors for effective wearable applications. From developing our own printable carbon-based ink, to screen-printing the electrodes, to functionalising each electrode into a specific biosensor, and finally to multiplexing and integration; we show how these devices can potentially add value to home-based biomarker monitoring. Secondly, we look at a variation of our flexible electrode, a graphite/carbon fiber (G/CF) hybrid resembling a super-efficient 3D highway network where ample expressways (CF) run through numerous small factories (locally distributed graphite flakes) for rapid goods pick-up and transportation (electron transfer).[5] Lastly, we zoom in on the top-most layer of the device, the Kirigami paper sweat channel, critical in enabling real-time fresh-sweat reading.[6,7]

[1] A graphite-based paste/ink for electrochemical sensors, WP Goh, CY Jiang, Y Yu, XT Zheng, YX Liu, L Yang, PCT/SG2022/050407, Singapore (*filed, secondary*), 2022.
[2] XT Zheng, WP Goh, CY Jiang, Y Yu, YX Liu, L Yang et al, *Manuscript in preparation*.
[3] Stretchable biochemical interface for solid epidermal analytes, YX Liu, WP Goh, XT Zheng, Y Yu, SCL Tan, CY Jiang, RT Arwani, L Yang, SG-10202202318P, Singapore (*filed, primary*), 2021.
[4] RT Arwani, WP Goh, CY Jiang, XT Zheng, Y Yu, YX Liu, L Yang et al, *Manuscript in preparation*.
[5] Y Yu, L Yang et al, Materials Today Advances, 14, 100238 (2022).
[6] A kirigami paper fluidic channel for sweat sensors, CY Jiang, WP Goh, XT Zheng, Y Yu, YX Liu, L Yang, SG-10202113328Q, Singapore (*filed*), 2021.
[7] CY Jiang, WP Goh, SCL Tan, XT Zheng, Y Yu, YX Liu, L Yang, *Manuscript in preparation*.

9:30 AM SB04.01.06
PEDOT:PSS Based Soft, Healable and Highly Adhesive Films for Monitoring Human Health Fabio Cicoira; Ecole Polytechnique de Montreal, Canada

Flexible, soft, self-healing, and adhesive conductive materials with Young's modulus matching biological tissues (with a moduli of 0.5-500 KPa)[1] are highly desired for applications in bioelectronics. Here, we report self-healing, stretchable, highly adhesive and conductive films obtained by mixing tannic acid (PVA), ethylene glycol, and Poly (3,4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS).[2] Our films demonstrated remarkable self-healing and self-adhesiveness, compliance on skin, outstanding stretchability, high adhesion on skin , and low Young's modulus. Our films were used to fabricate electrophysiological epidermal patch electrodes, which exhibited high-quality recording of electrocardiography (ECG) and electromyography (EMG) signals, like commercial Ag/AgCl gel electrodes.

9:45 AM SB04.01.07
Pressure-Sensor-Integrated Smart Bandage for the Management of Diabetic Foot Ulcers Xueju Wang; University of Connecticut, United States

Diabetic foot ulcers (DFUs) have affected millions of people in the U.S. and posed heavy burdens to patients and the healthcare system due to their being slow to heal, high recurrence rate, and potential risk of amputation and even premature death. A mainstay of DFU therapy is mechanical offloading to mitigate pressure at the ulcer, which, however, is usually not effective due to patients' diminished sensation capabilities on the foot and low adherence to offloading recommendations. I will present our recent effort in developing a soft, flexible, wireless pressure-sensor-integrated smart bandage system for continuously monitoring the pressure on the foot and alerting the users to offload under exceeded pressure. The pressure sensor exhibits high linearity, negligible hysteresis, fast response time, and excellent water-proof properties relevant to this application. Wireless data transmission onto a smartphone via Bluetooth enables the display and interpretation of the measured pressure with the option of a preset pressure threshold, when exceeded, an alert will be generated for immediate notifications. Trials on healthy subjects demonstrate reliable monitoring performance and effectiveness in aiding offloading. The developed smart bandage system represents a significant advance in the prevention and management of DFUs and other pressure injuries as well as compression therapy corrections.

10:00 AM BREAK

10:30 AM *SB04.01.08
High-Detectivity Wearable Organic Photodetectors for Self-Powered Pulse Rate and Oximetry Measurements Thuc-Quyen Nguyen; University of California, United States

Wide-range light detection from the visible to the near-infrared (NIR) region is central to many applications such as high-speed digital cameras, autonomous vehicles, IR sensing, and wearable electronics. Recently, organic photodetectors (OPDs) were shown to be a promising platform for these applications. However, the conventional OPDs are often limited by low responsivity, narrow absorption range, large dark/noise current under applied bias, and large-scale production of these devices require halogenated processing solvents that have a negative environmental impact. In this talk, I will discuss strategies to reduce dark current in NIR OPDs based on a bulk heterojunction (BHJ) comprised of a polymer donor and a non-fullerene acceptor and the molecular design rule for processing OPDs from a green solvent, 2-methyltetrahydrofuran (2-MeTHF). Our OPDs exhibit an excellent specific detectivity (D*) over a broad wavelength range (400 -900 nm) and is comparable to those of commercial silicon-based photodiodes. We demonstrate that the PM7-D5:Y12 OPDs can be used as wearable self-powered devices to monitor heart rate and blood oxygen saturation.

11:00 AM SB04.01.09
Discovering Giant Magnetoelasticity in Soft Matter for Bioelectronics Guorui G. Chen and Jun Chen; University of California, Los Angeles, United

States

Conventional magnetoelasticity, defined as the change in magnetic property in certain materials under mechanical stimulations, is usually observed in rigid alloys such as $Tb_xDy_{1-x}Fe_2$ (Terfenol-D) and Ga_xFe_{1-x} (Galfenol). However, interfacing electronic devices based on these rigid alloys with the human body might hurt the surrounding tissues and the resulting scars will damage or even disable the devices. Herein, we discovered the giant magnetoelasticity in soft matter and achieved a magnetomechanical coupling factor of up to 6.77×10^{-8} T/Pa without the need of an external magnetic field, which is up to five times larger than that of traditional rigid metal-based counterparts.[1] Meanwhile, the soft matter with the giant magnetoelasticity demonstrates a strain of up to 500% and a Young's modulus as low as 166.2 kPa, which is well comparable to the human tissue and skin. To elucidate the fundamentals of giant magnetoelasticity in soft matter, we established an analytical model based on the magnetic particle and dipole interaction, which is well consistent with the experimental observation.

Then we explored our discovery in bioelectronics by coupling it with magnetic induction to invent a textile magnetoelastic generator (MEG) for biomechanical-to-electrical signal conversion. The human body is particularly rich in biomechanical energy,[2] which can be explored to power bioelectronics for *in vivo* and *in vitro* diagnostics and therapeutics. Intimately interfacing the textile MEG with the skin, the relevant body movements could deform the device and strongly alter its magnetic flux density, thereby inducing a current in the textile coil with a density of 1.37 mA/cm^2. The collected electricity in the capacitor could drive a commercial thermometer for personalized sensing.

Meanwhile, the textile MEG can work as a self-powered sensor for *in situ* biomechanical signal analysis.[1,3] Textile-based bioelectronics can realize wide biomedical applications while maintaining their initial wearing comfort.[4-8] Thus, we seamlessly sewed the textile MEGs on the chest area of clothes for respiratory monitoring.[1] With a fundamentally new working mechanism, the textile MEG demonstrated an intrinsic waterproof property, an sensitivity of 0.27 mA/kPa, a signal-to-noise ratio of 61.8 dB, and a response time of 15 ms, which could continuously monitor the strength, frequency, and patterns of various respiratory activities on heavy perspiration skin without any encapsulation. Assisted by a machine learning algorithm, respiration abnormalities, such as cough and rapid breathing, can be recognized with an accuracy of up to 90.89%, hence allowing a personalized and timely detection of respiratory diseases. Thus, we believe that the discovery of giant magnetoelasticity can branch out into broader soft-matter systems, illuminating the future of biomedical society by developing human-body-centered bioelectronics for personalized healthcare.

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(*equal contribution)

11:15 AM SB04.01.10
Albumin-Based Antifouling Coating for CRISPR-Based Electrochemical Detection of SARS-CoV-2 Jeongchan Lee; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

As modern history progresses, the emergence of new viruses and the global outbreak of related diseases pose a serious threat to public healthcare issues. Recently, coronavirus disease 2019 (COVID-19) has become a global pandemic. Currently, the gold standard for COVID-19 diagnosis is quantitative reverse transcription-polymerase chain reactions (qRT-PCRs). However, it is time-consuming and requires laboratory-based hospitals, making the countries with poor infrastructures struggle to control the spread of virus.

We here present a method to formulate a thick (>1 μm) antifouling coating with macro- and nano-scale pores for electrochemical diagnostic sensors with ultrahigh sensitivity using an emulsion ink. Traditional antifouling coatings such as poly(ethylene glycol) (PEG) and bovine serum albumin (BSA) have several limitations in biomedical applications: they physically adsorb onto the sensing surfaces, which cannot ensure full blocking of the active surfaces and they may detach from the surface, 2) they hinder electron transfer in the electrode surfaces, reducing the electrochemical signal. Oil-in-water emulsion can be utilized to form the multiscale porous antifouling coating at any thickness desired and the highly porous nature of the material greatly increases its surface area available for bioreceptor presentation and interactions with analytes. We designed CRISPR-based sensors for detection of SARS-CoV-2 RNA using an electrochemical (EC) enzymatic sandwich detection assay, which allows us to detect the SARS-CoV-2 without electrode surface inactivation. It is also desirable as an antifouling coating as it can be rapidly applied using nozzle-assisted printing in a form that is highly sensitive and robust, plus functional nanomaterials can be embedded within the layer.

11:30 AM SB04.01.11
A Flexible and Switch-Matrix Addressable Active Electrode Array Based on Complementary Organic Electrochemical Semiconductor Technology Ilke Uguz[1], David Ohayon[2], Sophie Griggs[3], Iain McCulloch[3], Sahika Inal[2] and Ken Shepard[1]; [1]Columbia University, United States; [2]King Abdullah University of Science and Technology, Saudi Arabia; [3]University of Oxford, United Kingdom

While there has been considerable recent interest in flexible and conducting polymer (CP)-based implants for interfacing with the brain, nearly all of these studies have focused on passive electrode arrays with low channel counts. Active integration of CP-based electronics for large-scale recordings, on the other hand, is limited, as the current library of active organic electronics is restricted to organic electrochemical transistors (OECTs). OECT gating is traditionally achieved over a common gate electrode and electrolyte, which limits the control of individual components in a large array. In addition, when OECTs are used for active switching operations, ion uptake of CPs poses a major issue for *in vivo* neural applications where the high ionic transients (~μA) result in the undesired activation of nearby neurons and lead to high ionic-electronic cross-talk with the adjacent OECTs. Therefore, there is a significant need for generation of alternative CP-based circuit components to generate complex organic circuitries capable of operation with internal ions to avoid interference with the measured media. In this work, we introduce a new class of organic semiconductors which can be operated by controlling the electrophoretic drift of the internally trapped cations in the channel to generate unidirectional conductivity with electrical output analogous to silicon-based diodes. We tune these organic diodes to work in complementary regime with the existing OECT configuration and demonstrate that this circuit architecture can be used to generate a switch matrix for electrode selection on the neural interface with minimal crosstalk between adjacent pixels. We further show that this topology enables the generation of ultra-thin (50-μm x 8-μm), flexible neural implants with high channel counts (32) that acquire local field potentials with high signal-to-noise ratio. To the best of our knowledge, this work is the first demonstration of active organic electrochemical circuits integrated in the front-end pixel of a fully implantable shank. Owing to their ionic-electronic conductivity, solution-based processability, and integrability with flexible, biocompatible substrates, unlike most inorganic circuit elements, CP-based circuitries are ideal to use on the neural interface.

SESSION SB04.02: Device Design for Bioelectronic Sensing
Session Chairs: Tzahi Cohen-Karni and Luisa Torsi
Monday Afternoon, April 10, 2023
Moscone West, Level 3, Room 3004

1:30 PM *SB04.02.01
Real-Time Biosensor Technology H. Tom Soh; Stanford University, United States

A biosensor capable of continuously measuring specific molecules in vivo would provide a valuable window into patients' health status and their response to therapeutics. Unfortunately, continuous, real-time molecular measurement is currently limited to a handful of analytes (i.e. glucose and oxygen) and these sensors cannot be generalized to measure other analytes. In this talk, we will present a biosensor technology that can be generalized to measure a wide range of biomolecules in living subjects. To achieve this, we develop synthetic antibodies (aptamers) that change its structure upon binding to its target analyte and produce an electrochemical current or emit light. Our real-time biosensor requires no exogenous reagents and can be readily reconfigured to measure different target analytes by exchanging the aptamer probes in a modular manner. Using our real-time biosensor, we demonstrate the first closed loop feedback control of drug concentration in live animals and discuss potential applications of this technology. Finally, we will discuss methods for generating the aptamer probes which are at the heart of this biosensor technology.

2:00 PM SB04.02.02
***In Situ* Swelling of Cartilage Explants for Osteoarthritis Through Graphene Strain Sensing** Charles Dhong; University of Delaware, United States

Osteoarthritis (OA) is a widespread disease which involves the degeneration of cartilage. Healthy cartilage derives its function from a combination of mechanical integrity of the collagen matrix and the physiochemical contributors of negatively charged aggrecan contained inside the matrix. While mechanical integrity via cartilage stiffness is a commonly used biomarker—primarily due to the wide availability of indentation tests—there are few approaches which focus on restoring the aggrecan content, which manifest as the swelling behavior of cartilage in response to different osmotic environments. The challenge is that cartilage explants—which have high physiological relevance—are too large for sensitive instruments and swelling changes are too little for simple visual or mass-based techniques. Here, we developed a platform which uses embedded graphene strain sensors to measure the swelling behavior of equine cartilage explants in real time. By simulating OA-like degradation through a series of enzymes, we were able to identify distinctive swelling profiles of explants undergoing proteoglycan digestion versus broad spectrum matrix damage. This parallel and scalable platform would enable new approaches to OA regeneration based on restoring proteoglycan content.

2:15 PM SB04.02.03
***In Situ* Surface Engineering, Processing and Characterization of Flexible PLA-Based Biocompatible Composites Using Confined Micro-Plasma-Based Technique—For Applications as Embedded Wafers for Targeted Drug Delivery** Manan Sehgal[1], Prakhyat Gautam[1], Mai T. Yang[1], Edgar Perez-Lopez[2], Edbertho Leal-Quiros[2], Saquib Ahmed[3,3] and Sankha Banerjee[1,4]; [1]California State University, Fresno, United States; [2]University of California, Merced, United States; [3]Buffalo State College, United States; [4]University of California, Davis, United States

The following work focuses on the surface modification and processing of flexible PLA and PLA-Graphene composites using room temperature and confined micro plasma-based Townsend discharges in ambient conditions. The work includes in-situ-based processing using a proprietary plasma-integrated 3D printing system developed in the Energy Devices and Plasma Applications Laboratory at California State University, Fresno. The current-voltage characteristics of the plasma are varied based on the use of a quasi-static DC and a pulsed discharge with a variable voltage of 1 kV to 2.2 kV and with currents below 1mA. The micro plasma-based discharges integrated with the additive manufacturing process can tailor the surface characteristics of the composites by modification of their surface energies. The surface characterization of the 3D printed geometries is performed using profilometry, scanning electron microscopy, and electrical impedance spectroscopy. The surface energy and wettability characteristics are studied using contact angle characteristics. The micro plasma is characterized using high voltage probes, and visible spectroscopy. These 3D-printed geometries can be used as embedded wafers for targeted drug delivery.

2:30 PM SB04.02.04
A Very Large-Scale Integration of High Performance, Low Leakage Internal Ion-Gated Transistors (IGTs) for Wireless, Battery-Free Implantable Bioelectronics Claudia Cea, Zifang Zhao, Jennifer Gelinas and Dion Khodagholy; Columbia University, United States

Organic material-based conformable electronics are optimal candidates for components of bioelectronic circuits due to their inherent flexibility and soft nature. We have shown that internally ion-gated organic electrochemical transistors (IGTs) operate by leveraging ion reservoirs inside their channels to dramatically improve the operation speed and integration capacity of this ion driven transistor. In order to establish IGTs as versatile building blocks of bioelectronics, it is critical to establish fabrication strategies to enable IGT-based high-density integrated circuits for creation of fully implantable, wireless, and battery-free devices. Here, we report a scalable, self-contained, and integrable sub-micron internal ion-gated organic electrochemical transistor with vertical channel (v-IGT). Owing to the sub-micron channel size, v-IGTs can operate in the MHz range, surpassing any other electrochemical device while maintaining a high amplification. Furthermore, we analytically and experimentally derived the non-linear relationship between transistor speed and contact area as a function of gate and channel capacitance. The device is encapsulated using long-term implantable grade (parylene-C) material ensuring operational stability of over 1 year. We also developed a micron-scale perforation strategy to ensure intact hydration paths for transistor channels while maintaining effective isolation of densely packed adjacent transistors and minimizing potential for cross-talk and gate current leakage. The presence of this hydration via does not cause a detriment to the device characteristics due to the hydrophilicity and sufficient containment of ion reservoirs in the channel. We fabricated a conformable v-IGT-based array with 155k transistor/cm2, highlighting the viability and feasibility of IGTs as transistor architecture for a majority of flexible electronics applications. We further showcase their functionality by creating high-gain multi-stage amplifiers, oscillators, and multiplexers. Finally, we created a novel wireless, battery-free strategy for electrophysiological signal acquisition, processing and transmission that employs v-IGTs and ionic communication (IC). The wirelessly-powered v-IGTs were able to acquire and modulate neurophysiological data *in-vivo* and transmit them across the dermis, eliminating the need for any hard Si-based electronics in the implant.

2:45 PM SB04.02.05
Quantum-NanoElectroPore Platform for Single-Molecule Conductance and Raman Detection of Biomolecules Sanjana Mukherjee[1], Ching-Wei Tsao[1], Lucas Domulevicz[2], Josh Hihath[1] and Quan Qing[1]; [1]Arizona State University, United States; [2]University of California, Davis, United States

The great advancement in nanopore technology has enabled real-time sequencing without the need for sample amplification with long read length. However, the ionic-current-based readout has limitations in the specificity and resolution, leading to higher error rate. The growing interest in analyzing other biomolecules such as proteins using nanopore configurations also demands integration of additional readout mechanisms such as recognition tunneling and metal-gap enhanced Raman. However so far there is very little success in the integration of single-molecule delivery, and multi-mode detection of the same molecule. We recently developed a new strategy to fabricate a single-molecule sensing microchip platform, Quantum Tunneling NanoElectroPore (Q-NEP), which integrates inside a nanofluidic channel a pair of tunneling electrodes self-aligned with a nanopore, by combining standard top-down lithography on standard semiconductor substrates with *in situ* reversible electrochemical deposition with feedback control. We have demonstrated simultaneous detection of DNA translocation events from coincidental ionic and tunneling current signals, and successfully obtained quantized conductance from short thiolated oligonucleotides bridging the tunneling gap as they were delivered through the nanopore. In addition, metal-gap enhanced Raman signals are also obtained from L-cysteine molecules through the device. These results provide the first step for the integration of ionic, tunneling current and Raman multi-mode analysis of individual molecules on the Q-NEP platform, and reveal the promising potential for a unified microchip platform for multi-omics analysis with high resolution and specificity.

3:00 PM BREAK

SESSION SB04.03: Bioelectronic Sensors
Session Chairs: Thuc-Quyen Nguyen and Sabine Szunerits
Monday Afternoon, April 10, 2023
Moscone West, Level 3, Room 3004

3:30 PM *SB04.03.01
Single-Molecule Reliable Detections with a Large-Area Electronic Interface Luisa Torsi; University of Bari A. Moro, Italy

A large millimeter-wide electronic interface can detect at a single-molecule/entity limit-of-detection. The technology is called SiMoT - Single-Molecule with a large Transistor.[1] So far, antigens (Immunoglobulins, C-reactive proteins, spike 1, HIV p-24), antibodies (anti-immunoglobulins, anti-spike1), peptides, viruses (SARS-Cov-2), bacteria (Xylella fastidiosa), and even DNA strands (KRAS, miR-182) have been detected. Selectivity is assured by covering the gate electrode with a large number (10^{11}-10^{12}/cm^2) of recognition elements to affinity binding the target element.

SiMoT detects directly in a droplet (0.1 mL) of a real fluid such as saliva from COVID-19 patients, blood serum, pancreatic cysts juice, and olive saps from infected trees. Relevantly Brownian diffusion enables the entity to statistically hit the millimeter-wide interface in a few minutes.[2]Considering the footprint of a molecule on a millimeter-wide interface, it is like spotting a droplet of water falling on the surface of a 1 Km wide lake as depicted in the graphical abstract.

The applications span from a handheld intelligent single-molecule binary bioelectronic system for fast and reliable immunometric point-of-care testing of COVID-19 patients[3] and Xylella fastidiosa single bacterium detected in infected plants sap. The phenomenon enabling such outstanding performance level was discovered in 2018.[4] While still under investigation, it is supposed to involve an amplification that starts from the single affinity binding that triggers a propagating collaborative response.

Future actions include the deepening of our understanding of the sensing mechanism and the engagement in a campaign of thousands of clinical trials that will bring SiMoT beyond TRL5.

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4:00 PM SB04.03.02
Flexible, Implantable, Pulse Oximetry Sensors for Continuous Monitoring of Arterial Blood Oxygen Levels Joseph Troughton[1], Pauline Brige[2] and Marc Ramuz[1]; [1]MINES Saint-Étienne, IMT, France; [2]Aix-Marseille Université, France

Pulse oximetry is the most widespread method of monitoring patient heart rate and blood oxygen levels in both clinical and non-clinical settings. These devices tend to be ridged, bulky, and therefore suitable only for short-term use. In addition, they suffer degraded performance due to movement and changes in ambient light levels, and can present variability from one individual to another. To facilitate long-term monitoring of physiological parameters, including heart rate and oxygen saturation, implanted devices are required. Implantation removes interference from external light sources, eliminates sensitivity to skin pigmentation, and allows enhanced performance during movement associated with greater sensitivity.
Here we demonstrate a low cost, ultra-flexible pulse oximetry probe. The hybrid flexible devices are fabricated on 5 µm thick Parylene C using laser ablation to define the circuit design, and integrate a small ridged photodetector and LEDs using a flexible adhesive. Finally, contact between the probe and the processing board is achieved using a flat flexible cable and anisotropic conductive film. Devices are demonstrated *in vivo* on a sedated porcine subject and calibrated against a standard peripheral SpO_2 meter while the subject's oxygen intake was varied. In addition to demonstrating the functionality of these implanted devices, we show that the implementation directly on the femoral artery of our devices records a more acute response to the variation in oxygen intake compared to the peripheral measurements.
These devices are low cost and based on biocompatible materials, and can be easily implanted during cardiovascular surgery. This offers a route towards long-term implantation of devices for continuous patient monitoring.

4:15 PM SB04.03.03
A Skin Compatible Meta Structured E-Skin Patch for Long-Term Monitoring of Bio-signals Juhee Kim[1,2], Wonseop Hwang[3], Hyunjung Yi[1] and In-Suk Choi[2]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of); [3]Hanyang University, Korea (the Republic of)

In this presentation, we introduce a skin-compatible meta-structured e-skin patch that only consists of commercial adhesive dressing and FPCB for continuously collecting electrocardiographic signals over five days. In terms of long-term monitoring, it is crucial for the on-skin sensors to stably monitor bio-signals without any skin discomfort. Our approach presents a practical and cost-effective way to manufacture a skin-compatible wearable sensor system, making use of conventional materials that were difficult to include due to their high elastic modulus.

To rationally design the metal structural pattern of a stretchable sensor patch suitable for skin movement, we measured and analyzed the deformation field around the chest by using digital image correlation method and finite element simulation. Among many possible patterns, we chose the Kagome-based structure for the adhesive dressing that can well accommodate the deformation of the skin as well as give breathability to the patch due to its high porosity. We further devise a tethering scheme of attaching the FPCB to the adhesive dressing. The results showed that our sensor patch system greatly improved skin comfort and was able to monitor ECG signals for five days without any discomfort.

4:30 PM SB04.03.04
Wearable Non-Invasive Biosensors for Health Monitoring at the Molecular Level Hnin Y. Nyein; The Hong Kong University of Science and Technology, Hong Kong

The rather reactive and centralized medical approaches in today's healthcare system prevent individuals from obtaining diagnosis and treatment in a timely and accessible manner. Presently, commercially available devices for remote health monitoring are majorly limited to body's vitals and glucose levels, limiting access to healthcare. In this talk, I will present the wearable biosensors which utilized sweat to extract individual's biomolecular information. These sensors integrate flexible electronics and solid-state electrochemical sensors in a single robust platform to achieve reliable analyte quantifications at the site of sweat collection. Specifically, the wearable ultralow-volume sweat sensors make sweat a viable mode of health monitoring at the molecular level across activities, whether active or sedentary, and across user groups, whether young or old, healthy or ill. By using the sensors, continuous sweat analysis can be used to study how the body's endogenous and stimulated sweating response relates to stress, metabolic conditions, and potentially neurological afflictions through multiplexed quantification of ions, metabolites, and drugs.

4:45 PM SB04.03.05
Printed Carbon-Based Biosensors for Diagnostic and Cell Cultures Probing Mario Caironi[1], Adrica Kyndiah[1], Fabrizio A. Viola[1], Francesco Modena[1], Cristiano Bortolotti[1], Giulia Z. Zemignani[1], Gabriele Tullii[1], Francesco Galeotti[2], Carlotta Ronchi[1], Luca Sala[3] and Maria Rosa Antognazza[1]; [1]Istituto Italiano di Tecnologia, Italy; [2]Consiglio Nazionale delle Ricerche, Italy; [3]Istituto Auxologico Italiano IRCCS, Italy

Printed carbon based electrolyte-gated transistors represent ideal ionic/electronic hybrid devices that bridge biology and electronics. These devices are being investigated for a wide range of applications, from drug delivery to neuromodulation and highly sensitive biosensing. Here we report our recent progress in printed devices based both on thin films of polymer semiconductors and randon-networks of carbon-nanotubes. In particular, we show how large-area printed arrays of electrolyte-gated polymer transistors can enable future diagnostic tools to target specific biomarkers at clinical level. At the same time we propose printed carbon-nanotubes as an alternative approach for highly stable biosensors operating in acqueous environment. Besides their use to target biomarkers, we also show how such printed carbon-based transistors can be employed to monitor cell cultures proliferation over consecutive days. Remarkably, we also demonstrate that, despite the planar geometry of the device, spontaneous recording of intracellular action potentials of cardiomyocytes can be detected. Such results show that printed carbon-based electrolyte-gated transistors have great potentials for many aspects of future large-area bioelectronics, including diagnostic and parallel probing of electrogenic cell cultures.

SESSION SB04.04: Bioelectronic Interfaces
Session Chairs: Sahika Inal and H. Tom Soh
Tuesday Morning, April 11, 2023
Moscone West, Level 3, Room 3004

10:30 AM *SB04.04.01
Toward Flexible Multimodality Sense (and actuate)—Materials and Platforms Tzahi Cohen-Karni; Carnegie Mellon University, United States

My team's efforts are focused on the development and engineering of nanomaterials-based flexible platforms to interrogate and affect the properties of tissue, with a specific goal to understand signal transduction (chemical or electrical) in tissue or complex 3D cellular assemblies. Highly flexible bottom-up nanomaterials synthesis capabilities allow us to form unique hybrid-nanomaterials that can be used in various input/output bioelectrical interfaces, i.e., bioelectrical platforms for chemical and physical sensing and actuation. We developed a breakthrough bioelectrical interface, a 3D self-rolled biosensor arrays (3D-SR-BAs) of either active field effect transistors or passive microelectrodes to measure both cardiac and neural spheroids electrophysiology in 3D. This approach enables electrophysiological investigation and monitoring of the complex signal transduction in 3D cellular assemblies toward an organ-on-an-electronic-chip (organ-on-e-chip) platform for tissue maturation investigations and development of drugs for disease treatment. Utilizing graphene, a two-dimensional (2D) atomically thin carbon allotrope, we can simultaneously record the intracellular electrical activity of multiple excitable cells with ultra-microelectrodes that can be as small as an axon (ca. 2μm). The outstanding electrochemical properties of the synthesized hybrid-nanomaterials allow us to develop highly efficient catalysts, and electrical sensors and actuators. We demonstrated sensors capable of exploring brain chemistry and sensors/actuators that are deployed in a large volumetric muscle loss animal model. Finally, using the unique optical properties of nanocarbons in the form of graphene-based hybrid-nanomaterials and 2D nanocarbides (MXene), we have formed remote, non-genetic bioelectrical interfaces with excitable cells and modulated cellular and network activity with low needed energy and high precision. In summary, the exceptional synthetic control and flexible assembly of nanomaterials provide powerful tools for fundamental studies and applications in life science and potentially seamlessly merge nanomaterials-based platforms with cells, fusing nonliving and living systems together.

11:00 AM SB04.04.02
Printed Organic Electronic Devices for Plant Health Monitoring and Precision Agriculture Elliot Strand[1], Eloise Bihar[1], Sanggil Han[2], Catherine Crichton[1], George G. Malliaras[2], Robert Mcleod[1] and Gregory L. Whiting[1]; [1]University of Colorado, United States; [2]University of Cambridge, United Kingdom

Low-cost, flexible, and lightweight electronic biosensors offer an exciting pathway to future products for environmental and plant health monitoring. Organic electrochemical transistors (OECTs) are particularly favorable sensing platforms due to their high sensitivity, low power requirements, and use of soft, biocompatible materials. Furthermore, OECTs can be manufactured with scalable printing techniques, which makes them suitable for large-area electronics (LAE) applications. This presentation will describe the development of fully printed, flexible OECTs that can accurately detect a suite of analytes (e.g., nutrients, pH, temperature) that are relevant to plant health. For example, the devices were used to accurately detect macronutrient concentrations in whole plant sap and hydroponic fluids in real-time. The rheological and electronic properties of the OECTs were tuned by doping the semiconducting channel with sugar alcohols, super absorbing polymers and thickening agents. These additives boosted the transconductance and sensitivity of the transistors, which led to a super-Nernstian response to the target analyte. By utilizing ion selective membranes (ISMs), we fabricated OECT-based ion sensors that demonstrate selectivity to the target ion against similar ions over five orders of magnitude in concentration and a limit of detection (LOD) as low as 10 µM. The results confirm that lightweight, printed organic electronics are a suitable path to high-throughput, low-cost assessment of plant health, which could lead to massive efficiency gains in agriculture.

11:15 AM SB04.04.03
Flexible Graphene-Based mHealth and Wearable Sensors for Disease Monitoring and Management Jiaobing Tu, Rebeca M. Torrente Rodríguez and Wei Gao; California Institute of Technology, United States

With the emphasis of healthcare shifting towards prevention and early detection of diseases and monitoring of chronic conditions, there is a growing need for hassle-free telemedicine sensor technologies that can be seamlessly integrated into daily life. While significant progress has been made in the development of wearable sweat and salivary biosensors to meet this need for rapid, real-time collection of physiological information, the majority of current epidermal sensing systems are unable to detect trace-level disease-relevant biomarkers accurately in biofluids and cannot be mass produced. To meet this demand for low-cost, mass-producible mHealth devices for at-home settings, we developed several fully-integrated laser-engraved graphene-based biosensors for the detection of low-concentration sweat and salivary analytes including hormones (e.g. cortisol) and proteins (e.g. SARS-CoV-2 nucleocapsid protein and C-reactive protein). Several graphene surface engineering strategies are investigated for the sensitive and selective detection of targets. System-level engineering and microfluidic designs are explored to achieve on-demand sweat induction and harvesting under sedentary settings, automated sweat and reagent routing, and in situ signal correction and analysis for facile operation on the skin. The utility of these fully integrated flexible mHealth systems is evaluated through multiple human studies involving healthy and various patient subgroups towards stress assessment, rapid COVID-19 diagnosis and severity assessment, as well as the monitoring and management of various chronic conditions including chronic obstructive pulmonary disease, heart failure, and inflammatory bowel diseases. These fully integrated mHealth devices demonstrate an enabling technology that can be easily adapted to monitor a broad spectrum of disease-specific proteins, cytokines, and hormones, advancing future applications in personalized disease diagnosis, management, and prevention.

11:30 AM SB04.04.04
Wearable Electrochemical Biosensors for Real-Time Health Monitoring in Daily-Life Jayoung Kim; Yonsei University, Korea (the Republic of)

Wearable biosensors represent a promising opportunity to monitor human physiology through dynamic measurements of (bio)chemical markers in biofluids such as sweat, tears, saliva, and interstitial fluid in a continuous and non-invasive way. Such new platforms can thus offer real-time (bio)chemical information toward a more comprehensive view of a wearer's health, performance, or stress at the molecular level in daily-life. Continuous biomonitoring addresses the limitations of traditional invasive blood testing and provides the opportunity for early diagnostic and therapeutic interventions. My research is focused on developing wearable electrochemical biosensors towards non-invasive health monitoring opportunities and evaluating the potential impact of such wearable point-of-care devices on our daily life. The innovative biosensing technology was demonstrated by successful electrical/electrochemical signal transduction of biomolecular/biocatalytic reactions. It was further developed into various wearable form factors using printing technology, offering wearer conformity, flexibility, and stretchability. The wearable biosensors could measure a broad spectrum of biomarkers such as metabolites, electrolytes, hormones, and various small molecules in non-invasive biofluids, demonstrating clinical values through human studies. Furthermore, our recent outcomes will be discussed in this talk covering the discovery of new biomarkers and their underlying mechanisms utilizing various wearable form factors, such as mouthguards, contact lenses, and epidermal patches.

SESSION SB04.05: Flexible Bioelectronic Devices I
Session Chairs: Wolfgang Knoll and Sabine Szunerits
Tuesday Afternoon, April 11, 2023
Moscone West, Level 3, Room 3004

1:45 PM *SB04.05.01
Smart Skin Electrodes for Electrophysiological and Circulatory Monitoring of Freely Behaving Humans Yael Hanein; Tel Aviv University, Israel

Wearable devices are becoming ubiquitous. They are used extensively by consumers and are becoming more noticeable in the medical domain. But contemporary wearable devices are still relatively bulky and often have limited equivalence to medical gold standards. Skin patches with chemical, mechanical, and electrophysiological sensors offer new opportunities for future sensors. These devices can be designed to seamlessly interact with the user while also providing high quality and long-term data. In combination with miniaturized low power electronics and powerful data analysis algorithms these devices have the potential to provide continuous measures of various physiological parameters from freely behaving humans. In this presentation I will discuss some of our recent achievements in monitoring the electrophysiology (EEG, EOG, EMG and ECG) of freely behaving humans during rest, overnight sleep and during movement. I will also present recent progress towards simultaneous measurements of electrophysiology and blood pulsation at the arm, neck, and face.

2:15 PM SB04.05.02
Fully Implanted Battery Free Chronic Organ Interfaces Philipp Gutruf; University of Arizona, United States

Materials and fabrication concepts for the creation of soft electronics coupled with miniaturization of wireless energy harvesting schemes enable the construction of high-performance electronic and optoelectronic systems with sizes, shapes and physical properties matched its biological host[1]. Applications range from continuous monitors for health diagnosis to minimally invasive exploratory tools for neuroscience[2]. Translation of these approaches towards neuroscience tools to enable advanced insight into the central and peripheral nervous require means to enable full subdermal implantation and operation to enable naturalistic behavior which often is the readout of circuit level behavioral experiments that are critical to decipher function. This talk presents science and engineering approaches for the creation of soft devices with near field power transfer and data communication capabilities[3] and discusses application in devices for the stimulation and recording of organ systems such as the brain, the peripheral nervous, cardiovascular and the musculoskeletal system. We introduce a series of advances in subdermally implantable device technologies that enable digitally controllable subdermal platforms with multimodal optogenetic and electrical stimulation capabilities[4][5] with the ability to provide stimulus without the physical penetration of the blood brain barrier. Additional to these stimulation capabilities we demonstrate new capabilities in biointerfaces with the cardiovascular and musculoskeletal system[6] that enable recording of organ health as well as closed loop operation chronically in freely moving subjects. Because of the minimally invasive nature of these tools we show chronic neuromodulation capabilities over months in freely moving subjects enabling a digital disease models as well as platforms that can be rapidly translated to large animal models.

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2:30 PM BREAK

3:00 PM *SB04.05.03
Paper-Based Devices for Flexible and Wearable Applications Seokheun Choi; Binghamton University, The State University of New York, United States

Paper-based devices have recently emerged as a simple and low-cost paradigm for flexible and wearable applications. Paper is a flexible and low-cost game-changing substrate for next-generation electronics because of its excellent mechanical and dielectric properties with chemical and thermal stability. The biodegradability of paper-based electronics has attracted much attention as the future of green electronics, reducing the dramatic increase in electronic waste. Concurrent with advances in paper-based electronics, remarkable efforts have been dedicated to paper-based microfluidics for next-generation point-of-care (POC) diagnostics, particularly in limited-resource and remote regions. Fluidic components, patterned in paper, allow for instrument-free liquid transport via capillary wicking and storage of biological and chemical reagents within their 3-D fiber network of paper. A merged system incorporating paper-based electronics and paper-based microfluidics will have the transformative potential to yield exceptionally powerful functions and performances. In this invited talk, he will present many innovative paper-based electronics and paper-based microfluidics that his research group recently developed especially for flexible and wearable applications. Details of the frontier of research to improve the performance of the devices will be discussed, followed by a critical perspective on strategic future directions.

3:30 PM SB04.05.04
Ion-Based Conformable Integrated Wireless Neural Implant Zifang Zhao[1], Claudia Cea[1], Jennifer Gelinas[1,2,2] and Dion Khodagholy[1]; [1]Columbia University, United States; [2]Columbia University Medical Center, United States

Understanding how neural activity evolves in a developing brain is of great scientific value and clinical importance. However, chronic *in-vivo* monitoring of neural activity in a fetal animal requires a minimally invasive, conformable, and miniaturized device. Here, we introduce a fully conformable, battery-free, implantable bioelectronics device integrating a neural probe, internal gated ion transistor(IGT), and ionic communication circuit(IC). We hypothesize that IGT could be wirelessly powered by a pair of IC electrodes sensing externally generated electrical potential energy within polarizable media, and IGT enables modulation of the IC current by electrophysiological signal that can be sensed externally. To validate this hypothesis, firstly, we have characterized IGT's performance under IC operation frequency. IGT shows no transconductance decrease when powered with 1MHz sine wave, compared with DC power. We have characterized the power efficiency and signal-to-noise ratio of this system. We demonstrated IC could effectively transmit mill-watt power to an implantable device and IGT could effectively modulate IC current with sub-millivolt gate signal. Finally, we fabricated a fully conformable, implantable device and implanted the device in baby mice. We demonstrated chronic recording of high-quality electrophysiological signals, including local field and action potentials over 30 days. In this work, we have demonstrated a fully conformable neural implant that establishes a safe, long-term pathway to the signal inside biological tissues.

3:45 PM SB04.05.05
Biocompatible Printed Adhesive Devices for Electrical Stimulation of Plants Eloise Bihar, Megan N. Renny, Elliot Strand, Catherine Crichton, Robert Mcleod and Gregory L. Whiting; University of Colorado-Boulder, United States

Understanding the chemical signals governing plant physiology is critical for environmental monitoring and protection. Electrostimulation of electrical networks in plants can be linked to ion transport and the activation of ion channels, and can trigger biological activities such as gene expression or plant movements. Electrical currents have also been used to enhance plant growth. Here, we present a new technique to fabricate biocompatible adhesive sensors that can be placed as wearable dressing, and stimulate or relay signals emitted by the plant. The customizable sensors are used to induce electrostimulation and can be controlled wirelessly for over 1 week. This work represents a stepping stone toward understanding the biological mechanisms of plants, and evaluating their defense response when subject to stress.

4:00 PM SB04.05.06
Soft MXene Filament Microelectrodes for High-Resolution, Localized Detection of Neural Transmitters and Electrical Signals Lingyi Bi[1], Kseniia Vorotilo[1], Natalia Noriega[2], Ruocun (John) Wang[1], Bhavik A. Patel[2] and Yury Gogotsi[1]; [1]Drexel University, United States; [2]University of Brighton, United Kingdom

The development of soft neural interfaces opens opportunities for long-term studying and modulating brain functions and diseases with fewer side effects by minimizing the mechanical mismatch between artificial devices and soft tissues. However, few designs have enabled both electrical and chemical sensing – necessary for capturing the diverse neural signals *in vivo* – as simultaneous high conductivity and redox surfaces are required for such multifunctional electrodes. Here we report a novel method leveraging the unique combinations of electrical conductivity, functional surfaces, and solution processibility of MXenes, an emerging class of 2D nanomaterials, to produce a thin conformal MXene coating on nylon filaments (30-300 µm in diameter) at a fast speed (up to 15 mm/s). The highly aligned MXene coatings provide the microelectrodes with an electrical impedance as low as 3Ω at 1kHz. In addition, the MXene coating provides ample redox surfaces for the detection of neural transmitters such as dopamine and 5-hydroxytryptamine. These MXene filament microelectrodes offer a robust, miniaturized platform for the monitor and stimulation of neural activities at the cellular level, facilitating a greater understanding of health and disease.

4:15 PM *SB04.05.07
Wearable Microfluidic Electrochemical Biosensor for Automatic Molecular Monitoring Wei Gao; California Institute of Technology, United States

Wearable and flexible biosensors for the continuous monitoring of metabolites in sweat can detect a few analytes at sufficiently high concentrations, typically during vigorous exercise so as to generate sufficient quantity of the biofluid. I will introduce the design and performance of a wearable electrochemical biosensor platform for in situ analysis, in sweat during physical exercise and at rest, of trace levels of multiple metabolites, nutrients, and proteins. The biosensor consists of laser-engraved graphene electrodes that are functionalized with target-specific natural or synthetic receptors, and integrated with modules for iontophoresis-based sweat induction, microfluidic sweat sampling, signal processing and calibration, and wireless communication. The clinical value of our wearable systems is evaluated through human studies toward metabolic/nutritional assessment and disease management. These wearable technologies could open the door to a wide range of personalized monitoring, diagnostic, and therapeutic applications.

SESSION SB04.06: Poster Session: Flexible Bioelectronic Devices
Session Chairs: Wolfgang Knoll and Sabine Szunerits
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SB04.06.01
Multimodal Neruonal Function Monitoring of hiPSC-Derived Organoids on *In Vitro* Platform Namyun Kim, MinJin Kang, Yamujin Jang, Nakwon Choi and Yi Jae Lee; Korea Institute of Science and Technology, Korea (the Republic of)

Neuron-on-a-Chip technology has been intensively studied in medical and pharmaceutical fields to understand and explore complex neurological systems in a controlled in vitro platform. This platform provides a biocompatible cell culture dish with multiple electrodes that can transmit bioelectrical signals and well for nourishing, guiding, and proliferating the neurons. Recently, many researchers studied and investigated three-dimensionally cultured organoids derived from human induced pluripotent stem cells (hiPSC) in in vitro systems. The organoids showed much similar behavior to in vivo systems than 2D cultured cells due to their capability of mimicking organ cell formation with cell-to-cell interaction. However, due to their self-organizing characteristics while development and proliferation, the design of the multielectrode array (MEA) and microfluidic channels should be considered an important factor in realizing practical preclinical models.
In this paper, we developed a MEA chip consisting of a total of 130 electrodes that each can act as an electrically stimulating or recording site and dumbbell-shaped microfluidic channel to investigate hiPSC-derived motor nerve organoids placed in two wells. To minimize the contact impedance of the electrodes, the opening area (9 um diameter) is covered with platinum black. The organoids were cultured for one month in vitro and organoid formation and axon growth were investigated. The results showed that the axons from the organoids extended ~3 times longer in narrow fluidic channel (300 um width) than inside the well (2 mm diameter). Developed MEA chip showed simultaneously detection of multiple neuronal activities with a low background noise level. Also, from the electrical stimulation tests, neuronal network activities including conduction behavior were measured and analyzed. Further improvements to the MEA chip including 3D shaped electrode array and microfluidic channel variation may provide a basis for an advanced preclinical model platform for regenerative medicine and human disease modeling in the future.

5:00 PM SB04.06.02
A Form Factor-Free Musculoskeletal Sensor Platform for Predicting Behavioral Intentions YunJeong Kim, Yulim Min, hanbit Jin, Chanhwa Hong, Saerom Seo, Chaehyun Lim and Hye Jin Kim; Electronics and Telecommunications Research Insitute, Korea (the Republic of)

As the aging of society proceeds and the healthcare market has been significantly growing, it is essential to develop a musculoskeletal biological signal monitoring platform. Although most semiconductors or MEMS sensors for acquiring biosignals have excellent sensitivity and accuracy, they have the limitation of form factor for long-term attachment to human bodies [1]. In this study, we demonstrated a formfactor-free musculoskeletal platform integrating four types of sensors on a stretchable substrate that is stretched up to 20 % through an in-situ process. The stretchable substrate fabricated with serpentine electrode structure showed almost no change in the resistance of the electrode when it was increased up to 20 % strain, a highly reliable biological signal can be eventually obtained. Also, the sensors of Mechanomyography (MMG), Forcemyography (FMG), Electromyography (EMG), and accelerometer are integrated with one stretchable substrate, and the correlation between the sensors is analyzed to monitor the biological activity with high accuracy. In particular, MMG sensors are required high sensitivity and SNR to detect extremely low amplitude vibration signals inside the skin. Most MMG sensors are used ceramic-based microphones of accelerometers which are highly sensitive and accurate. However, it is not conformally adhered to human skin due to the rigid type of ceramic-based devices, thereby there is a constraint of data reliability caused by motion artifacts. To enhance the reliability of data, a stretchable 10-um-thick MMG patch sensor was fabricated by screen printing based on flexible 0-3 nanocomposite piezoelectric materials. Moreover, the SNR of the signal was improved by more than 3.5 times with the bump structure to the sensor. The pressure sensitivity was 395 mV/N (0%) and 407 mV/N (20%), respectively, before and after a stretch of 20 %, which confirmed negligible hysteresis with a delta value ($\Delta< 3$). The MMG sensor can detect dynamic vibrations in the working frequency range from 1 Hz to 100 Hz. Finally, it was applied to recognize or predict motion intention by analyzing the correlation of biological activity through the four types of sensor signals acquired by isometric contraction and relaxation of flexor digitorum longus.

Acknowledgement
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5:00 PM SB04.06.04
Polymerized Ionogels for Wearable Chemical Biosensors Detecting Biomarkers in Exhaled Breath Sang-Joon Park and Tae-Jun Ha; Kwangwoon University, Korea (the Republic of)

Wearable chemical biosensors detecting low concentration of biomarkers which can indicate health disorders such as asthma, cystic fibrosis, and bronchiectasis have attracted considerable attention in the field of bioelectronics [1]. To improve the sensing performance, various materials including nanostructured metal-oxide semiconductors and low-dimensional nanomaterials have been extensively investigated as promising active sensing channels owing to their high reproducibility and large surface-to-volume ratio [2]. However, the chemical biosensors based on these materials inevitably require high operating temperatures and complicated fabrication processes, which can limit the applicability of wearable electronics in the systel level [3]. Recently, polymerized ionogels exhibit great potential in ionotronic applications owing to their high chemical stability, mechanical flexibility, and ionic conductivity in addition to molecular interactions [4]. In this presentation, we will demonstrate polymerized ionogels consisting of ionic liquids (ILs) incorporated with 3 dimensional polymeric neworks which immobilize the ILs while maintaining distinctive their properties. We will also demonstrate chemiresistive-type wearable chemical biosensors based on polymerized ionogels, which can detect biomarkers of nitrogen oxide molecules in exhaled breath down to ppb-level and exhibit excellent operational stability under various environmental and mechanical conditions such as humidity, temperature, and physical deformation. We believe that this work can stimulate the field of ionotronic biosensors based on polymerized ionogels for human breath analysis underlying biomarkers.

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5:00 PM SB04.06.05

Pinch Gripper with Multi-Sensor Capable of Detecting Embolism and Monitoring Pulse Wave in Blood Vessel Daseul Lim, Yeonwook Roh, Doohoe Lee, Insic Hong, Dohyeon Gong, Dongjin Kim, Dongwook Shin, Seongyeon Kim, Je-Sung Koh, Daeshik Kang and Seungyong Han; Ajou University, Korea (the Republic of)

During sugery, various diseases can occur dut to abnormal blood vessel. Thrombosis and air embolism occurs frequently. Diagnosis of thrombosis and air embolism is CT or Doppler examination is typically used. These diagnosis are difficult to detect immediately during surgery and cost a lot of time and money. In this paper, a device capable of pinch grip propose to stable hold blood vessel without damage. The device has a capacitance sensor and crack-based strain sensor to measure a pulse wave and detect substance in the blood vessel. An in vivo experiment using the carotid artery of a pig was conducted to demonstrate the potential of use in bio medical device. As a result, the strain sensor has same pulse wave as commercial BP monitoring system. At the same time, it was cofimed through the C-arm that the capacitance sensor detects air embolism. It was possible to predict the occurrence of a stroke. In the future, the pinch gripper can be used as a biomedical device for a innovative blood vessel monitoring system in surgery. Our device can prevent dagerous complications such as hypotension, stroke, and heart attack in transplant and long time surgery.

5:00 PM SB04.06.07

Micro Plasma-Based Surface Modification of Soft Biocompatible Polymers and Composites Towards the Modification of Surface Properties for Biomedical Applications—Development of Correlations Between Plasma Properties and Surface Characteristics Using Machine Learning Manan Sehgal[1], Prakhyat Gautam[1], Andres Raymundo[1], Edgar Perez-Lopez[2], David Ryman[1], Edbertho Leal-Quiros[2], Saquib Ahmed[3,3] and Sankha Banerjee[1,4]; [1]California State University, Fresno, United States; [2]University of California, Merced, United States; [3]Buffalo State College, United States; [4]University of California, Davis, United States

The use of 3D printing scaffolds and interfaces has become popular due to its optimal customization and process time. Polylactic Acid (PLA) is a commonly used biocompatible and biodegradable filament material in 3D printing. However, PLA is naturally hydrophobic. Cell growth and cell adhesion on biocompatible polymers are affected by the surface energy properties and the interface. This study is focused on mitigating these problems by incorporating plasma micro-discharge surface modification to tailor the surface roughness characteristics of soft PLA and soft PLA composites toward the development of biocompatible substrates for enhanced cell adhesion and growth. There is limited research exploring how changes in plasma parameters affect the wettability and surface energy characteristics of materials. The current work involves the development of correlations between plasma properties and surface characteristics using machine learning models. Consequently, this work will also review the changes of 3D printed PLA in wettability, surface roughness, and surface morphology as the input voltage of the plasma micro-discharge treatment (confined micro plasma-based Townsend discharges) is varied.

5:00 PM SB04.06.08

Study of the Efficacy of a Flexible Active Polymer-Based Non-Invasive Glucose Monitoring System—Towards the Development of Embedded Devices Using Refraction and Photoacoustic Characteristics David Ryman[1], Muhilan Manimaran[1], Edgar Perez-Lopez[2], The Nguyen[1], Saquib Ahmed[3,3] and Sankha Banerjee[1,4]; [1]California State University, Fresno, United States; [2]University of California, Merced, United States; [3]Buffalo State College, United States; [4]University of California, Davis, United States

The current work focuses on the development of a flexible non-invasive glucose monitoring device embedded in an active polymer matrix (e.g. PVDF-TrFE or PVDF-BaTiO3). The device consists of an embedded circuit with a pulsed laser and a continuous LED light in the near infrared range. This light source is incident on a glucose control solution to mimic a range of glucose concentrations in blood (in the range from 0 - 500 mg/dl). The glucose levels are detected by a perovskite-halide optoelectronic sensor (refraction) and are validated by a perovskite oxide transducer (photoacoustic) while using the active polymer matrix as a energy conversion media. Correlations between the output voltage and the glucose concentrations are developed using machine learning methods. The active properties of the polymer matrix is also characterized using electrical impedance spectroscopy.

SESSION SB04.07: Virtual Session
Session Chairs: Sahika Inal, Wolfgang Knoll, Sabine Szunerits and Robert Wagner
Wednesday Morning, April 26, 2023
SB04-virtual

10:30 AM SB04.07.02

From Disposable to Wearable Bioelectronics Using Paper-Derived Laser Induced Graphene Rodrigo Martins, Tomás Pinheiro, Ana Carolina Marques and Elvira Fortunato; CENIMAT\i3N Nova School of Science and Technology, Portugal

Laser-induced graphene (LIG) has established itself as a very attractive material for electrode fabrication, within several applications in bioelectronics. The straightforward, high throughput graphitization of several precursor materials using this laser conversion process allows for the simultaneous synthesis and

patterning of this 3D graphitic material with diverse electrode architectures, to target several biosensing applications, from biophysical to biochemical monitoring.
Recently, paper has appeared has a viable alternative to conventional petroleum-based plastic polymer precursors, such as polyimide. This is due to the possibility to photothermally convert aliphatic cellulose monomers into graphene lattices, using several cellulose substrate treatment strategies. Application of fire-retardant chemical modifications and external aromatic moieties improves the graphitization potential of cellulose, to reach LIG films with 5 ohm.sq^{-1} sheet resistance and conductivities as high as 67 S.cm^{-1}.
With these improved conductive properties of paper derived LIG, this precursor material can be easily employed for the fabrication of disposable biosensing units, where paper acts as both the support substrate and precursor material for conductive electrodes fabrication, without the need for more intricate printing techniques. Alternatively, strategies can be employed to separate converted and unconverted phases, through transfer methods, to make this material compatible with wearable applications.
In this presentation, we report the use of cellulose as a material in the toolbox of LIG precursors, aimed at the development of both disposable and wearable biosensing applications. Paper-based electrochemical sensors using this material are presented, aiming at disposable sensor development for different analytes. Glucose and pH electrochemical sensors were fabricated, showing the compatibility of the material with several sensing strategies, such as enzymatic and non-enzymatic sensing. To translate patterned electrodes for wearable applications, a straightforward transfer method is presented, using a water-induced peel-off method. This method is capable of efficiently separating unconverted cellulose and converted LIG phases, allowing for the transfer of LIG patterns onto flexible, conformable and elastomeric substrates with adhesive properties, for example medical grade adhesives. Using this method, electrochemical biosensors, strain sensors for biophysical monitoring and electrodes for electrophysiological signal monitoring are presented.
In conclusion, the concepts explored herein show the applicability of LIG towards the fabrication of robust point-of-care, disposable analytical devices, but also the its potential for integration in wearable sensing systems, aiming at more sustainable, accessible bioelectronic applications.

SYMPOSIUM

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SESSION SB05.01: Designing Materials for Healthcare I
Session Chairs: Gemma-Louise Davies and Taeghwan Hyeon
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2016

10:30 AM *SB05.01.01
Design and Biomedical Applications of AIE-Active Nanoaggregates Ben Zhong Tang; The Chinese University of Hong Kong, China

Nanomedicine is an emerging and fast-growing field in which the application of nanotechnology to healthcare offers numerous improvements to medical diagnosis, therapy, etc. The design and development of novel fluorescent nanomaterials for biomedical applications have become one of the most important aspects of nanomedicine and have attracted increasing research interest. Previous studies have mainly focused on fluorescent inorganic nanoparticles, such as fluorescent carbon dots, metallic nanoclusters, etc. The major issues for their practical biomedical applications, especially *in vivo* applications, are still challenging, mainly due to their notorious toxicity to living organisms. As alternative nanomaterials for various biomedical applications, fluorescent organic nanoparticles have emerged and gained significant interest because of their various interesting optical properties, facile fabrication, and excellent biocompatibility. However, the fluorescence of most conventional organic dyes is quenched in the aggregate state or at high concentration, which is named aggregation-caused quenching (ACQ). This ACQ effect seriously hampers their potential applications in nanomedicine, such as bioimaging, diagnosis, and therapy. By contrast, aggregation-induced emission luminogens (AIEgens) are weakly emissive when molecules are uniformly dispersed in solution but “light up” when forming (nano)aggregates. With the significant advantages of high emission efficiency in the aggregate state, low background noise in dilute solution, excellent photostability, and large Stokes’ shift, AIEgens and AIE nanoparticles are especially suitable for bioimaging, diagnosis and therapy. AIEgens with various skeletons are designed as superior agents for biological process monitoring and disease theranostics. Moreover, AIEgens and AIE nanoparticles can be conveniently incorporated into the present theranostic platforms by combining them with various imaging and therapeutics modalities, such as multiphoton imaging, photoacoustic imaging, photothermal imaging, chemotherapy, photodynamic therapy, photothermal therapy, gene therapy, etc.

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11:00 AM SB05.01.02
Lanthanide-Doped Nanomaterials as Potential Bioprobes Eva Hemmer; University of Ottawa, Canada

The remarkable optomagnetic properties of the lanthanides (Ln) make Ln-based materials ideal for biomedical applications, including diagnostic (for instance, imaging or thermal sensing) and therapeutic (for instance, drug delivery and photodynamic therapy) approaches. This is due the unique electronic properties of the Ln (f-elements) allowing for upconversion and near-infrared emission under near-infrared excitation as well as high magnetic moments. Sodium lanthanide fluorides ($NaLnF_4$) are our favorite materials, and we developed a fast and reliable microwave-assisted synthetic approach allowing crystalline phase and size control in the sub 15 nm realm. Such control is crucial for the understanding of fundamental structure-property relationships and to optimize their optical and magnetic properties, when aiming for the design of next-generation optical probes or contrast agents for magnetic resonance imaging (MRI). For instance, $NaGdF_4$ nanoparticles (NPs) are gaining interest as alternative MRI contrast agent, while co-doping with emitting Ln^{3+} ions endows the NPs with luminescent properties for applications as optical probes. The hexagonal crystalline phase of $NaGdF_4$ is known as the more efficient host material for upconversion emission (i.e., the emission of one higher energy photon following excitation with two or more lower energy photons). In contrast, we observed that the cubic phase of $NaGdF_4$ shows superior performance as MRI contrast agent.
Having a fast and reliable synthetic route towards $NaLnF_4$ NPs on hand, we now explore various nanoparticle architectures and compositions with the goal to optimize their optomagnetic properties, ultimately resulting in the design of biocompatible multimodal bioprobes. This includes MRI contrast agents based on Gd- and Dy-containing NPs, and novel near-infrared emitters based on Ho or Pr for deep tissue optical bioimaging under near-infrared illumination, matching the biological transparency windows. In this presentation, we will also have a look at luminescent $NaLnF_4$ NPs with various surface-modifications and the suitability of hyperspectral imaging to study their nano-bio interactions.

11:15 AM SB05.01.03
Opening the Fourth Biological Window—Novel Lanthanide-Doped Near-Infrared Emitting Nanoparticles Abigale Puccini, Nan Liu and Eva Hemmer; University of Ottawa, Canada

Trivalent lanthanide (Ln^{3+})-based nanoparticles (NPs) are outstanding candidates for a wide range of sensing, imaging, diagnostic and therapeutic applications. Characterized by an incomplete 4f shell shielded by the outer $5s^2$ and $5p^6$ shells, the influence of the host lattice and surrounding environment on the optical properties of lanthanide ions is minimized. This results in long excited-state lifetimes and narrow absorption and emission bands that favour the use of excitation wavelengths in the near-infrared (NIR) region and leads to the emission of light in the ultraviolet (UV), visible, and NIR regions. By tailoring the choice of Ln^{3+} dopants, NIR-to-NIR wavelength conversion becomes possible, allowing for both the excitation and emission wavelengths to be compatible with the so-called biological transparency windows (NIR-I to NIR-III: 700 to 1870 nm). These optical properties make Ln^{3+}-based NPs favorable fluorescent probes for biological and biomedical applications. The use of NIR light is of particular interest for overcoming some of the limitations of conventionally used organic molecular fluorescent probes, which require excitation with UV light, including photobleaching, tissue autofluorescence, phototoxicity and limited tissue penetration depths. NIR light matching the biological transparency windows suffers from less scattering and absorption by water and biological tissues, which in turn improves spatial resolution and sensitivity and allows for deeper light penetration depths. Current and past research efforts have primarily focused on the development of fluorescent materials that emit at wavelengths longer than 1000 nm in the NIR-II (1000 to 1350 nm) and NIR-III (1550 to 1870 nm) region, under excitation with NIR-I light (700 to 950 nm). Recently, a fourth biological window (NIR-IV) has been suggested, centered at 2200 nm, but there still presents a significant lack of optical probes, specifically at the nanoscale.
To close this gap, here, we propose novel Ln^{3+}-doped NIR-IV emitting NPs to open the fourth biological window for exploration. Using the fast and reliable microwave-assisted thermal decomposition method, NIR-IV emitters praseodymium (Pr^{3+}) or holmium (Ho^{3+}) and sensitizing ytterbium (Yb^{3+}) and/or neodymium (Nd^{3+}) were doped into sodium rare earth fluoride ($NaREF_4$) host lattices to form sub-15 nm NPs. Co-doping with Yb^{3+} allows for 980 nm NIR excitation, while the absorption and scattering of the excitation light by biological tissues can be further reduced when using 808 nm excitation, which is achieved through co-doping with Nd^{3+}. This presentation will shed light on the influence of NP composition, surface chemistry, and aqueous versus non-aqueous media for NP dispersion on the optical properties, i.e., sought after NIR-IV emission. Seeking potential biomedical (and beyond) applications, we further assessed the performance of these NIR-IV emitters as nanothermometers. Optical thermal sensing allows to extract information on the local temperature of a given system at the nanoscale, including thermal irregularities related to various diseases. Overall, the developed NPs are highly promising to open the fourth biological window for imaging and sensing, and thus, potential innovative biomedical applications.

11:30 AM SB05.01.04
A Biomineral-Inspired Approach of Synthesizing Multicolor Colloidal Persistent Luminescent Nanophosphors and Mechanoluminescent Fluids as Intravital Light Sources Fan Yang; Stanford University, United States

Light is used in a wide range of biotechnologies, such as fluorescence imaging and optogenetics, yet a critical challenge of applying light *in vivo* arises from the poor penetration of photons in biological tissue due to scattering and absorption. Therefore, delivering photons deep into the body from an external light source requires invasive procedures, such as craniotomy, to surgically remove overlying tissues. Besides conventionally used external light sources, trap-engineered materials with persistent luminescence (PerL, as known as afterglow) and mechanoluminescence (ML) represent an arising opportunity for light delivery in deep tissue owing to their ability to store photon energy in their host structures. However, materials with strong short-wavelength PerL and ML are usually bulk particles (> 10 µm) synthesized via solid-state reactions at > 1000 °C to facilitate uniform doping and desirable polymorphs. Their large sizes prevent the formation of stable colloids in aqueous environment and prohibit their biological applications.
To address this challenge, here we report a bioinspired demineralization (BID) approach to synthesize stable colloidal solutions of solid-state PerL and ML nanoparticles with tunable wavelengths and remarkable luminescence intensity. Specifically, the BID approach is inspired by the strategy of biomineralization in nature: Biominerals, such as apatite in the dental enamel, can be gradually dissolved to nanostructures in a mildly acidic environment yet are resistant to further dissolution. This unconventional dissolution process, unlike the self-accelerating dissolution of soluble salts, is facilitated by the formation and growth of pits on the surface. The low solubility and thus high interfacial tension of biominerals results in a large critical size of 10 to 100 nm, below which the growth of dissolution pit is kinetically suppressed. In the BID approach, we demonstrated that sparingly soluble solid-state PerL and ML particles, similar to biominerals, also exhibited kinetically suppressed dissolution. Specifically, we used a citrate buffer to mimic the undersaturated

environment and produce colloidal nanoparticles down to 20 nm from their solid-state precursors with emission wavelengths covering the entire visible spectrum, including $Sr_2MgSi_2O_7$:Eu,Dy (470 nm), $Sr_4Al_{14}O_{25}$:Eu,Dy (490 nm), ZnS:Cu,Al (534 nm), ZnS:Mn (578 nm), $CaTiO_3$:Pr (610 nm), and $Ca_{0.85}Sr_{0.15}S$:Eu,Tm (650 nm). Furthermore, these BID-produced nanoparticles can be stably suspended in aqueous solution, while preserving the optical properties of their solid-state precursors, including strong PerL or ML intensities.
Additionally, we demonstrated the utility of BID-produced colloids in biology via excitation-free imaging and ultrasound-mediated non-invasive optogenetics. On one hand, owing to their exceptionally bright luminescence, BID-produced PerL nanophosphors exhibited the highest signal-to-background ratio for *in vivo* imaging among reported materials, and yielded the first example of transcranial afterglow imaging of cerebral vessels in the mouse brain. Furthermore, the bright short-wavelength PerL nanophosphors acted as an intravital light source and provided internal excitation for genetically encoded fluorescent reporters in a mouse brain through the intact skull, thus enabling afterglow imaging of fluorescent proteins for the first time. On the other hand, the BID-produced ML fluids acted as an ultrasound-mediated light source in the body after systemic delivery. We were able to visualize the ultrasound-mediated light emission from the ML fluids in the vascular systems of multiple mouse organs (including brain, liver and kidney) for the first time, and used this light emission for non-invasive optogenetics stimulation in transgenic mice expressing light sensitive ion channel ChR2.
The manuscripts based on these results were recently published in *Sci. Adv.* (DOI: 10.1126/sciadv.abo6743) and *JACS* (DOI: 10.1021/jacs.2c06724).

11:45 AM SB05.01.05
Design and Study of Hybrid Multifunctional Nanoparticles for Cancer Diagnostic and Treatment Through Spectral Photo Counting Scanner CT and X-Rays Activated PDT Frederic Lerouge[1,2], Loic Cuau[2], Frederic Chaput[2], Szilvia Karpati[2], Stephane Parola[2], Sylvain Bohic[3], Ludwig Dubois[4], Ala Yaromina[4], Pia Akl[5], Salim Si-mohamed[5] and Philippe Douek[5]; [1]Université de Lyon, France; [2]Laboratoire de Chimie ENS Lyon, France; [3]INSERM, France; [4]Maastricht University, Netherlands; [5]CHU de Lyon, France

General context
Cancer is one of the major societal issues of the century . Even if several strategies of treatments exist, the conditions of life of the patient during and after the treatment are deteriorated by side effects of heavy therapies such as radiotherapy (use of X rays of High energy). The need to propose new strategies of therapies is therefore of great interest.
Introduction
We are aiming at a technology that will ensure efficient treatment of cancer with low side effects, allow to perform accurate diagnostic and give access to in situ monitoring of the treatment. Our goal is based on the association of two cutting-edge technologies: spectral photon counting scanner CT (SPCCT) which is a ground-breaking imaging modality and a new X-ray based treatment known as X-rays activated Photodynamic Therapy (X-PDT). The perfect match between these two technologies will be ensured with specifically designed nanoprobes probes acting both as contrast media and therapeutic agents(1).

The possibility to use new treatments such as XPDT is raising a great interest. PDT alone is a clinically approved cancer treatment but, the strong absorption of light by tissues limits its use to rather superficial tumors. X-PDT is a new technology involving the same mechanisms but spreading the potential of this treatment. The principle of XPDT is to irradiate with low energy X-Rays hybrid nanoprobes consisting in an inorganic core functionalized with organic moieties (Photosensitizers-PS). Upon excitation the inorganic particle will emits light (scintillation) which will be absorbed by the PS. The latter will reach an excited state, making it able to react with surrounding oxygen and leading to the production of reactive oxygen species able to kill tumor cells.(2)

Spectral Photon Counting Computed Tomography (SPCCT) is a new imaging modality, currently in development. The SPCCT scanner is an evolution of the conventional CT scanner, with a totally new type of detection chain designed to provide high count-rate capabilities while offering energy discrimination with high spatial resolution. Its main asset is the ability to map and quantify elements based on their K-edge. For that modality, the traditional iodine based contrast agents are not particularly suited due to iodine's K-edge being outside the clinical X-ray spectrum, the use of new types of contrast agents is therefore necessary. (3)
Results
Based on our previous works on the design and surface modification of lanthanide fluoride nanocrystals (4) we describe the design of hybrid terbium (III)-doped gadolinium fluoride nanoparticles (NPs) which act as contrast media for spectral CT scanner and show scintillation properties (emission of light under low energy X-rays excitation). These nanoparticles can be considered as interesting nanoplatforms for further development related to X-Rays based imaging and treatment.
This presentation will first aim to highlight the results obtained concerning the luminescent properties of NPs under UV and X-ray excitation and their properties as contrast agent for spectral CT scanner (5). It will also describe the different strategies of surface modification for biocompatiblity and their effects on the optical properties of NPs. The proof of concept of the use of the nanoparticles as contrast agent in vivo as well as their ability to emit light when submitted to X-rays will be demonstrated. Finally, the functionalization of NPs by a PS will be discussed and results about in cellulo studies and singlet oxygen generation will be described.
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SESSION SB05.02: Designing Materials for Healthcare II
Session Chairs: Gemma-Louise Davies and Nicholas Kotov
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2016

1:45 PM *SB05.02.01
Designed Synthesis and Assembly of Inorganic Nanomaterials for Medical and Healthcare Applications Taeghwan Hyeon[1,2]; [1]Seoul National University, Korea (the Republic of); [2]Institute for Basic Science, Korea (the Republic of)

Over the last 20 years, our laboratory has focused on the designed chemical synthesis, assembly and medical applications of uniform-sized nanocrystals. We demonstrated that ceria nanoparticles and ceria–zirconia nanoparticles can work as therapeutic antioxidants to treat various nasty diseases, including ischemic stroke, Alzheimer's disease, sepsis, and Parkinson's disease, rheumatoid arthritis, and radioprotectants.[1] We developed a click reaction-assisted immune cell targeting (CRAIT) strategy to deliver drug-loaded nanoparticles deep into tumor interiors, reducing tumor burden in an aggressive 4T1 breast cancer model without any systemic toxicity.[2] We synthesized $MnFe_2O_4$-anchored mesoporous silica nanoparticles to overcome hypoxia, and consequently enhancing the therapeutic efficiency of photodynamic therapy.[3] We reported a heterogeneous chemodynamic therapy system based on copper-iron peroxide nanoparticles (CFp NPs) for tumor microenvironment-mediated synergistic cancer therapy.[4] We report a highly sensitive and selective K^+ nanosensor that can quantitatively monitor extracellular K^+ concentration changes in the brains of freely moving mice experiencing epileptic seizures.[5] We fabricated ultraflexible and/or stretchable soft-electronic and optoelectronic devices integrated with various functional nanomaterials and their applications to wearable and implantable medical and healthcare devices.[6] We introduced electromechanical cardioplasty using an epicardial mesh made of electrically conductive and elastic Ag/Au nanowire-rubber composite material to resemble the innate cardiac tissue and confer cardiac conduction system function.[7] We fabricated highly conductive and elastic nanomembrane for skin electronics.[8] We synthesized a flexible, sticky, and biodegradable electronic patch for controlled drug delivery for GBM treatment.[9] We developed a microneedle-based delivery method of theranostic NPs and high-energy photons to treat two types of brain tumors.[10] Recently, we synthesized an injectable hydrogel nanocomposite for intracortical drug delivery to treat deep-seated brain tumors.[11]

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2:15 PM SB05.02.03
Synthesis of Silicon-Metal Hybrid Hollow Nanostructures and Their Bio-Application Jeonghun Choi, Insu Lee and Nitee Kumari; Pohang University of Science and Technology, Korea (the Republic of)

Silicon nanostructures have been attractive materials in various field due to their unique properties such as large surface area, photoluminescence, semi-conductor. Despite enormous interest, synthesis of nanoscale (<100 nm) silicon nanostructures is challenging. Herein, we present the synthesis method of silicon nanostructures under 100nm through magnesiothermic reduction by handles of silica nanoparticles composition. During pretreatment of silica nanoparticles under vacuum condition, metal (Pd, Pt, Ni)-silicide and void space in silica nanoparticles play a key role to keep structures after conversion. We identified the optical properties of the silicon nanostructures and it is looking forward to giving high performance to Bio-application.

2:30 PM SB05.02.04
Antioxidative and Anti-Inflammatory WS_2 Nanosheets for Effective Wound Treatment Yoonhee So, Sin Lee, Chanhee Choi, Lee Hyun ji and Jong-Ho Kim; Hanyang University, Korea (the Republic of)

Deep partial- and full-thickness burn injuries are complicated traumas accompanying the severe failure of antioxidation, anti-inflammation, and inherent defense mechanisms against external bacteria. Accordingly, it is required to suppress oxidative stress and promote the recovery of intrinsic defense systems in burn wound lesions, but previous topical antipyrotics have been designed to date only to prevent bacterial infections. For this reason, it is an essential task to develop new efficient topical materials that can improve the intrinsic antioxidative and cellular defense mechanisms for the effective curing of deep burn wounds. Herein, we developed ultrathin WS_2 nanosheets exfoliated and functionalized with PCL-*b*-PEG (2H-WS_2) in aqueous solution, exhibiting superior scavenging ability and sustainability for a wide range of reactive oxygen species (ROS) and reactive nitrogen species (RNS) in keratinocytes. The functionalized WS_2 nanosheets were found to scavenge intracellular ROS and RNS as well as extracellular reactive species, suppressing oxidative stress in the wound lesions of mice. At the same time, the representative antioxidases, including CAT and GPx, were largely up-regulated in the presence of 2H-WS_2 nanosheets in burn wounds, improving the inherent resistance to oxidative stress. The 2H-WS_2 nanosheets also attenudated inflammatory cytokine secretion along with the inhibition of the extrinsic pathway of apoptosis in wound lesions. Moreover, the 2H-WS_2 nanosheets stimulated the production of innate antimicrobial peptides in burn wounds, enhancing the intrinsic resistance of cellular systems to external bacteria. All these integrated effects triggered by 2H-WS_2 nanosheets resulted in the successful healing of deep burn wounds. 2H-WS_2 nanosheets can be extended for the therapy of other diseases induced by oxidative stress and inflammation.

2:45 PM SB05.02.05
Laser-Assisted Surface Alloying to Enhance Antibacterial Properties and Bone-Cell Mineralization of Titanium Implants Sotoudeh Sedaghat, Vidhya Selvamani and Rahim Rahimi; Purdue University, United States

Orthopedic implants are commonly used to improve the patient's quality of life. Titanium-based alloys are widely employed in surgical implants due to their cytocompatibility and appropriate mechanical properties. However, the most common perspective problem that orthopedists face is implant-associated infection (IAI), which can lead to serious impacts such as the need for complex revision procedures, patient suffering, and even death. These complications that arise from the poor antibacterial property of titanium implants can be addressed by introducing antibacterial components such as silver. While researchers show the application of silver particles as an efficient anti-infection agent for Ti-based orthopedic implants, most of the developed products suffer from complicated and long fabrication/modification techniques, multi-step processing, high cost, unintended alteration in mechanical properties, unstable antibacterial effect, and leaching of the silver ions. Here we offer a simple and fast two-step technique for surface modification of the Ti-based implants using laser-assisted alloying (LAA). In this work, a nanosecond Nd:Yag laser was applied via optimized laser power for alloying of the coated Ag-ink film on the Ti surface. Besides, this prompt laser processing developed a micro/nano roughness on the Ti surface which was beneficial for osseointegration and cell mineralization. The Ti-Ag LAA samples prepared using a range of laser powers (8, 16, 24, 32, and 40 W) were characterized via various techniques. The scanning electron microscopy (SEM) images showed a developed hierarchical micro/nanostructure on the LAA surfaces. Energy-dispersive X-ray mapping and X-ray diffraction (XRD) results demonstrated enhanced oxygen level and Ag-Ti alloying. The Rockwell hardness tests of the Ti-Ag showed preserved bulk hardness of the samples with an average hardness of about 31 ± 1 HRC. This observation revealed a superficial alloying of the laser-assisted method which is essential for the Ti-based implant modification. The optimized Ti-Ag LAA sample (prepared with 32 W laser power) showed over 6-fold enhancement in antibacterial effect compared to the pristine Ti sample. This antibacterial property was shown to be effective on both gram-negative (E. coli) and gram-positive (S. aureus) bacteria during the test period of 12 days. On the other hand, the cell mineralization test showed over 2-fold increase in cell mineralization of the Ti-Ag LAA as compared to the pristine Ti sample which is due to the developed micro/nano features that provide active sites for cell attachment and growth. Moreover, the antibacterial effect of the developed surface helps the natural body cells to succeed in the competition on the implant surface toward the bacterial cell. The long-lasting antibacterial properties of the prepared Ti-Ag LAA samples along with cytotoxicity as low as 5- 10 % originated from the properly anchored Ag inside the Ti structure originated from the efficient laser surface alloying.

3:00 PM BREAK

SESSION SB05.03: Nano at the Biointerface

Session Chairs: Gemma-Louise Davies and Ben Zhong Tang
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2016

3:30 PM *SB05.03.01
Predictive Interactions of Chiral Nanoparticles and Proteins—From Catalysis to Vaccines Nicholas A. Kotov; University of Michigan, United States

Biomimetic nanoparticles (NPs) are known to serve as nanoscale adjuvants, enzyme mimics, and amyloid fibrillation inhibitors. Their further development requires better understanding of their interactions with proteins. The abundant knowledge about protein-protein interactions can serve as a guide for designing protein-NP assemblies, but the chemical and biological inputs used in computational packages for protein-protein interactions are not applicable to inorganic NPs. Analyzing chemical (CH), geometrical (GE), and graph-theoretical (GT) descriptors for protein complexes, we found that GE and GT descriptors that are uniformly applicable to biological and inorganic nanostructures can predict interaction sites in protein pairs with accuracy >80% and classification probability ~90%. We extended the protein-trained machine learning algorithms to inorganic biomimetic NPs and found a nearly exact match between experimental and predicted interaction sites with proteins. These findings can be extended to other organic and inorganic NPs to predict their assemblies with chemically dissimilar structures.[1]
The design principles of and predictictive capabilities of NP-protein interactions have been utilized for formation of complexes of plasmonic NPs with proteins. They enabled polarization-based drug discovery platforms for Alzheimer syndrome,[2] materials for chiral catalysis,[3] and chiral antiviral vaccines.[4]
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4:00 PM SB05.03.02
Boron Nitride Nanosheets Can Induce Water Channels Across Lipid Bilayers Leading to Lysosomal Permeabilization Xuliang Qian[1], Matteo Andrea Lucherelli[2], Wenpeng Zhu[3], Paolo Samorì[4], Huajian Gao[1,5], Alberto Bianco[2] and Annette von dem Bussche[6]; [1]Nanyang Technological University, Singapore; [2]CNRS, Immunology, Immunopathology and Therapeutic Chemistry, France; [3]Sun Yat-sen University, China; [4]University of Strasbourg, France; [5]A*STAR, Singapore; [6]Brown University, United States

While the interaction between two-dimensional (2D) materials and cell membranes is of key importance to the development of nanomedicines and safe applications of nanotechnology, still very little is known about the biological interactions of many emerging 2D materials. Here we investigate how hexagonal boron nitride (hBN) interacts with the cell membrane by combining molecular dynamics (MD), liquid phase exfoliation and in vitro imaging methods. MD simulations reveal that a sharp hBN wedge could penetrate a lipid bilayer and simultaneously form a cross-membrane water channel along its exposed polar edges, while a round hBN sheet does not exhibit this behavior. We hypothesize that such water channels could facilitate cross-membrane transport, with important consequences including lysosomal membrane permeabilization (LMP), an emerging mechanism of cellular toxicity that involves the release of cathepsin B and generation of radical oxygen species leading to cell apoptosis. To test this hypothesis, we prepared two types of hBN nanosheets, the former with a rhomboidal, cornered morphology and the latter with a round morphology, and exposed human lung epithelial cells to both hBN nanosheets. The cornered hBN with exposed polar edges resulted in a dose dependent cytotoxic effect, whereas round hBN did not cause significant toxicity, thus confirming our hypothesis. The described water channel mechanism suggests various applications including the development of hBN-based drug delivery systems and safe design of future advanced hBN containing composites and devices.

4:15 PM SB05.03.03
Nanoparticle Interaction with Extracellular Matrix Stabilizes Cartilage Tissue Integrity Ula von Mentzer, Gizem Erensoy, Stefanny de Fatima Guedes Cunha, Sara Yousefialdashi and Alexandra Stubelius; Chalmers University of Technology, Sweden

Statement of Purpose: Arthritic disorders are a leading cause of disability worldwide[1]. Current treatments result in unsatisfactory outcomes due to the lack of specificity, fast clearance, and inability to penetrate biological barriers. Advancements in nanotherapeutics have shown that electrostatic interactions and nano-sized particles are able to target and penetrate dense, negative tissues such as the joint cartilage[2]. Previously, we have shown that nanoparticles (NPs) interact with proteins in the joint space, which dictate the NPs' interactions with cells and cartilage tissue[3]. As it is known that NPs must interact with the cartilage extracellular matrix (ECM) proteins prior to reaching their cellular target, this study aimed to demonstrate that the NPs' interactions with ECM can be used as a means to stabilize the tissue and reduce degradation.
Methods: A cationic NP panel that differed in size and charge was synthesized based on either poly(amidoamine) (PAMAM) dendrimers (DendritechR, Midland, MI, USA) or poly(lactic-co-glycolide) (PLGA; ResomerR, Essen, Germany) polymer particles (formulated by nanoprecipitation) decorated with either PEG or polyethylenimine (PEI)-PEG modifications. All particles were fluorescently labeled with FITC. NP size and charge were characterized by dynamic light scattering (DLS) as well as electron microscopy. To mimic the thickness of human cartilage, porcine articular cartilage explants were used in this study, and subjected to arthritis-relevant enzymes such as ADAMTS5 for 1 or 2 hours, followed by NP treatment of equivalent duration. Released ECM components including sulfated glycosaminoglycans (GAGs) were assessed by colorimetric assays and polyacrylamide gel electrophoresis (PAGE). NP tissue uptake was evaluated by confocal microscopy, while aggregate formation and tissue topography were determined by atomic force microscopy

(AFM). The interactions between the NPs and ECM proteins were evaluated by isothermal titration calorimetry (ITC) and quantitative proteomics.
Results: Physicochemical characterization of PAMAM particles revealed sizes of 7.2 nm and 11.0 nm and zeta potentials of +17.0 mV and +4.0 mV for non-PEGylated and PEGylated NPs respectively. Control PLGA-based NP size varied between 270 nm and 264 nm with their respective zeta potentials exhibiting +22.2 mV and +3.78 mV. By treating porcine explants with the different particles after enzymatic stimulation, we measured a reduction of GAG concentration in the supernatants after 2- and 4-hour treatments compared to the control. To investigate the level of engagement between the particles and the tissue, we tracked the fluorescently labeled NPs using confocal fluorescent microscopy. To further analyze the specific interactions with the ECM proteins and individual NPs, proteomic analysis revealed several highly abundant integrity-associated proteins that could account for the NP-matrix stabilization interactions including proteoglycans such as biglycan and fibromodulin, as well as collagen-binding proteins such as matrilins that are essential for tissue integrity.
Significance: Soluble GAG concentration was inversely correlated to particle cationic charge, suggesting an effect based on electrostatic interactions with the anionic ECM components. NPs are usually studied as carriers for drug delivery applications, yet their physicochemical effects on the ECM are rarely reported. This study aims to be the first to demonstrate that interactions between cationic NPs and ECM components such as anionic GAGs can result in cartilage tissue stabilization in the catalytic proinflammatory arthritic environment.

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4:30 PM SB05.03.05
Assessing Toxicity of Fullerene Nanostructures Using Human Proteins by Combined Computational Chemistry and Cheminformatics Approach
Mariam Zamani[1,1], Stephen Szwiec[1,1], Gerardo Casanola-Martin[1], Natalja Fjodorova[2], Marjana Novič[2], Katja Venko[2], Melek Türker[3], Gulcin Tugcu[4], Safiye S. Erdem[5], All Toropova[6], Andrey A. Toropov[6] and Bakhtiyor Rasulev[1,1]; [1]North Dakota State University, United States; [2]National Institute of Chemistry, Slovenia; [3]Bogazici University, Turkey; [4]Yeditepe University, Turkey; [5]Marmara University, Turkey; [6]Istituto Di Ricerche Farmacologiche Mario Negri IRCCS, Italy

In recent years nanomaterials have found a widespread application in material science, pharmaceutical, biomedical and medical fields. Various nanomaterials are applied, as well as in development, as high effective drugs or as drug delivery agents for targeted treatment, including cancer, viruses and etc. Here we show how the combination of computational chemistry, data mining and cheminformatics approaches can help in assessment of toxicity and virtual screening of fullerene nanostructures for combined drug-like and toxicity properties. We demonstrate how the combination of inverse molecular docking, quantum chemistry and machine learning methods can be applied to investigate these nanostructures. A high-throughput virtual screening was applied to both large set of fullerene nanostructures and known biological targets (human proteins), to assess binding scores and to investigate the potential interactions with biological targets. We show several case studies, including analysis of aquatic toxicity of fullerene derivatives, since it is crucial to understand their fate in the environment, particularly their effects on aquatic organisms. Regression models were built and artificial neural network algorithms were applied for property prediction and screening FDs for structural features responsible for binding activity and then highlighted the most active fulleren derivatives that may have the greatest impact on aquatic organisms.
The outcome of this study has the potential to reveal which structural features of fullerene nanostructures have the main impact on toxicity, to be able to decide what fullerene derivatives should be prioritized first. This will help to decrease the need for animal testing and make decisions on applications in advance of manufacturing.

SESSION SB05.04: Poster Session I: NanoBio Interactions I
Session Chairs: Gemma-Louise Davies and Sarah Stoll
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SB05.04.01
Anti-Bacterial Surface Based on Nanostructurs and Biocompatible Materials for Surgical Titanium Plate *In Vivo* Jeong-Won Lee[1], Chang-Hun Lee[2] and Sung Jae Kim[3]; [1]Chosun University, Korea (the Republic of); [2]Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of); [3]hallym University, Korea (the Republic of)

In the modern era, the anti-bacterial efficacy of surgical implants in the body is attracting great attention. The method is to modify the surface of the implant to reduce the adhesion of bacteria to limit the formation of a biofilm or, on the other hand, to coat the implant with a functional material that kills the surrounding bacteria. However, most of these research results are difficult to mass-produce, or there are hurdles in practical application as materials that have not yet received FDA approval in the human body. In the case of the SLIPS surface, which has recently attracted attention, its excellent effect has been demonstrated by applying a physical barrier that bacteria cannot settle. However, in the case of an actual infection model, not only the problem of biofilm formation on the surface, but also the occurrence of infection around the implant, so simply a physical barrier on the surface cannot prevent the deterioration of the affected area. Additionally, fluoroalkyl silane used in the SLIPS method applied to implants is a material that has not yet been approved. Therefore, for practical application, the use of materials available to the human body, prevention of biofilm formation on the surface, and prevention of bacterial infection in the vicinity should be provided.
In this study, we used TiAl6V4 implant, which is currently the most used material in the medical industry, and manufactured an innovative coating that overcomes both infection models using only materials approved for the human body. In addition, SLIPS surfaces with proven superior function was fabricated, and comparison and efficacy were demonstrated through in vivo experiments.
TiAl6V4 plates were immersed in NaOH solution with 0.5 mol concentration at 180°C in the oven for formation of nanostructure. The formation of 20 nm scale structures of titanium dioxide (TiO_2) is a process of dissolution and precipitation reactions. Next, a mixture of Poloxamer 407, Octanoic acid, and EGCG was coated on the nano Ti surface. Poloxamer 407 and EGCG are mixed and placed in an oven at 100°C for about 30 minutes to liquefy. Since the mixed solution of Poloxamer407 and EGCG has a very high viscosity and is difficult to use for coating, Octinoic acid is used to dilute it.
The usefulness of titanium implant with nano-structure having a sustained-release coating of Poloxamer/Octanoic Acid both was verified in vitro and in vivo. In particular, we made a rabbit surgery model similar to fracture surgery performed in humans. We confirmed the usefulness of our coating by inducing Pseudomonas aeruginosa infection and biofilm formation. Our results confirmed that the poloxamer/octanoic acid coating material lowered the infection rate and had a low toxicity. We propose that a titanium implant with a nano surface structure having a poloxamer/octanoic acid coating could be a novel alternative for surgical metal processing.

5:00 PM SB05.04.02
Fabrication of Antiviral/Antimicrobial Metal Nanoparticle-Embedded Polyelectrolyte Coatings for PPE Substrates Elayaraja Kolanthai, Andrew Sanford, Craig J. Neal, Udit Kumar, Candace Fox, Griffith Parks and Sudipta Seal; University of Central Florida, United States

The emergence of the novel severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) brought a global pandemic as a result of the virus's ease of spreading and its potential to incubate in asymptomatic hosts. Coronavirus disease (COVID-19) can be developed when infected by the virus, resulting in potentially lethal respiratory distress. A human gets infected when exposed to infectious respiratory fluids. Therefore, the use s of personal protection equipment (PPE), such as masks, can protect from the direct route of infection. PPE are critical to the well-being of essential healthcare workers and the general public, reducing the spread of the virus. Given the magnitude of SARS-CoV-2 transmissibility, novel precautionary efforts are necessary to kill or halt the virus's spread even in the current pandemic or for future unknown emerging virus diseases. Recent involvements in nanotechnology have effectuated need-based virus-resistance face masks/shields developed through the addition of nanomaterial coatings or impregnating nanomaterials in the masks/shields to combat the virus and augment protection levels. We hypothesized that modifying existing PPE materials with engineered antiviral/antimicrobial nanoparticles could produce substantial improvement in the material's efficacy in preventing transmission. The layer-by-layer (LbL) coating technique is a user-friendly and low-cost method chosen for PPE surface modification without using any acid or heat treatment. A wet chemistry method was used to synthesize the antiviral nanoparticles (<100 nm, silver, and gold). Synthesized nanoparticles added to cationic (chitosan, CHI) and anionic (poly(acrylic acid), PAA) polymer solution and co-solution were used to produce LbL coatings. Initially, PPE materials were applied to polyethyleneimine (PEI) or sulfuric acid treatment based on turning charge on the surface. The wet surface of face mask and face shield were immersed in the nanoparticles/CHI solution for 15 min followed by immersion in PAA for 15 min using the LbL coating technique. The fabricated thin films were characterized by XPS and SEM. Biological studies were performed using *E. coli* as a model bacterium to assess the fabricated coatings' antimicrobial activity. Coated PPEs exhibited considerable bacterial inhibition. Antiviral assays were performed with calicivirus as a model virus, and similar trends in antimicrobial results were obtained. According to these findings, silver and gold nanoparticle-based PPE coatings fabricated via LBL appear promising for COVID-19 prevention.

5:00 PM SB05.04.03
Versatile Phenol-Incorporated Nanoframes for *In Situ* Antibacterial Activity Based on Oxidative and Physical Damages Pei Liu and Paul K. Chu; City University of Hong Kong, Hong Kong

Gold nanoparticles (GNPs) with oxidase and peroxidase properties are great candidates for antibiotic-mimicking materials due to reactive oxygen species (ROS) production. However, the bioenzymic properties are not long-lasting due to the short lifespan of ROS and have only been observed from GNPs with a size of less than 20 nm, thus making the synthesis laborious and inefficient. Herein, GNPs with controllable size and effective ROS utilization are synthesized by an environmentally green process using natural phenols extracted from plants as the reducing and capping reagent. Functional metallic ions are chelated by taking advantage of the coordinating properties of phenols to form the versatile nanoframe (pGNP-Fe) that can self-assemble onto bacteria due to the inherent attraction rendered by phenols, and the physical pressure causes bacterial membrane damage. During internalization in bacteria, the cascade process resulting from the enzyme-like properties generates cytotoxic reactive ROS via oxidization, and the Fenton reaction enhances the antibacterial efficiency. This dual physical/chemical antibacterial process obviates the need for external antibiotics and antibacterial agents, which may otherwise pose toxicity in vivo. The fabrication strategy and materials properties described here provide insights into the design of antibioticmimicking materials based on enzymatic and physical effects.

5:00 PM SB05.04.06
Development of Antimicrobial ZnO Nano-Spine Thin Film on Commercial Air Filter Dae Hoon Park, Younghun Kim, Gunhee Lee, Inyong Park, Sang Bok Kim and Bangwoo Han; Korea Institute of Machinery and Materials, Korea (the Republic of)

COVID-19 is a disease caused by the novel coronavirus SARS-CoV-2. According to the U.S. Centers for Disease Control and Prevention (CDC), SARS-CoV-2 is transmitted by exposure to infectious respiratory fluids caused by infected individuals talking, coughing, or sneezing, thus, spreading the virions in airborne droplets (~370 virions in 1 μm and ~360,000 virions in 10 μm) and in aerosol forms, which are called 'bioaerosols'. Bioaerosols are one of the particulate matters (PMs) carrying living organisms from biological sources which include fungi, bacteria, and viruses. To reduce the exposure of biological PMs in indoor air condition, an air filter could be applied in air conditioning system in order to collect the bioaerosols on the surface of the filter membrane. However, previous studies report that viruses remain infectious on various surfaces such as polymeric fibrous filters for a few days. That triggered a tremendous effort to develop antimicrobial fiber-based filters for prevention of infectious virus transmission by fomites. Herein, we present antimicrobial thin film of zinc oxide (ZnO) nano-spines on commecial fiber-based filters and its potential for infection prevention. By developing a novel technique of dry aerosol coating process, (Zn) nano-seed was well-covered on the commercial filter fiber. After hydrothermal treatment, high aspect-ratio ZnO nano-spines were densely exhibited on the filter surface, which have significant antimicrobial effect to airborne pathogens due to. their spiky morphology. This novel thin film hold potential for airborne microbial disinfection, and the design of microbicidal materials with wide applicability to commercial air filter.

5:00 PM SB05.04.07
Harnessing the Bio-Nano Interactions of Natural Clay for Advanced Antimicrobial Solutions Ofer -. Prinz Setter[1], Alva -. Gilboa[1], Iser Snoyman[1], Ghazal Shalash[1] and Ester Segal[1,2]; [1]Technion - Israel Institute of Technology, Israel; [2]The Russel Berrie Nanotechnology Institute, Israel

Biological cells have evolved alongside of natural mineral clay (layered aluminosilicates) leading to intriguing interactions from beneficial to bio-adverse. Specifically, bacteria were shown to adhere to clay particles and even incorporate them into their biofilm[1]. We endeavor to direct these interactions to neutralize a specific pathogenic bacterial srain in a heterogenous culture, maintaining the non-pathogenic populations unharmed and mitigating the global surge in antibiotic resistance. To that end, we utilize Halloysite nanotubes (HNTs), which are 600-900 nm long and 50 nm wide, and exhibit a hollow lumen with an inner diameter of 15 nm. This intrinsic mesoporous morphology of HNTs combined with their adsorptive silica surface renders the clay ideal for carrying various antimicrobial cargoes. The desired specific antibacterial effect is based on the selective binding of the clay to the target bacteria which is realized by antibodies we immobilize onto the HNTs' surface[2]. Next, we investigate the loading of the antibody-functionalized HNTs with two separate antimicrobial payloads: (1) the potent antibiotic ciprofloxacin (CIP) to be gradually released near the target bacteria[3], or (2) plasmonic gold nanorods (AuNR) to be activated by near-infrared irradiation for a local photothermal effect.

The selective binding of the Ab-functionalized HNTs to their target bacteria is confirmed by fluorescence and electron microscopy along with high-throughput imaging flow cytometry[4]. Consequently, CIP-loaded Ab-HNTs exert a two-fold higher potency against the target bacteria, whereas in the same heterogeneous culture, the inhibition of non-target bacteria is decreased by 50-90%. Regarding the AuNR-Ab-HNTs hybrids, upon irradiation with a near-infrared laser, a superior antibacterial activity is observed in comparison to free AuNR, despite the 5-fold higher increase in bulk temperature induced by the latter[4]. In addition, the biocompatibility of the multifunctional clay is studied towards a physiologically relevant co-culture of human colon epithelial cells (Caco-2 / HT29) and the localization of the particles after administration is investigated.

In this presentation, I will discuss our findings as well as the preceding considerations involved from the bioconjugation step to the loading of the clay for obtaining the desired bio-nano interactions. We believe this work signifies the potential in comprehending the interface between biological cells and natural nanomaterials, which are abundant and easily obtainable, to utilize the latter for novel biomedical applications.

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5:00 PM SB05.04.08
Neoteric Silver-Ceria as a Rapid, Residual Antibacterial Agent for Abiotic Surfaces Abinaya Sindu Pugazhendhi[1], Craig J. Neal[1], Udit Kumar[1], Fei Wei[1], Elayaraja Kolanthai[1], Andrew Andy[1], Candace Fox[1], Christina Drake[2], Griffith Parks[1], Sudipta Seal[1] and Melanie J. Coathup[1]; [1]University of Central Florida, United States; [2]Kismet Technologies, United States

Introduction: High rates of mortality and morbidity due to hospital acquired infectious (HAI) disease remains a serious problem in the healthcare sector. The application of nanotechnology as a novel antimicrobial agent has proven effective and is of high interest. Among them, cerium- and cerium oxide-based (ceria) nanoparticles (CNPs) have received much attention owing to their unique surface kinetics *via* auto-catalytic cycling between two oxidative states ($Ce^{4+} \rightarrow Ce^{3+} \rightarrow Ce^{4+}$). CNPs have been shown to be less toxic to mammalian cell lines but effective in eradicating bacteria through the formation of reactive oxygen species (ROS). Nano-based silver is also known for its efficient antimicrobial action. The aim of this study was to investigate the antibacterial activity of silver-doped ceria nanoparticles (AgCNPs) on three bacterial genera both in a liquid and dry form and its potential role as a novel, self-disinfecting and residual coating for high-touch abiotic surfaces. We hypothesize that through heightened generation of ROS, AgCNPs interact with the bacterial membrane leading to oxidative stress and bacterial death.
Materials and Method: AgCNP was synthesized using a base-mediated forced hydrolysis method and material characterization performed. The minimum inhibitory concentration (MIC) of AgCNPs and CNPs was determined for *Pseudomonas aeruginosa* (PA), *Staphylococcus aureus* (SA), and methicillin resistant *Staphylococcus aureus* (MRSA). Experiments were conducted with AgCNP and CNP at concentrations of 100 µg/mL (PA), 300 µg/mL (SA and MRSA), $AgNO_3$ (20 µg/mL) and gentamicin (20 µg/mL). Cell viability, a time-scale assay using TEM, intracellular ROS, DNA, and membrane damage were analysed. The ability of each agent to generate superoxide ($O_2^{\bullet-}$) and hydroxyl ($OH^\bullet$) radicals, RNS, and H_2O_2 was determined. To test each agent's residual antibacterial activity, solid surface (individual and multiple species) re-challenge tests were carried out with four cumulative doses (~10^8 cells/mL) of bacteria. Biofilm from each bacterial species was allowed to form followed by treatment with each agent for three days at intervals of 24 h. Biofilm thickness and bacterial viability was assessed. All experiments were carried out in triplicate and a Mann-Whitney U test was used for statistical analysis where p values < 0.05 were considered significant.
Results: AgCNP consisted of particles composed of 53.7% Ce^{3+}:Ce^{4+}(%Ce^{3+}) and 14.6% [Ag]/[Ag+Ce]. Treatment with AgCNP resulted in significant PA cell death (100%) after 60 mins ($p < 0.0001$) and SA and MRSA death after 180 mins (both $p < 0.0001$). AgCNP significantly induced ROS generation when given to all three bacteria (PA (~20-fold), SA (~7.4fold) and MRSA (~21fold)) when compared to control (all $p < 0.0001$). TEM analysis showed AgCNPs localized onto the bacterial membrane resulting in a significant and fatal increase in cell size (PA ($p<0.01$), SA and MRSA ($p<0.05$)). Results also revealed a significant increase in DNA damage following AgCNP treatment in all groups when compared to control (all $p < 0.0001$). Further, AgCNP induced a significantly increased amount of $O_2^{\bullet-}$, $OH^\bullet$, H_2O_2 and RNS compared to all other agents. An AgCNP-coated glass slide surface re-challenge test showed 100% inhibition of PA, SA and MRSA both individually and as a multispecies inoculation. Finally, AgCNPs were able to disrupt pre-formed biofilm in all three species and significantly eradicated shielded bacteria within (all $p < 0.0001$). AgCNPs outperformed CNPs, $AgNO_3$ and gentamicin.
Discussion and Significance: This study showed that AgCNPs, whether in a liquid or dry form, were able to eradicate *S. aureus*, MRSA, and *P. aeruginosa*. AgCNPs displayed synergistic and augmented antibacterial activity when compared to Ag or CNPs alone. We have demonstrated that AgCNP coatings may offer a new type of continuous disinfectant that leaves behind a continually disinfecting film with excellent antibacterial efficacy.

5:00 PM SB05.04.12
Investigating the Effect of Surface Chemistry of Mesoporous Silica Nanoparticles (MSNs) on MRI Performance Connor Wells[1,2], Danielle Winning[3], Dermot F. Brougham[3], James Wilton-Ely[2] and Gemma-Louise Davies[1]; [1]University College London, United Kingdom; [2]Imperial College London, United Kingdom; [3]University College Dublin, Ireland

Magnetic resonance imaging (MRI) is a leading non-invasive medical imaging technique due to its well established spatially resolved images. To aid this diagnostic tool further, contrast agents have been designed to improve the quality of the images, with nanostructured MRI contrast agents showing exceptional promise in image enhancement at extremely low doses.[1] Relaxivity is the term used to assess the effectiveness of an MRI contrast agent on signal enhancement. Taking advantage of their generally high surface areas, nanostructured contrast agents often host large numbers of paramagnetic centres thereby increasing sensitivity through increased local concentration. Importantly, their bulky size improves relaxivity by contributing to slower rotational correlation time, resulting in longer T_1 relaxation times.[2] There is also increasing evidence that nanoscale design features, such as pore size and surface chemistry can influence water mobility and hence affect the ultimate capability of these nanostructures as MRI contrast agents.[2,3] Surface modifications can not only impact water diffusion, but also directly affect the local tumbling rate of a chelated paramagnetic centre.[4,5] However, understanding the structure-property relationship of designed nanostructured contrast agents is still relatively poor and therefore a more thorough investigation is required in order to improve their potency.
The objective of this work is to explore how nearby surface modifications could influence the relaxation of Gd^{3+}-chelates loaded in mesoporous silica nanoparticles (MSNs). We seek to gain a better grasp of how a gadolinium complex interacts with neighbouring functional groups, such as hydrophilic thiols or bulky phenyls, across a range of molar percentages present in the pores, to probe water diffusion and effects on local tumbling, and understand the resulting impact on relaxivity. As well as full structural characterisation, single-field and fast-field cycling relaxometry (SFR and FFC-NMRD, respectively) have been used to analyse the water diffusion/exchange behaviour within these composites. It was found that modifying the molar percentages of either functional group did not significantly affect the colloidal stability of the particles, nor their particle size, as determined by TEM. Functionalised particles displayed differing behaviour when analysed using SFR; the relaxivity of phenyl-functionalised MSNs did not exhibit a linear trend with an increasing number of phenyl groups present, indeed showing no influence from the bulky ligand, whereas the thiol-MSNs gave lower

relaxivities as the thiol molar percentage increased. This is potentially due to the hydrophilic nature of the thiols and thus their interactions with water affecting the exchange rate. FFC-NMRD analysis revealed that both sets of functional groups influenced the paramagnetic Gd^{3+}-chelate compared to non-functionalised MSNs. This work provides valuable insights into the importance of nanomaterial design features, in particular the location and nature of functional groups in MRI contrast agent design. An improved understanding of the interplay between these factors should prove useful in the development of such agents for diagnostics and sensing.

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5:00 PM SB05.04.13

Application of Porous Nanomaterials in Filtration of Biological Systems Alexandra Ten Bosch; Centre National de la Recherche Scientifique, France

Nanofiltration is shown to provide a way to test and measure nano-bio interactions between the nanofilter material and biological nanoparticles (NP). Nanofiltration is used in biotechnological and biopharmaceutical industries for separation and purification of biological molecules such as viruses, monoclonal antibodies, vaccines, blood plasma and therapeutic proteins. Other applications can be found in water purification, air filtration, biomaterial processing.. Membrane fouling limits use of nanofiltration in large low value applications such as wastewater treatment and has encouraged the development of better membranes. Nanofibers of polymers produced by electrospinning yield filters with higher flux and better mechanical stability. Ceramic membranes such as nanoporous zeolites improve selectivity. Recently Carbon nanotubes (CNT) and other nanotube materials have been explored and show promising properties. The interaction between nanofilter material and permeating biological nanoparticles determines the efficiency of the filtration process.
A theory for the efficiency and permeability of a nanomembrane is presented. The dynamic equations for flux and concentration profiles, derived from a kinetic theory of non-equilibrium statistical mechanics, are solved analytically. The penetration of the nanoparticles is determined by the ratio of the flux at the exit of the membrane to the flux at the entrance.
The theory is applied to two specific examples.
●Filtration of virus-like particles in air by a nanofibrous membrane with and without charge on fiber surfaces. The model treats the virus as a spherical particle of net surface charge and the polymer fiber as a neutral or charged line or plane. For like net charges on fiber and virus the electrostatic interaction between the NP and the fibers is shown to decrease penetration and impact NP aggregation, pertinant for the smallest NP sizes.

●Filtration of a polydisperse virus sample in water by a cylindrical CNT of radius H. The model demonstates a transition with increasing effective interaction from "hydrophobic" rejection of water molecules (diameter σ) for weak van der Waals forces with the carbon walls to notable penetrration with large flux and density, localized for $\sigma/H = 1$ at the center of the tube. Interactions between water molecules play an important role. The virus interacts with the pore material principally by a Lennard Jones type interaction. Viruses with effective diameter greater than H are inhibited from entering the CNT by steric effects and pure water exits the CNT pore.

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5:00 PM SB05.04.15

Molecular Investigation of The Interaction Between a Gold Nanoparticle and a Polymer in Aqueous Solution Roberta Cappabianca, Paolo De Angelis, Annalisa Cardellini, Eliodoro Chiavazzo and Pietro Asinari; Politecnico di Torino, Italy

Several experimental and theoretical challenges limit a more rational design of nanoparticles (NPs) with a specific target application, i.e., the preparation of NPs with different structures/properties for various final uses. The characterization of different nanoparticle suspensions in liquids has drawn significant attention in a wide range of engineering applications. Recently, many computational approaches concerning the interactions between soft materials and inorganic nanoparticles proved to be promising in guiding the experimental preparation of nano suspensions [1-3]. Due to their optical and electronic properties, gold nanoparticles (AuNPs) are interesting for several applications, ranging from energy (e.g., solar steam generation [4,5]) to medicine (e.g., cancer theranostics [6,7]). Regarding the latter, AuNPs often encounter biocompatibility and biodegradability issues that can be overcome by encapsulating them in a poly (lactic-co-glycolic acid) (PLGA) matrix. Understanding the self-assembly dynamics of PLGA on the AuNP surface is crucial to guide and optimize the design of AuNPs coated with a PLGA corona. In this work, we combine different computational techniques to understand the interactions of an AuNP with PLGAs, aiming at assessing the most efficient and effective AuNP shape for biological applications. Specifically, we first perform classical molecular dynamics simulations while tuning the PLGA concentration in an aqueous solution; second, relying on a recently developed unsupervised machine learning (ML) algorithm, we evaluate the time evolution and behavior of PLGA clusterization. Finally, we employ the umbrella sampling approach to explore the AuNP-PLGA free energy landscape; this, combined with a detailed analysis of the surface still accessible to the solvent, allow us to gain insight into the anisotropic adsorption behavior of PLGAs onto AuNP. Our results highlight that the shallow morphology, besides surface chemistry, can influence the adsorption phenomena: in particular, the tested AuNP topology present the Au {1 1 1} crystal planes as privileged adsorption sites. This modeling-based investigation offers a comprehensive methodological approach for the rational and functional design of PLGA-coated gold nanoparticles [8].

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5:00 PM SB05.04.16
Poly(acrylic acid)-Based Nanocomposite Hydrogel Prepared by Gamma-Irradiation Crosslinking for Sweat Urea Detection Nichaphat Passornraprasit[1], Tatiya Siripongpreda[2,1], Sumalee Ninlapruk[3], Nadnudda Rodthongkum[4,5,1] and Pranut Potiyaraj[4,5,1]; [1]Chulalongkorn University, Thailand; [2]Nanoscience and Technology Interdisciplinary Program, Thailand; [3]Office of Atoms for Peace, Thailand; [4]Metallurgy and Materials Science Research Institute (MMRI), Thailand; [5]Center of Excellence in Responsive Wearable Materials, Thailand

Nanocomposite hydrogel is fabricated via γ-irradiation crosslinking of PAA, graphene oxide (GO), and cellulose nanofiber (CNF) to serve as a sensing substrate for non-invasive dual detection of urea in sweat. In this work, CNF helps to improve the mechanical properties of the hydrogel whereas GO plays a key role in enhancing the detection signal of urea in laser desorption/ionization mass spectrometry (LDI-MS) and increases the hydrogel functionalities. The hydrogel possesses high water-sorption capacity and transparency suitable to accommodate coloring reagents and enzymes for the colorimetric sensor. The sensor exhibited vivid color change towards the increase of urea concentration in a linear range of 40–80 mM covering for chronic kidney disease (CKD) indication. Furthermore, the hydrogel can be directly applied as a substrate for the direct quantitation of urea by LDI-MS. In LDI-MS, it verifies that GO/CNF/PAA hydrogel can act as a direct matrix for promoting urea ionization, and these results corresponded well with the colorimetric sensor. Hence, this hydrogel patch might be a potential material to be applied in the non-invasive dual detection of CKD in medical diagnosis.

5:00 PM SB05.04.19
Design of Mesoporous Silica Nanoparticles for Crossing the Blood-Brain-Barrier by Modulating Surface Properties Zih-An Chen[1], Si-Han Wu[2], Chung-Yuan Mou[1] and Peilin Chen[3]; [1]National Taiwan University, Taiwan; [2]Taipei Medical University, Taiwan; [3]Academia Sinica, Taiwan

Mesoporous silica nanoparticles (MSNs) have been demonstrated as an excellent platform for drug delivery carriers in cancer treatment where tumor targeting is normally achieved via the enhanced permeability and retention (EPR) effect. However, it remains challenging for MSNs to deliver chemical drugs, nuclear acids, or proteins to reach brain tumors due to the presence of the blood−brain barrier (BBB). Here, we propose a simple strategy to modify MSNs to target brain tumors. Our strategy was to optimize the size of PEG on the surfaces of MSNs to overcome BBB. We first tested different sizes of PEG coating on the MSNS in the in vitro BBB model, where the smaller size of MSNs with near neutral charged ($RMSN_{25}$-PEG-TA) possesses higher transport efficiency to cross the BBB-mimicking endothelial cell layer. To evaluate the circulation of MSNs, we utilized two-photon microscopy. We observed that the MSNs stayed long enough in the circulation system (over 24 h) and could be accumulated outside of the cerebrovascular in mouse brains. We also examined the EPR effect with various functionalized MSNs. A particular modification in MSNs led to their abundant accumulation in tumor tissue. In a drug delivery study, we explored the potential of using MSNs to deliver drugs (DOX@MSN) into the glioma tumor. It has been observed that the functionalized MSNs with DOX significantly suppress the growth of orthotopic glioma tumors and improved DOX's severe side effects in vivo study. The biosafety result showed that the given dose of the functionalized MSNs appeared safe and decreased severe side effects caused by DOX in the animal models.

5:00 PM SB05.04.20
Tannic Acid-TiO_2 Heterojunction within Mesoporous Silica Particles for Reduced Photo-Induced Toxicity and Enhanced Sunscreening Effects Saehan Choi, Jeonga Kim, Rafia T. Rahman and Yoon Sung Nam; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Wide bandgap semiconductor nanoparticles, such as zinc oxide (ZnO) and titanium dioxide (TiO_2) nanoparticles, have been widely used as ultraviolet (UV) blocking materials due to efficient UV absorption and excellent stability. However, the high chemical potentials of the photo-induced electrons and holes unavoidably generate reactive oxygen species (ROS) that can induce adverse chemical and biological damage. Synthetic polymer encapsulation has been commonly used to suppress photo-induced ROS generation, but recent studies continue to warn against the use of synthetic polymers in cosmetic and personal care products. Here we present a new method to effectively minimize the photo-induced toxicity of TiO_2 using tannic acid, a bio-inspired adhesive antioxidant polyphenol molecule, that can strongly bind to TiO_2 nanocrystal surface via ligand-to-metal charge transfer (LMCT). SiO_2-TiO_2 particles were prepared through the *in situ* TiO_2 nanocrystal synthesis within mesoporous SiO_2 particles to minimize the photochemical reactivity of TiO_2. TA was spontaneously deposited on the TiO_2 surface by Ti-catechol and Ti-pyrogallol coordination to synthesize SiO_2-TiO_2-TA hybrid particles. TiO_2 nanoparticles penetrated the cellular membrane by endocytic internalization and accumulate around the endoplasmic reticulum and nucleus. Accordingly, fibroblasts treated with TiO_2 nanoparticles exhibited lower cell viability under UV or HEV light irradiation due to highly reactive ROS generation. However, SiO_2-TiO_2-TA hybrid particles did not penetrate the cell membrane but efficiently protected the fibroblasts against UV and HEV damage through the effective scavenging of photo-generated ROS. Additionally, the LMCT from the TA HOMO to the TiO_2 conduction band allowed a new absorption pathway, enhancing the UV-to-HEV blocking performance, which significantly increased the sunscreen performance of an emulsion formulation containing SiO_2-TiO_2-TA hybrid particles. This work demonstrated a new promising strategy of plastic-free sunscreen agents with enhanced sunblock performance and suppressed photochemically induced toxicity.

5:00 PM SB05.04.21
Towards the Development and Optimisation of Designer Nanocomposites for Biomedical Applications Sam Ackerley[1], Leslie P. Hughes[2], Duncan L. Browne[1] and Gemma-Louise Davies[1]; [1]University College London, United Kingdom; [2]AstraZeneca, United Kingdom

Flow chemistry is a fast-advancing field involving the continuous combining of reactants which are fed into a reaction chamber, followed by the continuous output of product. When compared to batch methods, flow chemistry boasts better mixing, more efficient heat transfer and the ability to undergo self-optimisation.[1] Typically synthesised in batch, nanoparticles which display superior properties (e.g. chemical, thermal, optical) to their molecular counterparts are becoming increasingly in demand, however their large-scale synthesis, necessary for industry, is currently limited. One significant benefit to flow is the ease of scale-up whilst still retaining the desired particle properties. A range of nanoparticles from metal oxides to polymers have been produced *via* flow techniques, for example microfluidics.[2] Moreover, in flow the user has much greater control over the experimental parameters, i.e. reaction time can be fine-tuned much more easily than in batch which is useful for reactions which occur in a matter of seconds.

Continuous stirred tank reactors (CSTR) are commonplace in many large process reactions such as pharmaceutical manufacturing where they are predominantly used to synthesise organic compounds on the molecular level. Whilst CSTRs are generally involved in batch reactions they can be utilised in continuous flow processes too. The fReactor™ represents a versatile piece of flow equipment consisting of five connected CSTR modules, each of which form a discrete reaction zone. Each module has multiple ports making telescoping of reactions possible. Offering alternative routes of synthesis, this equipment can be used to conduct both single and multiphasic reactions. Additionally, the fReactor allows for the exploitation of traditional chemical and physical principles but provides that critical level of control not seen in batch, owing to its small size and modular design. Thus, bridging the gap between batch and classical flow/microfluidics.

Using the fReactor, this work describes the optimisation of poly(lactic-co-glycolic) acid (PLGA) nanoparticle synthesis by nanoprecipitation. This polymer presents itself as an ideal candidate for encapsulating active pharmaceutical ingredients owing to its biocompatible and biodegradable nature, coupled with its FDA approval for use *in vivo.*[3] Initial optimisation experiments allowed the formation of spherical nanoparticles ~200 nm with polydispersity indices of 0.05, a significant improvement over the polydispersity observed when prepared using traditional bath methods. Furthermore, we describe a methodological design which was carried out as a systematic study to assess several parameters including type of PLGA, solvent, flow rate, residence time, agitation speed, use of surfactants, and encapsulation ability. Notably we found that as agitation speed within the fReactor was decreased in regular intervals from 1500 to 500 rpm during the synthesis, nanoparticles size increased linearly ($R^2 = 0.98$). However, for speeds lower than 500 rpm this control was lost and an increase in particle polydispersity was observed. A full comparison against PLGA prepared through batch nanoprecipitation demonstrated that this flow technique has the ability to tune particle properties readily, through greater control over process parameters and produced nanoparticles with a smaller size distribution.

We have further demonstrated the broad utility of this cascade of small volume CSTRs by optimising the synthesise of superparamagnetic iron oxide nanoparticles (8 nm diameter) and mesoporous silica nanoparticles with tuneable pore diameters, which can be used as medical imaging agents and drug delivery carriers, respectively. All particles made in the fReactor were comparable to the equivalent batch materials.

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5:00 PM SB05.04.22

Graphene Oxide Nanoplatforms to Enhance Cisplatin-Based Drug Delivery Silvia Panseri[1], Arianna Rossi[1,2], Ludmila Zarska[3], Darren Beirne[4], Giada Bassi[1,5], Andrea Ruffini[1], Monica Montesi[1], Diego Montagner[4] and Vaclav Ranc[3]; [1]Consiglio Nazionale delle Ricerche, Italy; [2]University of Messina, Italy; [3]Palacký University Olomouc, Czechia; [4]Maynooth University, Ireland; [5]University of Chieti-Pescara, Italy

INTRODUCTION

Glioblastoma is a very aggressive type of cancer with a very poor life expectancy for patients and breast cancer often metastasizes into the liver, lungs, brain, and, in 70% of cases, to bones[1,2]. Chemotherapy is largely used to treat cancer and it is based on the use of molecules targeting the high cancer cell proliferation metabolism[3]. Platinum (Pt) and three of its isoforms (cisplatin, carboplatin, and oxaliplatin) are some of the most successful metal-based drugs to cure breast cancer and glioblastoma[4,5]. Despite Pt-based chemotherapeutics being effective, their side effects (high degradation before entering the cells, the off-target organs toxicity, and cell resistance) remain great drawbacks[6-9]. In this work, it was developed a Graphene Oxide (GO) nanoplatform functionalized with Pt as a promising smart delivery system that could increase the Pt cellular uptake reducing the Pt amount needed for cancer treatment and consequently the side effects.

EXPERIMENTAL METHODS

GO nanoplatforms were treated with 8-arm polyethylene glycol-amine (PEG) that permits to load Pt on the platform (GO-PEG-Pt) and an extensive *in vitro* screening was performed on two breast cancer cell lines with aggressive nature that lead to metastatic behavior (MDA-MB 231 and MDA-MB 468) and two glioblastoma cell lines (U87 and U118). The bioactivity of GO-PEG-Pt compared to Pt-free (15 µM, 30 µM, and 60 µM) was analyzed looking at the effect on cellular uptake (ICP-OES), viability (MTT Assay), morphology (DAPI and actin staining), and migration up to 72 hours (Scratch Assay).

RESULTS AND DISCUSSION

The cell viability was significantly lower in MDA-MB 468 and U118 cells at 30 µM for GO-PEG-Pt group compared to Pt-free (<75%), and even the cell morphology seemed to be compromised. These results were highly related to the cellular uptake of GO-PEG-Pt which is significantly higher compared to Pt-free after 24 hours. This data confirmed that our nanoplatform promotes drug delivery directly inside the cells. In addition, GO-PEG-Pt mostly affected the cell migration compared to Pt-free, in particular, MDA-MB 231 showed a migration reduction of 60%, and this could be a great advantage in reducing the metastasis process.

CONCLUSION

This study demonstrated that the combination of Pt onto PEG-functionalized nano-sized GO provided numerous advantages for tumor therapy such as minimizing toxicity, enhancing the cellular uptake, and consequently we could reduce the side effects because a lower amount of Pt is necessary.

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ACKNOWLEDGMENTS

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5:00 PM SB05.04.24

Mannose-conjugated Ferritin Nanocages for Targeted MRI of Atherosclerosis Tanvi S. Kaku and Sierin Lim; Nanyang Technological University, Singapore

Atherosclerosis is characterized by the recruitment of monocytes to the subendothelial space which then mature into macrophages in the presence of macrophage colony stimulating factors and under the influence of their microenvironment to either M1 or M2 phenotypes. Early detection of atherosclerosis is challenged by a phenomenon known as positive arterial remodelling. This phenomenon is characterized by outward expansion of arterial walls in response to development of plaques, thus retaining the lumen diameter and demonstrating no stenosis. It is one of the major causes for missing out the detection of atherosclerosis by techniques that rely on lumenography. This leads to the need for imaging agents capable of targeting and imaging plaque components. The current study aims at targeting one such plaque component, the M2 macrophages, that are prevalent in higher numbers during early-stage atherosclerosis and to image these macrophages using magnetic resonance imaging (MRI) to aid early detection and facilitate timely therapeutic intervention of atherosclerosis. The study employs ferritin, an iron storage protein, with its natural ligand, iron, for MRI contrast. M2 macrophages are known to express mannose receptors on their surface, and we thus aim at using mannose conjugated ferritin nanocages for targeted MRI of the M2 macrophages in the atherosclerotic plaques. Mannose-conjugation is hypothesized to increase accumulation of ferritin nanocages in M2 macrophages and therefore improve contrast by virtue of targeting.

5:00 PM SB05.04.25
Enhanced Immobilization of Glucose Oxidase by Ferrocene-Branched Chitosan for Non-Invasive Glucose Sensing with High Selectivity and Sensitivity Yi-Ting Lai[1], Tzuhsiung Yang[2] and Nyan-Hwa Tai[2]; [1]Ming Chi University of Technology, Taiwan; [2]National Tsing Hua University, Taiwan

Diabetes, one of the leading causes of death worldwide, is responsible for one-seventh of deaths in the global population each year. Non-invasive methods for sensing and screening glucose level are highly desirable due to the more comfortableness, simplicity, and no risk of infection. However, the insufficient accuracy and ease of interference limit the non-invasive sensing technique from practical medical applications. Here, we develop a non-invasive glucose biosensor for measuring glucose in saliva based on ferrocene-chitosan (Fc-Chit) modified carbon nanotubes (CNTs) electrode through a simple drop-casting method. Quantum chemical calculations as well as comprehensive experiments were conducted to optimize the electro-mediated Fc-Chit, demonstrating sturdy immobilization of glucose oxidase (GOx) on the electrode and leading to a better electron transfer process. Superior glucose sensing sensitivity of 119.97 μA/mMcm^2 in phosphate buffer saline (PBS) solution and 108.21 μA/mMcm^2 in artificial saliva, respectively, can be achieved in a wide sensing range of 20–800 µM. In addition, the electrode shows high stability (remaining 95.0% after three weeks) and high selectivity toward glucose in the presence of various interferences, including uric acid (UA), ascorbic acid (AA), and lactic acid (LA), which is attributed to the specific sites enabling GOx to be sturdily immobilized on the electrode. The results show that the proposed non-invasive glucose biosensor can serve as a technological solution for regular and accurate screening of blood glucose levels by saliva tests.

5:00 PM SB05.04.26
Albumin-Albumin/Lactosylated Core-Shell Nanovectors—Therapy to Treat Hepatocellular Carcinoma for Controlled Delivery of Doxorubicin Neyelli G. Teran-Saavedra, Jose A. Sarabia-Sainz and Alexel J. Burgara-Estrella; Universidad de Sonora, Mexico

Doxorubicin (Dox) is the most widely used chemotherapeutic agent and is considered a highly powerful and broad-spectrum for cancer treatment. However, its application is compromised by the cumulative side effect of dose-dependent cardiotoxicity. Because of this, targeted drug delivery systems (DDS) are currently being explored in an attempt to reduce Dox systemic side effects. In this study, DDS targeting hepatocellular carcinoma (HCC) has been designed, specifically to the asialoglycoprotein receptor (ASGPR). Dox-loaded albumin-albumin/lactosylated (core-shell) nanoparticles (tBSA/BSALac NPs) with low (LC) and high (HC) crosslink using glutaraldehyde were synthesized. Nanoparticles presented spherical shapes with a size distribution of 257 ± 14 nm and 254 ± 14 nm, as well as an estimated surface charge of −28.0 ± 0.1 mV and −26.0 ± 0.2 mV, respectively. The encapsulation efficiency of Dox for the two types of nanoparticles was higher than 80%. The in vitro drug release results showed a sustained and controlled release profile. Additionally, the nanoparticles were revealed to be biocompatible with red blood cells (RBCs) and human liver cancer cells (HepG2 cells). In cytotoxicity assays, Dox-loaded nanoparticles decrease cell viability more efficiently than free Dox. Specific biorecognition assays confirmed the interaction between nanoparticles and HepG2 cells, especially with ASGPRs. Both types of nanoparticles may be possible DDS specifically targeting HCC, thus reducing side effects, mainly cardiotoxicity. Therefore, improving the quality of life of patients during chemotherapy.

5:00 PM SB05.04.27
Pyrene-Perfluoroalkyl (PP)-Incorporated Liposomes for Improving the Oxygen-Enriched Photodynamic Therapy (Oxy-PDT) Kwang Min Kim, Manoj Manna, Mohammed Inayathullah, Kyle D. Brewer, Bhavika Mam, Kelly B. Mahaney and Jayakumar Rajadas; Stanford University, United States

The Oxygen-enriched Photodynamic Therapy (Oxy-PDT) is one of the emerging tumor-treating approaches, where the perfluorocarbon as a high-capacity oxygen carrier is conjugated to the photosensitizer that converts the carried triplet oxygens into reactive singlet oxygens, which kill cancer cells. However, the efficacy of Oxy-PDT in the biological system remains challenging because it is difficult to obtain cytosolic delivery of the Oxy-PDT agent into cells due to its low cell permeability. To overcome the issue, we synthesized the perfluoroalkyl-pyrene (PP) as the Oxy-PDT agent, which was further incorporated into lipid bilayers (DSPC and DPPC) for enhancing the delivery of the agent into cancer cells. Our results showed that the PP formed a well-ordered structure within a hydrophobic region of the DSPC-DPPC bilayers (Fluoroscence spectroscopy, DLS). We also confirmed that the PP incorporated into the liposomal bilayers successfully exhibited an excimer emission at 450 nm in aqueous solutions (Fluoroscence spectroscopy, DLS) and produced singlet oxygens ($^1O_2$) (UV-Vis absorption spectroscopy). Then, we applied our new Oxy-PDT to the human patient-derived cancer cells (i.e., glioma, a type of brain cancer) to evaluate the therapeutic efficacy. Using the immunocytochemistry and confocal microscopy, we demonstrated that the PP-liposomes were localized only within cancer cells and significantly decreased the number of cancer cells when irradiated with light. In this study, we are introducing a new class of small organic molecules for biomedical applications. We expect that our approach incorporating oxygen carriers, photosensitizers, and liposomes in one system would make a significant contribution to the study of the Oxy-PDT modality by improving the localization and timing of cancer killing agent delivery.

SESSION SB05.05: Nano in Tissue Engineering
Session Chairs: Gemma-Louise Davies and Sarah Stoll
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2016

8:45 AM SB05.05.01
Polymer Blended Membranes Bi-Functionalized with ZnO-NPs via Electrospinning for Periodontal Bone Tissue Regeneration—Antibacterial Effect and Osteogenic Differentiation Stimulation Gina Prado-Prone[1], Phaedra Silva-Bermudez[2], Sandra E. Rodil[3], Maria L. Focarete[4], Jorge A. García-Macedo[5] and Argelia Almaguer-Flores[1]; [1]Universidad Nacional Autónoma de Mexico, Mexico; [2]Instituto Nacional de Rehabilitación LGII, Mexico; [3]Universidad Nacional Autonoma de México, Mexico; [4]University of Bolognia, Italy; [5]Universidad Naciona Autónoma de México, Mexico

Periodontitis is a highly prevalent infectious disease that causes the progressive destruction of teeth-supporting tissues: alveolar bone, cementum, and periodontal ligament. If left untreated it can lead to tooth mobility and eventually tooth loss, impairing oral function, aesthetics, and the patient’s overall quality of life. Bone Tissue Regeneration (BTR) is a surgical therapy to restore the alveolar bone around the tooth for reducing its mobility or, if the tooth was already lost, for future implant placement. This periodontal therapy involves the use of a resorbable membrane that selectively excludes the relatively rapid epithelial and fibroblastic down growth into the bone defect, allowing the repopulation of the defect sites with slower migrating endogenous bone cells and stem cells to regenerate the affected tissues. Two of the major reasons for clinical BTR failure are the bacterial colonization of the membrane-defect area and the fast biodegradation of the membrane, causing postoperative infections and a premature rupture of the membrane, limiting the regeneration process.

In this work, we present the development of biodegradable polymer-blended membranes functionalized with ZnO-NPs via electrospinning to prevent local bacterial colonization and, simultaneously, favor bone growth.

The developed membranes were synthesized based on a homogeneous polymer blend of polycaprolactone and gelatin (PCL-G) and modified, via electrospinning, with different concentrations (1, 3, and 6 wt.%) of ZnO nanoparticles (ZnO-NPs). The chemical composition, micro-morphology, hydrophilic character, biodegradation rate, and thermal and mechanical properties of the membranes were analyzed under conditions similar to the physiological environment. The antibacterial effect of the PCL-G membranes modified with ZnO-NPs was evaluated using five bacterial strains, two important periodontal pathogens: *A. actinomycetemcomitans* serotype b and *P. gingivalis*; and three aerobic pathogens causing prevalent nosocomial infections: *S. aureus*, *E. coli*, and *S. epidermidis*. We also investigated whether the developed membranes could stimulate osteogenic differentiation, and consequently bone regeneration. For this, the expression of osteoblast markers (osteocalcin and osteoprotegerin) and calcium deposition in human bone marrow-derived mesenchymal stem cells (BM-MSC) after exposure to the membranes, were analyzed.

The developed membranes presented appropriate physicochemical properties to be potentially used in clinical treatments, mainly, the mechanical properties and biodegradation rates were satisfactory. All the PCL-G membranes modified with 1, 3, and 6 wt.% of ZnO-NPs showed a significant reduction in the planktonic and biofilm formation of the five clinically relevant tested. However, only the membranes modified with the lowest concentration of ZnO-NPs (1 wt.%) stimulated the production of osteoblast markers and calcium deposits in human BM-MSC and were biocompatible with human bone cells and gingival fibroblasts cells.

These results suggest that the PCL-G membranes with 1 wt.% of ZnO-NPs are high-potential candidates for BTR treatments, as they were the most effective in terms of better antibacterial effectiveness at biocompatible NPs-concentration while creating a favorable cellular microenvironment for bone growth.

9:00 AM SB05.05.02

Nano-Biofabrication Approaches Towards Human Eardrum Reconstruction Shivesh Anand[1], Cemre Günday[2], Nazende Günday Türeli[2], Thomas Stoppe[3], Marcus Neudert[3], Serena Danti[4], Lorenzo Moroni[1] and Carlos Mota[1]; [1]Maastricht University, Netherlands; [2]MyBiotech GmbH, Germany; [3]Technische Universität Dresden, Germany; [4]University of Pisa, Italy

Introduction: The human eardrum or tympanic membrane (TM), is a thin, conical tissue of the middle ear that captures sound waves and transforms them into mechanical motion. Successful transmission of these nano-vibrations to the inner ear is attributed to its precise three-dimensional (3D) design [1]. In this work, we investigated the integration of tissue engineering with different nanotechnologies for an accurate modelling and reconstruction of the human TM. Hierarchical scaffolds were biofabricated in this regard, and validated based on their mechanical, acoustical, and biological response [2]. Subsequently, antibiotic-loaded nanoparticles along with anti-inflammatory nanofillers were incorporated to prevent infections or immune reaction post implantation [3, 4].

Methods: A Python script was developed for modelling the anatomical architecture of the human eardrum. Computational simulations were performed on COMSOL Multiphysics to identify dominant structural attributes within the generated TM models. The selected geometries were fabricated using a combination of poly(ethylene oxide terephthalate)/poly(butylene terephthalate) (PEOT/PBT) with chitin nanofibrils (CN). A hybrid biofabrication approach combining electrospinning and additive manufacturing was implemented in this regard. 3D patterns with varying radial and circumferential arrangements were deposited on the nanofibrous electrospun membranes to replicate the collagen fibrils of the native tissue. A co-electrospinning setup was introduced for the incorporation of ciprofloxacin-loaded poly(lactic-co-glycolic acid) (PLGA) nanoparticles within these eardrum scaffolds. The mechano-acoustical response of the fabricated constructs was evaluated by applying the techniques of macroscopic indentation and laser Doppler vibrometry. Finally, human mesenchymal stromal cells (hMSCs) were cultured to assess their differentiation towards TM fibroblasts.

Results: Biomimetic eardrum scaffolds were fabricated using PEOT/PBT/CN nanocomposites. A three-fold reduction in the diameter of electrospun nanofibers was obtained upon the introduction of CN within the polymeric matrix. The co-electrospinning setup was successful in depositing and adhering PLGA nanoparticles onto the nanofibrous membranes. *In silico* investigation of the chosen TM models suggested a geometrical dependency of their mechanical and acoustical responses, which was further corroborated by the experimental measurements. In general, radially aligned constructs were noted to show a more comparable mechano-acoustical behavior with respect to the native tissue. *In vitro* studies performed with hMSCs revealed a favorable influence of 3D hierarchy on cellular alignment and extracellular collagen production. Moreover, a pronounced downregulation of pro-inflammatory cytokines was achieved with the inclusion of CN. Lastly, the ciprofloxacin-loaded TM scaffolds demonstrated the desired biocompatibility and drug release kinetics.

Conclusions and Outlook: The optimized nano-biofabrication strategies allowed the creation of biomimetic constructs within the anatomical dimensions of native eardrum. The addition of CN as a nanofiller within the PEOT/PBT matrix produced significant improvements in their mechanical and immunomodulatory capabilities. Besides, a tunable release of ciprofloxacin was achieved from the fabricated scaffolds. Finally, advanced 3D bioreactor platforms are currently under investigation to differentiate the cultured hMSCs toward TM-specific cells.

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SESSION SB05.06: Probing the NanoBio Interface
Session Chairs: Gemma-Louise Davies and Gareth Williams
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2016

9:15 AM SB05.06.02

Micro-Injection of Amphiphilic Nanoparticles into a Droplet Interface Bilayer Reveals Particle-Induced Reductions in Membrane Capacitance
Farzin Mashali, Colin Basham and Stephen A. Sarles; The University of Tennessee, Knoxville, United States

With their ability to passively enter cells, amphiphilic gold nanoparticles (AmNPs) functionalized with a striped pattern of hydrophilic sulfonate and hydrophobic octanethiol ligands show promise for enhanced drug delivery. However, the specific mechanisms of their passage through cellular membranes remain unclear, in part due to a lack of appropriate experimental tools. Ongoing work in the Sarles group at UTK seeks to reveal these interactions by leveraging the droplet interface bilayer (DIB) technique for model membrane formation and electrophysiological characterization. The advantages of the DIB method for assembling a lipid bilayer include the ability to independently control droplet and lipid leaflet compositions and membrane area. The DIB technique also permits the use of electrophysiology measurements to monitor changes in bilayer structure and transport properties, both of which may aid in the disclosure of NP-membrane interactions.
Herein, we utilize micro-injection to incorporate AmNPs into one droplet of a droplet interface bilayer *after* bilayer formation occurs and use electrophysiological measurements as well as brightfield imaging to assess NP-induced changes in bilayer properties. Post-bilayer-formation direct micro-injection of NPs allows for maintaining stable membranes needed to study NP-membrane interactions and permits before-and-after comparisons to be made on the same membrane. In this study, DPhPC model membranes are formed between 300 nL droplets in hexadecane. A pulled micropipette connected to a pneumatic injector is used to inject AmNPs without disrupting the membrane. Before injecting AmNPs, the electrical resistance and capacitance of the membrane are electrically tested using wire-type electrodes to establish baseline bilayer characteristics and, thereby, quantify NP-induced changes to the membrane after injection. This procedure reveals that AmNPs with 15 mol% OT ligands decrease the area-normalized capacitance of the bilayer by up to 20%, where the amount of reduction depends on the final AmNP concentration. When combined with other electrical measurements, this trend indicates that AmNPs spontaneously embed into the hydrophobic center of the bilayer, increasing its average thickness and reducing its capacitance per unit area. In contrast, no discernible changes in the bilayer's specific capacitance were observed after adding hydrophilic NPs lacking hydrophobic ligands. This implies that the hydrophobic ligands are responsible for the insertion of AmNPs into the bilayer. Moreover, AmNPs with 30 mol% hydrophobic ligands showed larger decreases in specific capacitance that occurred at a lower AmNP concentration) compared to 15 mol% OT AmNPs. Finally, we observed that AmNPs lowered the membrane resistance, resulting in increases in average ion current through the bilayer under an applied voltage. These changes also coincided with transient, discrete current spikes with durations of 3 and 12 ms. Unlike many works which leveraged qualitative experimental measures, our findings demonstrate how direct microinjection and electrophysiology measurements that specifically incorporate capacitance monitoring can be used to study NP-membrane interactions.

9:30 AM SB05.06.03
The Role of Fluid Dynamics and Particle Physicochemical Properties in Characterizing the Nano-Cellular Interface Within a Multi-Cellular *In Vitro* Model Kristen Krupa, Maggie Jewett, Hayley Jesse and Audrey Brackenridge; University of Dayton, United States

Due to their unique physicochemical properties nanomaterial (NM)-based technologies are growing exponentially in scope and economic importance. Additionally, due to their electric and antibacterial attributes silver NMs (AgNMs) are integrated into electronic, sensing, and consumer applications. This surge has resulted in significant degrees of NM waste and increased rates of human exposure. This has created a vital need to fully understand the potential biological consequences of NM exposure, characterize resulting NM-biological interfaces, and determine subsequent toxicological effects. NM safety assessments are currently being carried out in both cell-based in vitro and animal-based in vivo models, with limited correlation between the two models due to the fact that NM behavior is dependent upon environmental and exposure factors. Therefore, there exists a need for the development of an enhanced cellular model that preserves the advantages of in vitro systems while incorporating in vivo influences to produce an efficient, realistic, and relevant means for NM exposure and evaluation.

As such, the goal of this study was to design, optimize, and implement an enhanced in vitro microenvironment model to create a rapid, more realistic mechanism to evaluate the safety and nano-cellular interface of experimental NM constructs. Using perfusion plates, this model was comprised of three cellular compartments, dynamic flow to represent the cardiovascular system, and a combination of tissue-based and immune cell lines. The set-up selected for this study includes 1) initial NM exposure into an alveolar model, followed by 2) transport into liver then 3) skin compartments: representing initial inhalation, movement into the liver for waste removal, and relocation to the skin. AgNMs were incorporated into for this study, which are renowned for their ability to induce stress, genetic modifications, immune activation, and cytotoxicity. Furthermore, to effectively correlate NM deposition and physicochemical properties to bioresponses, two different AgNM sizes and surface chemistries were evaluated.

The results of this work demonstrated that the nano-cellular interface varied as a function of several influences, predominantly the presence of fluid dynamics and both primary size and surface chemistry of the AgNPs. One unique aspect of this study was the development of kinetic profiles of the nano-bio interactions within each, interconnected cellular compartment. Polymer coated AgNMs proved to be more adept in traveling between cellular compartments than their citrate coated counterparts, with a more evenly distributed. Looking at the toxicological profile following AgNM exposure, the cellular immune response was substantially decreased under dynamic conditions, as assessed via pro-inflammatory cytokine secretion rate. The degree of nano-bio interactions was directly linked to observed cellular outcomes, including intracellular stress and activation of signal transduction pathways; both of which were dependent upon exposure conditions and AgNM physicochemical properties. In conclusion, the enhanced in vitro model, which successfully incorporated multiple cellular components and fluid dynamics, resulted in a modified nano-cellular interface from a static, mono-cellular control. The evaluation of kinetic deposition rates, which varied with NM surface chemistry and primary particle size, were correlated to observed nanotoxicological outcomes. This work demonstrates that by including physiologically relevant modifications, in vitro models can be an effective tool in predicting nano-bio interactions, particle fate, and safety assessments within a biological system.

9:45 AM BREAK

SESSION SB05.07: Drug Delivery
Session Chairs: Weibo Cai and Gemma-Louise Davies
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2016

10:30 AM *SB05.07.01
Futureproofing Formulations, Fast! Claire Thompson; Agility Life Sciences, United Kingdom

The vast majority of new drug candidates are "badly behaved", either poorly soluble, poorly permeable, or both. The pandemic has increased the expectation from patients and investors that we develop medicines more quickly. So, how can we accelerate timelines while also giving drug candidates the best chance of success in preclinical and clinical studies? We will discuss case studies demonstrating how nano-enabled approaches can enable you to formulate fast while also futureproofing your products.

11:00 AM SB05.07.02
Lidocaine and Cyclodextrin Complexes as a Bio-Textile Patch for Fast-Releasing Topical Administration of Lidocaine Ankit Kirtania, Asli Celebioglu and Tamer Uyar; Cornell University, United States

Bio-textiles are primarily engineered for specific biomedical end-uses like textile-based drug-delivery carriers for appropriated *in-vivo* target sites while maintaining somatic harmony. The use of nanotechnology for fabricating such bio-textiles via electrospinning gained importance because of controllable nanoscale diameters, the encapsulation amount of active agents, and overall efficacy in targeted delivery overcoming first-pass metabolism barriers. Fine-tuning such parameters positively affects the morphology interface, imparts enhanced physiochemical properties, and facilitates bio-nano-interface construction. Responsive polymeric base materials as encapsulation agents for electrospun nanofibers for active agents like medicaments are preferred for their biocompatibility and homeostasis during interaction with bio-compounds. The large surface area and highly porous structure of the nanoparticles allow easier disintegration upon subjection to proximal physiological fluids. The protein corona expedites the stable transition of the nanoparticles to the target delivery site via endocytosis or direct penetration. The amorphized state of the active agent within the nanofibrous matrix allows easier adsorption into target organs. Apart from polymeric bases, cyclodextrins are a safe choice for nanofiber matrices to confine active agents via inclusion complexation (IC) within the hydrophobic truncated cone for drug delivery systems by amorphization of the crystalline active agents and enhancing its solubility, bioavailability, and stability. Cyclodextrins are more water soluble than polymers and become a better choice as an encapsulation agent because solubilizing polymers need toxic solvents sometimes. Cyclodextrin help in the fast or slow, or controlled release of the encased active agents leading to drug delivery in a similar fashion as the polymeric nanofibers. Cyclodextrin and active agent inclusion complexes can be electrospun into nanofibers in the form of strips or onto textile substrates to form bio-textiles. In this study, Lidocaine (Lid), a crystalline and poorly water-soluble amino-amide drug, was encapsulated within Hydroxypropylated Beta Cyclodextrin (HPβCyD) nanofiber matrices to enhance its topical bioavailability and solubility. Aqueous solutions of Lid/HPβCyD-IC in different molar ratios were electrospun into nanofibrous (NFs) strips and checked for their physiochemical properties to ascertain IC formation and understand the efficacy of encapsulation and amorphization of Lid in HPβCyD nano matrix through 1H-NMR, FTIR, XRD, DSC, and TGA. The Lid/HPβCyD-IC NFs were deposited on a non-woven cotton patch to create a bio-textile patch for topical administration. The *in-vitro* release performance was examined, and the findings corroborated the fast-release corollary.

11:15 AM SB05.07.03
Structure Optimized Lipid-Based Intradermal Delivery—Needle-Free Transdermal Drug Delivery Hyunro Kim[1], Jaeyi Choi[1], Jisung Shim[2], Jaegeun Noh[3], Byeong Ju Kwon[4], Sung Uk Kuh[4], Youngdo Jeong[1], Kwanhyi Lee[1] and Hojun Kim[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Korea University School of Medicine, Korea (the Republic of); [3]Hanyang University, Korea (the Republic of); [4]Yonsei University College of Medicine, Korea (the Republic of)

Transdermal drug delivery (TDD) exhibits high drug efficacy and minimized side effects over oral administration because it bypasses first hepatic metabolism and gastrointestinal tract. However, the outermost layer of the skin, the stratum corneum (SC; composed of thousands of lipid layers), is recognized as the major barrier in TDD.
With the recent FDA approval case, Microneedle (MN) is recognized as an effective solution for TDD. MN, however, also has an issue with remaining physical damage up to the dermis, where abundant immune cells reside. Therefore, MN can cause external infection and induce the hypersensitivity that can be fatal for children.
Here we devised a needle-free TDD based on lipid as a chemical penetration enhancer. Specifically, we designed structure of lipid nanoparticles with different fusogenicity (liposome < cubosome < hexosome). With structure engineered lipid nanoparticles, Structure Optimized Lipid-based Intradermal Delivery (SOLID) patch was fabricated. Our *in vitro* test revealed that cubosome- and hexosome-SOLID patch outperforms that of liposome in SC penetration. To understand behind principle of outstanding performance, we conducted *in situ* synchrotron SAXS study and found out both cubo- and hexo-some show much faster kinetics in SC lipid layer disruption over liposome. Our study indicates that structure engineering of lipid nanoparticle can be an effective approach for the development of needle-free TDD. We believe needle-free TDD can be an effective strategy for not only drug delivery, but many other applications including mRNA intradermal vaccine to prevent pandemic.

11:30 AM SB05.07.05
Nanoneedle-Decorated Bioresorbable Vascular Scaffold (BVS) Technology Priya Vashisth, Cong Wang and Ciro Chiappini; Kings College London, United Kingdom

Numerous advances and innovative therapies have been developed for interventional cardiology over the recent years, since the first introduction of balloon angioplasty. Among these, bioresorbable vascular scaffolds (BVS) represent a breakthrough technology, heralded as potential candidates to treat atherosclerosis (a cardiovascular disease related to the build-up of hypercholesteremic plaque in the dysfunctional arteries). Compared to permanent metal stents, BVS brings the promise of complete bio-sorption after regaining the normal blood flow through arteries, restoration of natural vasomotion, and the possibility of restenting at the same site (if needed) without the interference of previous treatments. However, this breakthrough technology is facing a serious issue of late-stent-thrombosis. The underlying causes of failure of this technology could be summarized as (1) delayed endothelialization, (2) recoiling after the implantation, and (3) ineffective, and uncontrolled release of cytotoxic drug which not only stops the proliferation of vascular smooth muscle cells but also affects the normal functioning of endothelial cells.
In this study, to address these key shortcomings, we introduce a unique platform for effective drug delivery only to the lesion site, through the integration of nanoneedles (NNs) within a poly L lactic acid (PLA) BVS.
The planar surface (metal or polymeric) of stents usually result in the non-specific burst release of the cytotoxic limus drug towards the vessel wall as well as to the lumen, leading to less efficient drug delivery and disruption of normal functions/tight junctions of endothelial cells. In contrast, the NNs can penetrate the vascular tissue in a minimally invasive way and precisely target and modulate the release of drugs, thus selectively treating the atherosclerotic vessel wall and minimizing systemic dispersion. As a proof of concept, here we demonstrated the interfacing of NNs with primary human vascular smooth muscle cells (HVSMCs: the cells of interest and the primary cause of in-stent-restenosis) and the capacity of NNs to deliver the GFP-mRNA to these cells. The biocompatibility of the fabricated NNs platform has been evaluated using human vascular endothelial cells (HUVECs). Results demonstrated no significant impact on cell viability, adhesion, spreading, proliferation, and most importantly on the formation of the tight junction between the endothelial cells.
Furthermore, we evaluated the bio-interfacing of NNs with vessel wall tissue compared to the plane PLA surface to estimate the impact on recoiling. The cells are known to grab and pull on individual nanoneedles, yielding significantly enhanced adhesion which can thus enhance the apposition to the vessel wall and minimize the issue of BVS recoiling The *ex vivo* interfacing experiments, performed using porcine artery wall and analyzed using histological assessment of the interfaced tissue specified an overall effect of nanoneedles on underlying and surrounding tissue.

The developed degradable platform can be potentially used to deliver the drugs to the target site with minimal side effects and also can help to solve the recoiling issue that exists with BVS technology. With directional and respective modifications, this platform can also be used to treat other peripheral blockage conditions where we need to open up the lumen and at the same time need to deliver the drug/s efficiently to cure the condition.

SESSION SB05.08: Theranostics
Session Chairs: Gemma-Louise Davies and Claire Thompson
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2016

1:30 PM *SB05.08.01
Polymer-Based Nanoscale Theranostic Formulations Ziwei Zhang, Connor Wells, Gemma-Louise Davies and Gareth Williams; University College London, United Kingdom

Most conventional chemotherapeutics have narrow therapeutic windows, and thus their delivery remains challenging and often raises safety and efficacy concerns. Theranostic platforms, with simultaneous encapsulation of therapeutic and diagnostic agents, have been proposed as next-generation formulations which can overcome this issue. We have shown in recent studies that co-encapsulation of superparamagnetic iron oxide nanoparticles (potent magnetic resonance imaging [MRI] contrast agents) and chemotherapeutic active ingredients into nanoscale fibers and nano-microscale particles produces formulations from which drug release can be directly quantified from the MRI signal. We have generated systems appropriate for both oral and implant delivery. This presentation will summarize our recent findings in this research, exploring the effect of formulation composition and morphology on the functional performance.

2:00 PM SB05.08.02
***In Vitro* and *In Vivo* Analysis of Pancreatic Cancer Chemotherapeutics Encapsulated in Metal-Organic Frameworks (MOFs)** Francesca Melle[1,2], Jon Ostolaza[1], Sergio Mercado[1], Xu Chen[1] and David Fairen-Jimenez[1]; [1]University of Cambridge, United Kingdom; [2]AstraZeneca, United Kingdom

Pancreatic cancer is one of the most lethal and aggressive tumors with a 5-year survival rate of 5%. Due to the complex and surgically inaccessible anatomical position of the pancreas, most cases are treated using chemotherapeutics. However, these drugs have several limitations such as low targeting specificity, high instability, severe side effects from the use of high doses, inability to bypass cell membranes, and poor pharmacokinetics. One strategy to improve the efficacy of chemotherapy drugs is their encapsulation into nanoparticle systems. Among different nanoparticle systems, metal-organic frameworks (MOFs) represent a promising opportunity for the treatment of cancer. MOFs are a new class of biocompatible nanoporous materials with exceptionally high surface area (>8,000 m^2/g) and drug loading capabilities (>70% drug weight), surpassing that of alternative drug delivery systems. Their chemical flexibility allows them to host virtually any therapeutic payload, including small molecules and macromolecules, and to be functionalized with different surface molecules (e.g., PEG), offering a platform with the potential to ultimately become a universal "plug-and-play" system.

In this work, the drug loading efficiency of the most common chemotherapeutic drugs for pancreatic cancer (gemcitabine, paclitaxel, and SN38) was assessed using a MOF named PCN222. PCN222 was first synthesized and characterized by DLS and SEM to confirm a size between 120-150 nm that ensures its ability to interact at a cellular level. PXRD and N_2 adsorption were used to confirm the crystallinity and the porosity of the material. The three drugs were then loaded independently into PCN222 followed by surface functionalization with PEG chains to increase both stability and biocompatibility of the drug-MOF complex. The drug loading efficiency was measured using UV-vis and HPLC while PEGylation and drug content were confirmed by ζ-potential, DLS, FT-IR, and TGA. Following the material characterization, the three drug-loaded PCN222 were tested for *in vitro* toxicity in pancreatic cancer cell lines (BxPC-3, Mia-Paca-2, and PANC-1) using live-imaging cell analysis and MTS end-point viability assays. Cell internalization was further studied using confocal microscopy. Subsequently, the most effective formulation was evaluated *in* vivo using a subcutaneous xenograft mouse model of human PDACs of BxPC-3.

The viability analysis showed that different pancreatic cancer cells tolerated high concentrations of the empty PCN222, highlighting its biocompatibility *in vitro*. The PEG coating improved the stability and the sustained drug-release capability of loaded PCN222 *in vitro*. In addition, PCN222 showed a high cell internalization efficacy in BxPC-3, Mia-PaCa2, and PANC-1 cells. The *in vivo* studies using human pancreatic cancer xenograft mouse models showed that the delivery of chemotherapeutics loaded in PCN222 led to enhanced antitumor efficacy when compared to the free drug.

PCN222 is a promising drug delivery system able to increase the efficacy and safety of current standard-of-care chemotherapeutics such as gemcitabine, paclitaxel, and SN38, paving the way toward the clinical translation of MOFs in pancreatic cancer and other hard-to-treat cancers.

2:15 PM SB05.08.03
7-Dehydrocholesterol Lipsome Nanoparticle as a Targeting Radiation-Induced Ferroptosis Radiosensitizer for Non-Small Cell Lung Cancer
Jianwen Li, Wei Yang, Shuyue Zhan and Jin Xie; University of Georgia, United States

Therapeutics that can be activated by radiation in situ to enhance the efficacy of radiotherapy are highly desirable. Herein, 7-Dehydrocholesterol (7-DHC), a biosynthetic precursor of cholesterol, is engineered in a liposome nanoparticle as a targeting delivered radiation-induced radiosensitizer (RIRS) towards non-small cell lung cancer (NSCLC). The studies show that 7-DHC can be activated and react with radiation-induced reactive oxygen species (ROS) and in turn promote lipid peroxidation, subsequently induce ferroptosis. For efficient delivery, 7-DHC is encapsulated into a liposome nanoparticle, and been tested in tumor bearing mice, results showed a significantly enhanced the efficacy of radiotherapy. After treatment, 7-DHC is converted to cholesterol, causing no detectable side effects or hypercalcemia. This new method represents a nature-inspired, safe RIRS with great potential in clinical translation.

2:30 PM SB05.08.04
Ultrasound-Triggered Piezocatalytic Cancer Therapy Using Piezoelectric Nanomaterials Quan Truong Hoang[1], Ravichandran Vasanthan[1], Thuy Giang Nguyen Cao[1], Min Soo Son[1], Hyeon Ju Kang[1], Ji Hee Kang[2], Young Tag Ko[2], Tae Il Lee[2] and Min Suk Shim[1]; [1]Incheon National University, Korea (the Republic of); [2]Gachon University, Korea (the Republic of)

Piezoelectric nanomaterials, which are capable of generating reactive oxygen species (ROS) via piezocatalytic redox reactions under mechanical stress have emerged as promising nanoplatforms for efficient cancer treatment. Herein, piezoelectric nanoparticles such as ZnO nanorods and metal sulfide nanoparticles were functionalized with poly(ethylene glycol) (PEG) and loaded with chemodrugs for ultrasound (US)-triggered combination chemo-piezocatalytic cancer therapy. The drug-loaded piezoelectric nanoparticles can efficiently induce piezoelectric polarization for the generation of ROS under US irradiation. In addition, the drug-loaded piezoelectric nanoparticles not only generated ROS under US irradiation but also improved the intracellular delivery of chemodrugs. In vivo study showed that drug-loaded piezoelectric nanoparticles effectively accumulated in the tumors and significantly suppressed the tumor growth under US irradiation without systemic toxicity. This study demonstrates the feasibility of piezoelectric nanoparticles as US-triggered piezocatalytic agents that can selectively and effectively eradicate tumors via chemo-piezocatalytic combination therapy.

2:45 PM SB05.08.05

Development of Thermo-Responsive Theranostic Mesoporous Silica Nanoparticles for Hepatocellular Carcinoma Marwa Rizk[1,2], Connor Wells[1], Gareth Williams[1] and Gemma-Louise Davies[1]; [1]University College London, United Kingdom; [2]Alexandria University, Egypt

Hepatocellular carcinoma (HCC) is commonly diagnosed in the late stages which restricts treatment options to the FDA approved drug sorafenib. However, sorafenib's low efficacy, poor solubility, and toxic side effects limit its performance to only 30% of patients. In addition, the lack of a proper diagnostic tool for either detecting the tumour in the early stages or to monitor the disease progression represents another barrier. [1-3]

This work aims to solve these problems by developing theranostic mesoporous silica nanoparticles (MSNs) that can enhance the therapeutic and diagnostic performance through combination therapy of doxorubicin.HCl and sorafenib tosylate as well as magnetic resonance imaging (MRI) contrast by loading of MRI-active gadolinium 1,4,7,10-tetraazacyclododecane-N,N',N'',N'''-tetraacetic acid (Gd^{3+}-DOTA) chelate. Therapeutic MSNs have been prepared and the effect of the pore size, internal pores' chemistry and solvent polarity (DMSO, DMF, ethanol, THF, acetone) on both drug loading and entrapment efficiency of sorafenib tosylate and doxorubicin.HCl has been studied. In term of diagnosis, MRI-active MSNs have been optimised by incorporating the MRI contrast agent (Gd^{3+}-DOTA) chelate to internal surfaces, at different locations where water gating can be exploited to provide an 'on/off' MRI signal switch for disease diagnostics. [4] In order to cap the pores, different molecular weights of UCST thermo-responsive polymers (poly(acrylamide-co-acrylonitrile)) were synthesized using reversible addition−fragmentation chain-transfer polymerization (RAFT); where design of experiment (DOE; central composite design) was applied to optimise the temperature at which the polymer will change its conformation from dehydrated to hydrated, allowing water access to the internally located paramagnetic species (turning 'on' the MRI contrast) and concurrent controlled drug release. [5,6]

Sorafenib tosylate loading capacity into MSNs has been highly affected by solvent polarity and pore size variation; where maximum drug loading was achieved upon using THF as a solvent and MSNs of narrow pore diameter of 3.5 nm. In the case of doxorubicin.HCl, the loading capacity was decreased 5 times upon scaling up, however other parameters showed no significant effect on its loading. The dual loaded optimised MSNs showed loading capacity and entrapment efficiency percentages of 29.1 % and 27.1 % for sorafenib tosylate and 17.4% and 9% for doxorubicin.HCl, respectively. MRI-active MSNs showed relaxivity values (r1) of 60.1 mM^{-1} s^{-1} at 0.47 T for internally located Gd^{3+} chelates on MSNs-Gd, compared to the commercially available Gd^{3+}-DOTA chelate (Dotarem®) of r1 3.4 mM^{-1} s^{-1} at 1 T. The molecular weight of the synthesised UCST thermo-responsive polymers (poly(acrylamide-co-acrylonitrile)) ranges between 84600- 164100 g/mol and their cloud points were characterised using dynamic light scattering (DLS) as well as turbidimetry, and found to range between 36.6–85.5 ^{o}C. As a final step, the behaviour of the optimised thermo-responsive polymer grafted onto the theranostic MSNs will be described, including studies on the efficacy and biosafety of the developed system on Hep-G2 cell lines.

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3:00 PM BREAK

3:30 PM *SB05.08.06

(Cancer) Theranostics with (Intrinsically) Radiolabeled Nanomaterials Weibo Cai; University of Wisconsin--Madison, United States

Radiolabeled nanomaterials have gained tremendous interest over the last 2 decades, which can play diverse roles in imaging, image-guided drug delivery, as well as theranostics of a number of diseases such as cancer. Some recent examples of radiolabeled materials from our recent work will be briefly described in this talk.

Although chelator-based radiolabeling techniques (commonly used for labeling nanomaterials with radiometals such as ^{64}Cu/^{89}Zr) have been used for decades, concerns about the complexity of coordination chemistry, possible alteration of nanomaterial pharmacokinetics, and potential detachment of radioisotopes have driven the need for developing a simpler yet better technique for future radiolabeling, which may facilitate future clinical translation.

The emerging area of intrinsically radiolabeled nanomaterials can take advantage of the unique physical and chemical properties of well-selected inorganic or organic nanomaterials for radiolabeling, and more importantly, offer an easier, faster, and more specific radiolabeling possibility to facilitate future clinical translation. Generally speaking, the four major categories of intrinsically radiolabeled nanomaterials include: 1) hot-plus-cold precursors, 2) specific trapping, 3) cation exchange, and 4) proton beam activation.

Representative examples of these strategies will be briefly illustrated in this talk, with the main focus on our own work that involves the radiolabeling of a variety of nanomaterials via "specific trapping". The nanomaterials investigated in our laboratory include silica/carbon-based nanomaterials, COVID-19 nano-vaccines, multifunctional/multimodal hybrid nanomaterials, iron oxide nanoparticles, micelles, DNA nanostructures, etc. **[1-10]**.

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4:00 PM SB05.08.07

Improving Surgical Treatment of Breast Cancer: Dual-Modality Nanocrystals for the Detection of Sentinel Lymph Nodes Loren Deblock[1], Benedicte Descamps[1], Glenn Vergauwen[1,2], Jens Debacker[1], Philippe Tummers[1,2], Isabel Van Driessche[1], Klaartje De Buysser[1], Jonathan De Roo[3] and Christian Vanhove[1]; [1]Ghent University, Belgium; [2]Ghent University Hospital, Belgium; [3]Universität Basel, Switzerland

Each year, more than two million women worldwide are diagnosed with breast cancer [1]. In the typical surgical treatment of this cancer the primary tumor is removed, together with the so called sentinel lymph nodes (SLNs), these are the lymph nodes that have the highest probability of being invaded by cancer cells. A combination of two methods has been established as the gold standard for the detection of SLNs. Metastable radioactive Technetium-99m (^{99m}Tc) labeled nanocolloids are either peritumoral or periareolar injected several hours before surgery and accumulate in the SLNs. A preoperative SPECT/CT is made to identify the exact anatomic location of the SLNs and during surgery, a handheld gamma counter is used as confirmation. SLN imaging is often supplemented by an intraoperative injection of a blue dye to visually guide the surgeon. Unfortunately, the current standard has several downsides; the radioactive nanocolloids have a short half-life (i.e. 6 hours), SPECT imaging has a spatial resolution in the mm-range and both the patient and the surgical team are exposed to ionizing radiation. In addition, the blue dye can only be detected at a depth of a few millimeters (increasing the risk of missing the SLN), is prone to leach from the lymphatic vessels, occasionally cause (severe) allergic reactions, and may cause a long-lasting blue stain remaining on the breast for several months. Therefore, there is a need for alternative imaging methods to identify SLNs.

As an improved alternative to the current clinical standard, we have developed dual-modality nanocrystals (NCs) for the detection of SLNs using X-ray Computed Tomography (CT) and near-inrared (NIR) fluorescence. By removing radioactivity from the equation, we could reduce overall patient radiation exposure and remove the need for high-cost SPECT scanners, and instead use more widely available and faster imaging techniques like CT or conventional radiography to identify SLNs. The second imaging modality, NIR-fluorescence, is part of the same imaging probe and as such does not suffer from undesired tissue extravasation like the currently used small molecule dyes do. To mimic the behavior of the currently used clinical nanocolloids, we synthesized high-density bio-inert nanocystals that are approximately the same size after surface functionalization (5 - 10 nm). Next, we functionalized the NCs with our recently developed catechol-derived ligands, providing colloidal stability in relevant biological buffers, such as phosphate buffered saline at concentrations up to 300 mg NCs/ml. In the following step, we further improved the surface chemistry of the NCs by synthesizing an azide-terminated catechol ligand and apply strain-promoted click chemistry to covalently link fluorophore molecules to the NCs to create a dual-modality imaging-probe. Following this, we performed an *in vivo* evaluation of the dual-modality NCs in mice, imaging the lymphatic system using CT and NIR-fluorescence. We found that the NCs drain to the SLN shortly after injection and provide high *in vivo* contrast enhancement and NIR-fluorescence. Contrast enhancement and fluorescence remain high over several hours, which could make the NCs useable for extended surgical procedures. We further confirmed our findings by performing a longitudinal statistical study between a test and control group. Finally, we directly compared the NCs in terms of lymphatic drainage, spatial resolution and image quality to ^{99m}Tc-Nanocoll, the most used radiographic compound for SLN identification in Europe, and found that the NCs show similar drainage behavior as the clinical standard while allowing for faster scan times at higher scan resolution.

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4:15 PM SB05.08.08

Engineered Multifunctional Superparamagnetic Copper Iron Oxide Nanoparticles (SCIONs) for a Combined Magnetic Hyperthermia and Immune Therapy of Metastatic Cancers Yuxin Cai and Pengyu Chen; Auburn University, United States

Metastatic cancer has remained one of the most lethal diseases worldwide for decades because of its complex pathophysiology. Given the great efforts and investment devoted, the remaining high mortality of metastatic cancer patients is certainly frustrating. Yet in recent years, cancer immunotherapy has been considered a promising cancer treatment regulating the immune system and stimulating innate immune responses to fight tumor cells. There are several strategies that achieved a certain level of clinical success. Even so, restrained by the complex tumor microenvironment, these strategies are still limited by the insufficient activation of the immune system, poor infiltration to the tumor microenvironment, and the inability to track the distribution of the anticancer ingredients. Consequently, combining treatments for metastatic cancer to enhance the infiltration to the tumor microenvironment and immune response has been paid noteworthy attention. Considering the severe side effects caused by radiotherapy or chemotherapy and the limited penetrating ability of near-infrared light, magnetic hyperthermia therapy (MHT) becomes a promising treatment to induce and promote an immunological response in the tumor microenvironment safely and effectively. Such a remote-controlled therapeutic system affords triggered release for high local effectiveness of the anticancer process with excellent tissue penetration and minimal damage to healthy tissue.

Hyperthermia is a cancer therapy raising the local tumor temperature and maintains 41 - 45 °C for a period to kill the tumor cells while sensitizing them to other treatments. For iron oxide nanoparticle-based MHT, the heat will be generated by the MNPs while an alternating magnetic field (AMF) was applied. By harnessing the unique property of superparamagnetism, the MNPs will be well-dispersed in the tumor microenvironment while avoiding the high cost and long preparation time of the regular methods for targeted drug delivery including the cell-specific ligands and pH-responsive. Additionally, the particles manipulated by a magnetic field indicate that precise targeting delivery and MHT cancer treatment can be realized at the same time.

In this study, we designed and synthesized the superparamagnetic copper iron oxide nanoparticles (SCIONs) and engineered them into a monodisperse multifunctional anti-cancer SCION complex, programmed for targeting delivery, hyperthermia therapy, and immune therapy of metastatic cancer treatments. The porous structure of our SCIONs provides multiple Cu^{2+} sites. When loading sodium diethyldithiocarbamate trihydrate (DDC-Na), the $[Cu(DDC)_2]$ complex will be self-assembled on the surface, which has been wildly proven as an effective anticancer ingredient. Compared to common combined magnetic hyperthermia and immune therapy where the high-performance-hyperthermia magnetic nanoparticles and the programmed checkpoint blockade therapy ingredients were treated to the tumor environment separately, each SCION complex is a multifunctional tumor cell treatment.

In the pre-clinical study of 4T1 tumors (murine breast cancer cells) on BALB/c mice, the MHT and anti-cancer immune therapy collaborate simultaneously. The inherent mechanism and the process of the anti-cancer effect are proposed following. Firstly, the SCION complex generates a considerable amount of local heat to eliminate tumor cells when AMF is applied. Meanwhile, the anti-cancer ingredients will continuously function in the tumor microenvironment inducing tumor cell death and apoptosis. Then, combined MHT and $[Cu(DDC)_2]$ complex treatment ablation of tumor cells could generate tumor-associated antigens, The antigens were uptaken by dendritic cells (DCs), which would lead to the activation of immunological cell death (ICD). Furtherly, the anti-cancer ingredients loaded on the surface of the SCION complex keep functioning to inhibit epithelial-mesenchymal transition

(EMT) to prevent cancer metastasis from happening.

4:30 PM SB05.08.09

Mxene Nanocomposites Based 3D Printed Scaffold Sensors for Cancer Metastases Study Danling Wang, Mahek Sadip and Kalpana Katti; North Dakota State University, United States

Breast cancer (BrCa) is the most common cancer worldwide and approximately 70% BrCa patients eventually develop bone metastasis. 80-90% of breast cancer (BrCa) patients die because of the skeletal complications due to the bone metastases. Therefore, the presence of bone metastases plays an important role in cancer patient's prognosis, quality of life, and the planning of the treatment. To better understand cancer metastases, it is critical to find an effective method of detecting the status of bone metastases and investigating the dynamics of breast cancer metastasis to bone in a timely and cost-effective manner. Current techniques including imaging techniques such as CT, MRI, particular skeletal scintigraphy, have been developed and used as an initial work-up for the detection and management of bone metastases from breast carcinoma. These techniques are accurate but cause concerns about high dose of radiation exposure, comprehensive operation, and expensive cost. The development of 3D models for cancer metastasis using scaffolds provide a way to recapitulate native microenvironment for the metastasis to bone. However, imaging techniques and 3D models using scaffolds both can not real-time capture and evaluate the circulating process of cancer cells to cancer tumor at the bone site.

This presentation focuses on developing a new MXene based 3D printed scaffold sensors to 1) real-time capture and evaluate the circulating process of cancer cells to cancer tumor at the bone site; 2) control tumor formation; and 3) find solutions of improving new drug response and delay metastases. We will take a two-pronged approach: (1) the 3D bone mimetic scaffold seeded with cancer cells, placed in a bioreactor to mimic physiological flow conditions, with embedded sensors for real-time monitoring will capture the chemical and biological signals during tumor formation, (2) keeping the same conditions as in the previous approach, anti-cancer treatments will be introduced in the bioreactor, and real-time monitored as the treatment inhibits tumor formation. These experiments, along with characterization techniques such as gene and protein expressions, and imaging will supplement the sensor data to develop the roadmap of tumor formation and assist in developing the design rules. This work will be to initialize a new research area of developing new functionalized sensing techniques that can sense the impact on osteogenesis of bone in tumor proximity and monitor new drug response to limit tumor formation and cancer metastases. In particular, this work will expect to design multifunctional 3D scaffolds as novel biomaterials with sensing capability and tissue-engineering performances.

4:45 PM SB05.08.10

Virus Like Shape Nanoparticles for Tuberculous Meningitis Treatment Alessandra Pinna[1,2], Ieva Ragaisyte[1], William Morton[1], Maddalena Cerrone[2], Alize' Proust[2], Rocco D'Antuono[2], Katalin Wilkinson[2], Jakson Luk[2], Robert J. Wilkinson[2,1,3] and Alexandra Porter[1]; [1]Imperial College, United Kingdom; [2]Francis Crick Institute, United Kingdom; [3]University of Cape Town, South Africa

INTRODUCTION

Tuberculous meningitis (TBM) is the most severe form of tuberculosis infection with very high mortality and accounts for 2-5% of all tuberculosis cases among children and HIV-positive adults, causing permanent neurological consequences and disability.[1]

TBM arises from mycobacterium tuberculosis (*M.tb)* release into the brain, which triggers an inflammatory cascade. TBM treatment is currently based on the treatment of pulmonary tuberculosis with combinations of antibiotics including first-line antibiotics drugs, such as rifampicin (RIF). Therapy using these drugs has poor outcomes because suboptimal drug levels reach the brain due to poor blood brain barrier (BBB) penetration. There is an urgent clinical need for alternative vehicles to deliver antibiotics and anti-inflammatory drugs inside the brain to treat TBM locally. In this work a biodegradable and monodisperse mesoporous silica nanostars (MSNS) have been proposed as a carrier of RIF (antibiotic) and cerium oxide nanoparticles (nanoceria, anti-inflammatory) with the aim of using the system to treat TBM.

EXPERIMENTAL METHODS

MSNS were synthesized using a sol gel single-micelle epitaxial growth approach[2]. In a typical synthesis CTAB is used as mesoporous template, NaOH as catalyst, n-hexane as co-solvent and TEOS as silica source. Temperature, aging time and stirring rate effects on MSNS diameter and spike length were investigated. The drugs, RIF and nanoceria, were encapsulated into MSNS using a passive diffusion method and post-synthetic impregnation respectively. The MSNS physicochemical properties were determined by using transmission electron microscopy (TEM), dynamic light scattering (DLS), Brunner-Emmett-Teller (BET) analysis and X ray diffraction spectroscopy (XRD). Encapsulation of RIF and cerium oxide were confirmed using high performance liquid chromatography (HPLC) and inductively coupled plasma mass spectrometry (ICP-MS).

The toxicity and immunogenicity of MSNSs were evaluated in PBMC, astrocyte, pericyte and microglia cells by MTS and Luminex assays. An *in vitro* BBB model was used to assess the BBB permeability to MSNS in comparison to spherical mesoporous nanoparticles (MSNP).

RESULTS AND DISCUSSION

The synthetic approach used in the present work to produce virus like shape nanoparticles allows to tune the size and the spike length of MSNS. Two types of nanoparticles, MSNS-1 with size of 83 ± 9 nm (spike length: 9 ± 2nm) and MSNS-2 72 ± 11 nm (Spike length:18 ±4 nm) were chosen for further experiemnts. XRD analysis reveals their amorphous structure while the BET demonstrates a high surface area of ~200 m^2/g which allows a high drugs encapsulation. RIF was successfully incorporated in both type of MSNS at concentration of 70 mg/300mg MSNS-1 and 220mg/300mg of MSNS-2. Furthermore, XRD and ICP-MS analysis show the successful incorporation of nanoceria into MSNS. MSNS Cellular toxicity was measured and the 1 µg/ml of MSNS was set do not induce any cellular toxicity and any immunogenic effect in PBMC cells and in the four types of cells that make up the BBB (astrocytes, pericytes, endothelial cells, and microglia). Moreover, the capability of MSNS to cross the BBB was assessed in a unique 3D *in vitro* model showing MSNS better crossing the BBB respect to the spherical MSNP.

CONCLUSION

The present work shows we can tune the size and the morphology of MSNS, RIF and nanoceria drugs were successfully incorporated into MSNS without producing any modification in the silica structure. MSNS tdid not induce any cellular toxicity and immunogenic effect and are able to better cross the BBB respect to the spherical counterpart. The preliminary results pave the way to a new therapy for TBM.

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SESSION SB05.09: Poster Session II: NanoBio Interactions II
Session Chairs: Gemma-Louise Davies and Sarah Stoll
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SB05.09.01

Functionalized Carbon Nanotubes for the Electrochemical Quantification of Renin as a Marker of Tissue-Perfusion Ariadna Schuck, Hyo Eun Kim and Yong-Sang Kim; Sungkyunkwan University, Korea (the Republic of)

Renin is an enzyme with the function to produce angiotensin I in plasma triggering a cascade of reactions that regulate blood pressure homeostasis. It is a useful marker of tissue perfusion plasma renin activity (PRA), but it was not well exploited in terms of electroactivity in human blood while evaluating the renin-angiotensin-aldosterone system. To quantify the renin levels in human plasma samples, a novel screen-printed carbon electrode (SPCE) sensor modified with doped multi-walled carbon nanotubes (MWCNTs) and polyethylene glycol (PEG) is proposed and experimentally demonstrated. PEG is a biopolymer commonly used to coat the surface of nanostructures to reduce nonspecific interactions and minimize aggregation promoting colloidal stability. The functionalized MWCNTs were first evaluated with Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) images. The structural analysis proved that there were no further effects on the size and shape of the carbon nanostructures. The doping was confirmed with the three-electrode cyclic voltammetry (CV) technique where the peak currents were amplified by almost 6.5× after the functionalization step. Afterward, the Human Renin Antibody Pair is immobilized on the nanocomposite film for 1 hour before the performance of the electrochemical measurements with the samples containing the enzyme. Differential pulse voltammetry (DPV) measurements were performed to quantify the Renin (0 ~ 2,000 pg/mL) in human plasma samples (<20 µl) that are injected into the device. The variation of the current peaks presented high linearity (linear regression coefficient (R^2) of 0.9890) with the levels of renin enzyme. The validation was obtained while comparing the results of the SPCE device with the gold standard method, Enzyme-Linked Immunosorbent Assay (ELISA), using the Bland–Altman plot with a good agreement between the two methods within a 95% confidence interval. Further studies involve the combination with the other inflammation-related markers already evaluated with our multiplexed electrochemical sensing device.

5:00 PM SB05.09.02

Nanoplasmonic Immunoassay Based Integrated Microfluidic Device for *In Situ* PD-L1-Exosome Mediated Cell Communication Visualization and Analysis Chuanyu Wang, Chung-Hui Huang and Pengyu Chen; Auburn university, United States

Cellular communication is an essential process to maintain cellular bio-function. Communication between cancer cells and immune cells has been investigated for decades. One of immune checkpoint cancer therapies is developed after fully understanding the communication between programmed death ligand 1 (PD-L1) from cancer cells and programmed death 1 (PD-1) on T cells. Cancer cells can remotely deactivate T cells by secreting soluble PD-L1 proteins and secreting extracellular vesicles (EVs) with exosomal PD-L1. Commercial immunoassays, such as enzyme-linked immunosorbent assay (ELISA), have been utilized to measure concentrations of PD-L1, IL-2, and IFN-γ for the demonstration of cellular interaction between cancer cells and T cells. However, commercial immunoassays cannot detect a diffusion path of proteins. A diffusion map of proteins is also significant information to understand how cells secrete proteins. Here, a specially designed on-chip device consists of cell isolation chambers and a gold nanosphere-based nanoplasmonic digital immunoassay, rendering *in situ* remote cell communication to visualize a diffusion map and quantify a concentration of proteins. A machine-learning-based image process method was utilized to generate a signal map translating a PD-L1- exosome-mediated communication between breast cancer cells and T cells. This developed platform provides new methods for visualizing cell-cell remote communication that has high potential as a characterization method for monitoring cellular progression.

5:00 PM SB05.09.03

Fluorogenic Immuno-Sensor Using Inverse Opal Hydrogel with Target Specific Aptamer Modification Jaewook Lim, Hyo Lee and Seungjoo Haam; Yonsei University, Korea (the Republic of)

Over 10million people have disabilities due to nervous system disorders. Alzheimer's, a representative degenerative brain disease, is characterized by irreversible cognitive dysfunction and occurs when amyloid plaque accumulates even before symptoms occur. Therefore, it is more important to prevent it through early diagnosis than to treat the disease. One of the early diagnosis system is Liquid biopsy that diagnoses using blood, urine, spinal fluid, etc. The aqueous humor is body fluid which fills the space between the lens and the cornea of the eye. The aqueous humor contains biomolecules come from central nervous system. Diagnosis platform using aqueous humor can be a promising platform for early diagnosis of neurodegenerative diseases.

Here, we made fluorescence aptamer conjugated inverse opal hydrogel lens (FAIOL). Intraocular lens are implanted for vision correction or cataract surgery at eye chamber which is filled with aqueous humor. FAIOL is aptamer conjugated intraocular lens system. When the biomarker approaches at FAIOL, quencher modified aptamer combines biomarkers and dissociates from fluorescence modified complimentary DNA. To raise specificity of FAIOL, AFIOL is made by MMA (methyl methacrylate) which is well known hydrophobic monomer. And for sensitivity of FAIOL, we applied inverse opal system that makes fluorescence signal amplification by photonic band gap. FAIOL can be a target independent sensor such as protein sensor by, DNA sensor, or RNA sensor. Early diagnosis of various neurological diseases will be possible through FAIOL

5:00 PM SB05.09.05

Acoustic Anti-Cancer Therapy Using Nanoparticles Yong-Gyu Jeong[1], Hyo-Soo Lee[2] and Dongwoo Khang[1,1,1]; [1]Gachon University, Korea (the Republic of); [2]Korea Institute of Industrial Technology, Korea (the Republic of)

Sonodynamic (SDT) has the advantage of localized anti-cancer treatment on the targeted tumor region and, can minimize the side effects for normal tissues. SDT is usually operated by ultrasound of 20 kHz or higher frequencies. However, biomedical research on audible soundwaves below 20kHz to control SDT were vailed. Herein, we report audible soundwaves that triggering the aggregation of the nanoparticles and, the aggregation behavior of the nanoparticles subsequently influenced the intracellular autophagy formation. Thus, the amplified autophagy by audible soundwave responsive nanodrug effectively increased apoptosis in cancer cells. In conclusion, obtained result clearly demonstrated the anti-cancer therapy using sub-audible ranges of frequency and suggested novel strategy for the treatment of anti-cancer therapy with noninvasive manner.

5:00 PM SB05.09.06

Cellular Uptake and Cytotoxicity of Varying Aspect Ratios of Gold Nanorods in HeLa Cells Yolanda Vasquez, Deshani Fernando and Shoukath Sulthana; Oklahoma State University, United States

Gold nanorods (GNRs) have received broad attention due to their tunable surface plasmon modes, which make them attractive candidates for applications in drug and gene delivery, biological imaging, and cancer treatments. In this study, we highlight the interactions of four different aspect ratios (ARs), 2.6, 3.2, 5.4 and 11.5, of GNRs with HeLa cells. Specifically, we study the uptake of the particles by HeLa cells while also considering the effects of other parameters such as the surface stabilizer, supernatant, and serum proteins present in the medium. From this work, it was determined that the cell viability depended on the chemical composition of the supernatant especially the amount of excess surfactant, hexadecyltrimethylammonium bromide (CTAB), used for the synthesis of GNRs; thus, the effect of aspect ratio of GNRs on endocytosis could not be directly discerned. For example, when exposed to GNRs of aspect ratio 11.5, HeLa cells showed higher cellular uptake compared to smaller aspect ratios, and also exhibited lower cytotoxicity due to the lower concentration of CTAB used in their synthesis. Gentler purification methods (sedimentation) appeared to be a factor in lowering the free CTAB concentration for experiments containing GNRs of aspect ratio 11.5. Overall, the synthesis protocols functionalization, purification processes, and the stability of GNRs in media have an effect on cellular uptake and viability. Our results suggest that the AR of GNRs may a role in endocytosis when mPEG, instead of CTAB, is used as a stabilizing ligand although an overall trend could not be unequivocally established. In future studies, sedimentation, contact time, and internalization kinetics need to be probed further using more biocompatible ligands and less inert ligands (mPEG) to determine the effect of AR on GNR internalization in HeLa cells.

5:00 PM SB05.09.07
Educational Stemsome Targeting and Destroying Pancreatic Tumor Jun-Young Park, Jun Young Park and Dongwoo Khang; Gachon University, Korea (the Republic of)

Currently, the survival rate of pancreatic tumors has not been improved despite development of therapeutic agents for other tumors, such as breast cancer, liver cancer, lung cancer, and stomach cancer. This is because ligand-antibody binding strategies cannot be applied for pancreatic tumors, and thus, targeting pancreatic cancer is not available yet. Due to the unique ability of stem cells for targeting the specific tumor environment, stem cell membranes (stemsome) with nano-encapsulated mediators can target tumor and can load active anticancer agents. In this study, a specific cancer targeting strategy for stemsomes prepared by extracting ectosomes from stem cells with improved pancreatic cancer targeting ability was demonstrated. Stem cell membranes with enhanced targeting ability to pancreatic tumor cells were encapsulated with doxorubicin-loaded PLGA nanoparticles, successfully targeted and reduced pancreatic deep tumor tissue. Considering that there are no known target proteins in pancreatic tumor cells, the proposed platform technology can utilize for targeting various malignant tumor possessing unknown surface target receptors on cancer cell membranes.

5:00 PM SB05.09.08
Tumor-Activatable Tissue-Adhesive Chitosan Nanodepots for Site-Directed Treatment of Cancer Yu Ri Jeon[1], Mou Seung Kim[1] and Yun Kee Jo[1,2]; [1]Department of Biomedical Convergence, School of Convergence, Kyungpook National University, Korea (the Republic of); [2]Cell and Matrix Research Institute, Kyungpook National University, Korea (the Republic of)

Even though chemotherapy is most commonly applied to treat cancer, the insufficient locoregional retention and systemic toxicity has remained to be solved. Naturally derived chitosan is a promising biomedical material due to its biocompatibility. However, pH and concentration-dependent solubility of chitosan has been restricted further applications to clinical settings. Here, we propose chitosan-based nanodepots containing Fe(III)-catechol complexes (Cat-CS NPs) as a tumor-activatable therapeutics delivery system to accomplish highly site-directed administration while minimizing adverse effects towards surrounding normal tissues, inspired by intriguing adhesion mechanism of marine mussels. The Cat-CS NPs fabricated through electrospray exhibited Spherical uniform size nanoparticles. Furthermore, they indicate improved adhesiveness on glass and porcine skin tissue model in aqueous conditions. The pH-dependent stoichiometry of Fe(III)-catechol coordination in the doxorubicin-loaded Cat-CS NPs (Cat-CS@DOX NPs) allows the triggered release of DOX in response to the acidic conditions around the tumor tissues. The Cat-CS@DOX NPs showed a significant inhibition of growth of cancer cell *in vitro* while exhibiting a good biocompatibility towards normal cells. In addition, they demonstrated superior adhesion ability to tissue substrates after local spray process *in vitro* and *in vivo*. Taken together, our polysaccharide-based sticky nanoparticles can be applied to open new avenues as a topical delivery system to adjuvant cancer therapy.

5:00 PM SB05.09.09
mRNA Encapsulated Ectosome-Liposome Hybrid for Anticancer Therapy Su Hyun Lim, Geunhye Kim and Dongwoo Khang; Gachon University, Korea (the Republic of)

Recently, artificial liposomes were developed as an effective carrier for the COVID-19 vaccine. However, liposomes are not sufficient to use for the treatment of diverse diseases due to the absence of the ability for targeting pathophysiological sites. In this regard, ectosomes, a type of nano vesicles composed of cell membrane can be endowed with target ability, is a promising drug delivery vector. In this study, macrophage derived ectosome shows greater cancer targeting efficacy. Macrophages can migrate to the cancer cells and additionally can release pro-inflammatory cytokines, such as TNF-a, IL-1b, and IL-6. Macrophage-derived ectosomes fused with liposomes, hybrid nano formation (ecto-liposome), enhanced the anticancer efficacy of delivery to malignant tumor tissues. Specifically, a mRNA, regulating signaling pathways involved in cancer, was encapsulated in ecto-liposome inhibited cancer cell growth and suppressed chance of metastasis. Obtained results in this study clearly suggested that the mRNA encapsulated ecto-liposome is highly effective and thus, represents a novel strategy for the treatment of anti-cancer therapy.

5:00 PM SB05.09.10
Mitochondria-Targetable Lysine-Based Biodegradable Nanogels Through Hydrophobic-Hydrophilic Conversion Hana Cho and Han Chang Kang; The Catholic University of Korea, Korea (the Republic of)

For several decades, to maximize the therapeutic efficacy of drugs, various drug delivery systems that target various cells or subcellular organelles (e.g., nucleus, mitochondria, lysosomes, endoplasmic reticulum, Golgi apparatus, etc.) have been developed. However, most targeted drug delivery systems use methods to directly conjugate the targeting moiety to the drug or to decorate the nanoparticle surface.

In this study, an ε-poly($_L$-lysine)-based mitochondrial targeted drug delivery system (i.e., REPL-NG) was developed by introducing hydrophobic and biodegradable disulfide bonds into a hydrophilic polymer without a mitochondrial targeting moiety. REPL exists in the form of nanogels in aqueous solution due to hydrophilic primary amines on the surface and hydrophobic disulfide bonds inside the core. Thus, hydrophobic drugs such as doxorubicin could be encapsulated into REPL-NG (i.e., DOX@REPL-NG) by hydrophobic interactions.

In HCT116 cell line, a human colorectal cancer cell line, DOX@REPL-NG was internalized by endocytosis and was able to escape the endo/lysosomes by the proton-buffering effect of the primary amine of REPL-NG. After internalization, DOX@REPL-NG favored mitochondria over the nucleus, and as a result, a greater amount of DOX was uptaken into mitochondria rather than the nucleus. In addition, in HCT116-xenografted nude mice, DOX@REPL-NG exhibited superior antitumor effect than free DOX-HCl by tumor accumulation and retention of DOX. In conclusion, DOX@REPL-NG could target mitochondria by modulating the hydrophobicity of lysine-based polymers without commonly used mitochondrial targeting moiety.

5:00 PM SB05.09.11
Advanced Delivery of Therapeutics Using Metal-Organic Frameworks (MOFs) in 3D *In Vitro* Respiratory and Cancer Cell Models Sergio Mercado, Francesca Melle, Jon Ostolaza and David Fairen-Jimenez; University of Cambridge, United Kingdom

Therapeutics used in the treatment of various types of cancer and respiratory diseases present significant drawbacks such as limited efficacy and severe off-target toxicity. These issues hinder their success and support the current need to develop enhanced formulations to improve the prognosis of patients.

Metal-organic frameworks (MOFs) have attracted much attention for biomedical applications since they can encapsulate and thus enhance the safety and efficacy of therapeutics. MOFs are a class of biocompatible nanoporous materials with exceptionally high surface area (>8,000 m^2/g) and drug loading capabilities (>70% drug weight).

In this work, molecular simulations were performed to find a MOF structure with a porosity compatible with different chemotherapeutics. PCN-222, a zirconium-based MOF with mesopore size (> 2 nm), was selected due to its high porosity and biocompatibility. Chemotherapeutics used to treat breast and lung cancer (fulvestrant and temozolomide, respectively) were then loaded into PCN-222. Subsequently, a PEG coating was applied to drug-loaded PCN-222 to improve stability and slow-release profile. The resulting PEGylated drug-loaded MOFs were characterized for drug loading capacity and physiochemical properties, including size, aqueous stability, crystalline structure, and porosity. Drug loaded-PCN-222 was tested using *in vitro* models of breast and lung cancer (MCF7 and A549 cells, respectively). The effects of this nanomaterial's characteristics (including size, composition, and surface characteristics) on toxicity were assessed by metabolic activity. Live-cell imaging and confocal microscopy were used to analyze internalization and cellular interactions of PCN-222.

PCN-222 characterization showed nanoparticles of 120-150 nm in a homogenous dispersion. Drug loading of fulvestrant and temozolomide into PCN-222 was successful for both chemotherapeutics, achieving a loading efficiency of more than 30%. The effect of this nanomaterial on cell toxicity was assessed by a metabolic activity assay and live cell imaging, showing that breast and lung cancer cells tolerated high concentrations of PCN-222. These results highlight the biocompatibility of PCN-222. The PEG coating improved intracellular stability and delayed drug-release capability. PCN-222 showed a high cell internalization efficacy in MCF7 and A549 cells, as seen by confocal microscopy.

PCN-222 showed biocompatibility, high loading capabilities, delayed drug-release, and efficacious cell internalization. Further works using *in vivo* mouse models are expected to confirm the previous *in vitro* data. Finally, PCN-222 is a promising nanocarrier able to increase the efficacy and safety of current standard-of-care chemotherapeutics and facilitate the progress of nanomaterials for medical applications.

5:00 PM SB05.09.12
Nano-Corona Anticancer Strategy Jun Young Park[1] and Dongwoo Khang[1,2,3]; [1]Gachon university, Korea (the Republic of); [2]Lee Gil Ya Cancer and Diabetes Institute, Korea (the Democratic People's Republic of); [3]gachon, Korea (the Republic of)

Nano-corona is induced by the interaction of nanoparticles with plasma proteins. Although the immune toxicity aroused by nano-corona has been intensively studied for the past decade, there were no reports on immunotherapy using nano-corona. It is widely believed that nano-corona invoke intrinsic and adaptive immune responses by conformation changes in the protein structures. In this study, the anti-cancer efficacy of nano-corona was analyzed in the tumor microenvironment in which the immune response was suppressed by cancer cells. Surprisingly, nano-corona significantly induced M1 differentiation from the M2 phenotype in the tumor microenvironment with a stimulated innate immune response. In addition, to examine the removal of the tumor tissue, combination therapies using nano-corona, photothermal therapy, and anti-cancer immune-therapy was conducted. Combinational therapies inhibited the growth of tumor tissues. Activation of NK cells and cytotoxic T cells that directly destroyed tumor cells and importantly, T_{reg} cells are reduced at the tumor microenvironment. Obtaimed results represent that the anti-tumor immune response enhanced by nanocorona. Importantly, the study suggested evidence that controlling of immune responses using nano-corona significantly influences the efficacy of anti-cancer therapy by switching immune regulation at the tumor environment.

5:00 PM SB05.09.13
Stabilization of a Synthetic Protein Nanoparticle by a Polycation for Gene Delivery Fjorela Xhyliu; University of Michigan, United States

Nanoparticles (NPs) have attracted significant attention in the field of gene therapy in recent years. Despite the many advances in NP-mediated non-viral gene delivery, the stability of the NPs, successful internalization of nucleic acids, and efficacy in delivery and transfection in cells remains an obstacle to their clinical translation. This work explores the surface-stabilization of a synthetic protein nanoparticle (PNP) with a polycation for improved NP stability and pDNA transfection *in vitro* and *in vivo*. Utilizing electrohydrodynamic (EHD) jetting, PNPs were used to encapsulate a large plasmid followed by stabilization by a polycation. The stabilization of the PNP in solution is enabled by the electrostatic interactions between the polycation and the protein. Electron microscopy, dynamic light scattering (DLS), and nanoparticle tracking analysis (NTA) confirm that the surface-stabilized PNPs (ssPNPs) have sub 200 nm diameters in their dry and hydrodynamic states. Additionally, it was determined that the ssPNP size and positive charge are stable in aqueous conditions for extended periods of time, without the addition of stabilizing agents. Utilizing NTA and UV-vis absorbance data, a method was established to determine the DNA amount per ssPNP, indicating an overall yield of 75-80%. In human HepG2 cells, more than 90% of cells take up the ssPNPs, partly due to the positive surface charge. Moreover, transfection of ca. 50% can be achieved while varying the amount of DNA and NP dosing, with negligible cytotoxicity. In a mouse glioblastoma model, ssPNPs demonstrated transfection effectiveness higher than JetPEI®, a commercially used product. This platform shows that using a polycation as a surface stabilizer allows for successful pDNA internalization, NP stability, and transfection efficacy. These findings demonstrate the capability of this new gene delivery system to overcome challenges that hinder the clinical translation of NPs, with the potential for the treatment of various cancers and diseases.

5:00 PM SB05.09.14
Mesenchymal Stem Cell Conjugated with Triamcinolone Loaded Gold Nanoparticles Attenuates Rheumatoid Arthritis Minjun Shin[1], Jun-Young Park[2], Youn Joo Kang[3] and Dongwoo Khang[1,2,1]; [1]Gachon University, Korea (the Republic of); [2]Lee Gil Ya Cancer and Diabetes Institute, Korea (the Republic of); [3]Eulji Hospital, Korea (the Republic of)

Unfortunately, conventional therapy for rheumatoid arthritis (RA), which is an autoimmune and inflammatory disease, was not enough to attenuate the RA patient with severe inflammatory symptoms. Mesenchymal stem cells (MSCs) are considered as a promising regenerative therapy for the treatment of RA due to their regenerative activity and ability to migrate toward damaged tissues, but the insufficient anti-inflammatory efficacy limited MSC application in various stages of RA patients. In this aspect, the combination of nano-drugs and MSCs can increase the anti-inflammatory response at the inflamed joints, and the severe stages of RA can be recovered. In this study, the inflammation-mediated education process without genetic engineering enhanced the migration ability of MSCs to inflamed joints. Star-shaped gold NPs (AuStar: AuS) were synthesized with the conjugation of Triamcinolone (TA), a glucocorticoid widely used for inflammatory disease. AuS-TA stably conjugated on the surface of MSCs, and inflammation-educated MSCs with conjugation of triamcinolone-loaded gold nanostar (Edu-MSCs/AuS-TA) elicited remarkable attenuation of RA in collagen-induced arthritis (CIA) mouse model. Furthermore, photothermal therapy (PTT) with the irradiation of near-infrared (NIR) laser on inflamed joints showed the maximized efficacy of the anti-inflammatory response for the treatment of the severe stage of the CIA model. Specifically, Edu-MSCs/AuS-TA promoted the repolarization of macrophages from the M1 to the M2 phenotype and decreased the recruitment of neutrophils in joints. Additionally, Edu-MSCs/AuS-TA significantly decreased pain and increased general locomotor activity levels and cartilage regeneration.

5:00 PM SB05.09.15

Designed Biosilica and Collagen-Coated Carrier to Deliver Growth Factor for Bone Regeneration Mi-Ran Ki, Sung Ho Kim, Seok Beom Rho, Ki Ha Min, Gyu Do Lee and Seung Pil Pack; Korea University, Korea (the Republic of)

Since the silica surface is generally composed of hydroxyl groups and ether bonds, it is considered to have a negatively charged surface that readily adsorbs oppositely charged molecules. The heparin-binding domain (HBD), mainly composed of positively charged residues, is present in many growth factors (GFs). It plays an essential role in the binding with the anionic sulfate of heparin/heparan sulfate. Based on this, GFs containing HBD may have an affinity for the anionic silica surface. We hypothesized that the silica coating would increase the association for the growth factors. To identify this, hydroxyapatite, currently used as a bone graft material and BMP2 carrier, was coated with bio-silica on the surface using a silica-forming peptide. By atomic force microscopy, we measured the binding force between GF, BMP2, and the silica surface, demonstrating that the biosilica surface showed an 8-fold higher binding strength than the HA alone. While the loading efficiency was increased due to the strong binding force, there was a problem in that the release rate was low. For effective delivery of GF by increasing diffusion rate, collagen was introduced. HA was coated with collagen and biosilica layer by layer according to collagen concentration and the number of coating layers. In the final biosilica-coated surface, the diffusion rate of two successive coatings of collagen and biosilica was higher than the one-time coating. Meanwhile, triple layers lowered the loading efficiency (LE%) and diffusion rate than the former coating. Double successive coatings of collagen and biosilica with 0.01% collagen displayed the highest LE% and diffusion rate. Hence, this formulation was selected as an optimal carrier for GFs. The carrier above demonstrated increases in cell proliferation, alkaline phosphatase activity, osteogenic gene expression, and calcium mineral precipitation in the osteogenesis of MC3T3 E1 cells compared to those of HA and one-time biosilica-coated HA. Therefore, the biosilica/collagen-coated HA can be an effective carrier for GF-employed therapy in bone regeneration.

5:00 PM SB05.09.16
RANKL Reverse Signaling Derived Bone Regeneration by Osteoclast Membrane Vesicle-Functionalized PLGA Nanoparticle Jae Won Jang[1], Hyunji Kim[1], Dongtak Lee[2], Yonghwan Kim[1] and Hyo Gi Jung[1]; [1]Korea University, Korea (the Republic of); [2]Brigham and Women's Hospital, United States

Controlling the bone formation and resorption processes by osteoblast and osteoclast is crucial for bone regeneration. Previously, it was solely reported that osteoblast secretes receptor activator of nuclear factor kappa-B ligand (RANKL) to differentiate osteoclasts. However, it is recently reported that RANKL reverse signaling mechanism which induce the bone formation by osteoclastic exosomes possessing RANK. Bioinspired by the RANKL reverse signaling pathway, we fabricated artificial osteoclastic exosomes to induce enhanced bone formation. In detail, we extracted osteoclast-derived cell membrane vesicles (OCMVs) which were functionalized on PLGA nanoparticle core. We successfully confirmed the synthesis of the OCMVs by the analysis of dynamic light scattering, zeta potential, and TEM imaging. In addition, the presence of RANK on OCMVs was verified via confocal microscopy and western blot. Finally, we validated the enhanced bone regeneration process by OCMVs using alkaline phosphatase (ALP) assay. The results show that the degree of bone regeneration by OCMVs significantly increased compared to that of bone morphogenic protein-2 (BMP-2). Our findings suggest that OCMVs have a potential to be utilized in biomedical application of bone regeneration.

5:00 PM SB05.09.17
DNA Origami—Increasing Functionality in Biological Settings Veikko Linko[1,2]; [1]University of Tartu, Estonia; [2]Aalto University, Finland

Sub-nanometer-precise DNA origami structures may serve as versatile high-resolution templates for engineering inorganic materials [1] and as components for bridging molecular and macroscopic scales [2]. For biomedical applications, DNA origami could be integrated into robotic devices [3], gene-editing tools [4], delivery vehicles [5], and diagnostic platforms [6]. However, under physiological conditions these structures may suffer from poor stability due to low-cation-induced denaturation and enzymatic degradation. Here, I will present some of our very recent results in the following topics:
(1) Structural design governs the folding [7] and environment-dependent stability of DNA origami [8].
(2) Superstructure of DNA origami can be harnessed in rational design of drug release profiles [9].
(3) Customized static [10-12] and stimuli-responsive [13] coatings can be used for targeting, for protecting DNA origami from degradation, and for increasing the immunocompatibility of DNA-based delivery systems.

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5:00 PM SB05.09.18
Highly Effective Porous Antimicrobial Coatings Saeed Behzadinasab, Myra D. Williams, Christopher Stoll, Joseph O. Falkinham III and William A. Ducker; Virginia Tech, United States

Antimicrobial surface coatings can be used to reduce the transmission of infectious diseases that are spread by contact. An effective coating should kill microbes in the time between users, which is minutes or less, and also continue to operate for an extended period. Fast killing is a transport problem, and our solution is a porous coating with the active material inside the pores. We use hydrophilic pores of dimensions 5-100 µm such that they infiltrate liquid droplets in seconds, and from there transport distances and times are short, defined by the pore size, rather than the droplet size. Our coating has two levels of structure: (A) a porous scaffold and (B) an antimicrobial coating within the pore structure containing the active ingredient. Two scaffolds are studied: stainless steel and poly(methylmethacrylate) (PMMA). The active ingredient is electrolessly-deposited copper. To enhance adhesion and growth of copper, a layer of polydopamine (PDA) is deposited on the scaffold prior to deposition of the copper. This porous copper coating kills 99.8% of *Pseudomonas aeruginosa* within three minutes, which is highly effective. Killing on this fast scale is appropriate for antimicrobial applications to prevent disease.

5:00 PM SB05.09.20
Mineralization Stimuli of Hydroxyapatite-Embedded Hierarchical Nanofibrous Scaffold Using Piezoelectric Protein for Tissue Engineering Ji

Yeon Lee[1], Chan Hee Park[2] and Cheol Sang Kim[2]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Jeonbuk National University, Korea (the Republic of)

The development of novel biomaterials that provide electrical potentials generated through bioactive scaffolds with respect to their appropriate effects on cell behaviors is essential for tissue engineering. In particular, piezoelectric biomaterials are attractive due to the possibility to produce electrical potentials for stimulation via cell motility. Despite their capacity to promote tissue regeneration through cell stimulation, synthetic piezoelectric biomaterials still face issues with poor biocompatibility and inflammatory response. Here, we designed a scaffold that supports cellular activity without eliciting any toxic effect on the host immune response by using a nature-derived piezoelectric protein and mimicked extracellular matrix microenvironment topologies using electrospinning to enhance cell adhesion. The scaffold enhanced piezoelectricity to overcome limited electrical signaling pathways of the nanofibrous membrane via alpha-helix to beta-sheet transition, and this led to elevated mechanical properties and wettability according to the morphological modification. In addition, the hierarchical structure of the scaffold induced a sequential release of hydroxyapatite and simvastatin by gradual biodegradation of the protein to accelerate homogenous growth in a higher local ion concentration during mineralization. Our scaffold is a promising candidate for tissue engineering and mechanoelectrical transduction platform due to its phased functionality in electrophysiological activity, biodegradability, and mineralization. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2021R1C1C2011542) and NRF-2017-Fostering Core Leaders of the Future Basic Science Program/Global Ph.D. Fellowship Program.

5:00 PM SB05.09.22

Carbohydrates-Modified Pt(IV) Pro-Drugs -Conjugated Graphene Oxide as a Novel Therapeutic Strategy to Target Osteosarcoma Giada Bassi[1,2], Ludmila Zarska[3], Eoin Moyinihan[4], Arianna Rossi[1,5], Andrea Ruffini[1], Silvia Panseri[1], Diego Montagner[4], Vaclav Ranc[3] and Monica Montesi[1]; [1]Institute of Science, Technology and Sustainability for Ceramics (ISSMC) National Research Council, Italy; [2]University of Chieti, Italy; [3]Regional Centre of Advanced Technologies and Materials, Palacký University, Czechia; [4]Maynooth University, Ireland; [5]University of Messina, Italy

INTRODUCTION

Osteosarcoma is the most common type of bone cancer diagnosed especially in children and young adults[1]. A combination of chemotherapy, radiotherapy and surgery is commonly used to treat this type of cancer[2,3]. In detail, chemotherapy is based on the use of molecules targeting the high cancer cell proliferation metabolism such as Platinum (Pt)-based drugs that binds nuclear DNA upon overpassing the cell membrane, causing its damage and the arrest of the cancer cell cycle at G2/M transition phase, leading to apoptosis[4-7]. Despite Pt chemotherapeutics are the most potent used anticancer drugs, their side effects (high degradation before entering the cells, the off-target organs toxicity, and cell resistance) remain great drawbacks[8-11].

EXPERIMENTAL METHODS

In this study, we synthetized Graphene oxide (GO)-based nanoplatforms as smart delivery systems of Platinum-based drug. In order to reduce GO cytotoxicity in health cells while promoting its cellular uptake in cancer cells, and to allow Pt loading on GO, 8-arm polyethylene glycol-amine (PEG) was used. The bioactivity of GO-PEG-Pt platforms were compared to Pt-free (15 µM, 30 µM, and 60 µM) on three osteosarcoma cell lines (MG63, U2 and SAOS-2). The in vitro analysis of cellular uptake (ICP-OES), viability (MTT assay), morphology (actin and DAPI staining) and migration (scratch test) was performed.

RESULTS AND DISCUSSION

A preliminary study showed that GO-PEG was not toxic for cells at any concentration tested compared to cells only. A significant cell viability reduction was detected at 30 µM GO-PEG-Pt for all cell lines compared to Pt-free, reaching 70% cell mortality in MG63 (p value ≤ 0.0001) and SAOS-2 (p value ≤ 0.001). Morphological analyses showed a round-shape cell morphology and cell number reduction in the presence of GO-PEG-Pt respect to Pt-free in a dose dependent trend. Cellular uptake of GO-PEG-Pt was significantly higher after 24h for SAOS (p value ≤ 0.05) and MG63 (p value ≤ 0.0001) cell lines than Pt-free. The cell migration was lower in Go-PEG-Pt than Pt-free in MG63 and U2 with overall more than 60% migration inhibition over time at 30 µM concentration.

CONCLUSION

The results confirmed that GO-PEG-Pt platforms work as promising anticancer delivery systems. In fact, all the three osteosarcoma cell lines showed higher susceptibility to GO-PEG-Pt in terms of lower metabolic activity and lower migration rates due to the higher GO-PEG-Pt uptake compared to Pt-free.

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5:00 PM SB05.09.23

Understanding the Host-Guest Chemistry of CuMOF-Gliotoxin Complexes by X-Ray Absorption and X-Ray Photoelectron Spectroscopy Izuchika Nduka, Sara Namvar and Rosa Arrigo; University of Salford, United Kingdom

Introduction: Gliotoxin, a secondary metabolite isolated from the fungi, *Aspergillus fumigatus* has shown cytotoxic activity against neuroblastoma (1), a type of cancer accounting for 15% of all childhood cancer-related deaths (2). But as with all other chemotherapeutic agents, this compound is toxic to both tumour cells and healthy cells. To minimize toxicity towards the healthy cells, a biocompatible nanoparticulate system is needed. For this reason, our study has explored the use of nanosized metal organic frameworks (MOFs) – a class of organic-inorganic hybrid materials made up of metal nodes held together

by organic bi or tridentate linkers, as drug delivery systems with the goal of achieving controlled delivery of gliotoxin to neuroblastoma cells. Amongst the MOF systems we have investigated, Cu-MOFs with RAWYAS and GIFKUC phases showed interesting results and are the focus of this contribution. By means of microwave-assisted solvothermal method, we synthesized some Cu-based MOFs at 1 (MOF1Cu), 5 (MOF5Cu), and 30 (MOF30Cu) minutes, using copper (ii) nitrate trihydrate as the metal ion and 5-aminoisophthalic acid as the ligand, and studied their structural characteristics by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD). We also explored their adsorption capacities using high performance liquid chromatography (HPLC) and investigated their cytotoxic effect against the SHSY-5Y neuroblastoma cell line by means of 3-(4,5-dimethylthiazol-2-yl)-2,5 diphenyltetrazolium bromide (MTT) assay. To rationalize our findings from the MTT assay, we sought to understand the nature of the intra-and inter-molecular interactions between gliotoxin and the synthesized Cu-MOFS by measuring the K-edges of Cu, C, N, O, and S of the MOF-gliotoxin complexes by means of soft and hard x-ray absorption spectroscopy (XAS) and x-ray photoelectron spectroscopy (XPS) in an ex-situ fashion.
Results: The MTT assay showed that upon immobilization of gliotoxin within the synthesized MOFs, its cytotoxic effect was increased. This enhanced cytotoxicity suggests that not only do the MOFs act as carrier systems, but they also provide a synergistic effect. The changes in the near edge x-ray absorption fine structure (NEXAFs) spectra on immobilization of gliotoxin within the synthesized Cu-MOFs showed that there is an interaction between the drug and the MOF systems. This is particularly evident in the N K edge spectrum of the MOF sample after immobilization of gliotoxin 1:5 ratio with a shift of the 1s→p* transition of the amino group of MOFs to higher energy. Moreover, the ratio between the 1s→p* and 1s→s* in the OK edge changes significantly upon immobilization of gliotoxin, indicating a significant structural modification of the MOFs. Also, marked changes can be seen in the S2p XPS spectra upon gliotoxin immobilization, which suggests a direct co-ordination between the sulphur of gliotoxin and the Cu metal sites of the MOFs. Based on these results, we posit that the interaction of the gliotoxin with the MOFs involves mainly the N site of the ligand. More investigations on the S L edge XAS will clarify any modification on the structure of the gliotoxin.
Conclusion: Taken together, our findings highlight an approach to enhancing the pharmacological activity of gliotoxin. As an outlook, we would further explore the nature of the host-guest chemistry between gliotoxin and the synthesized Cu-based MOFs from a computational viewpoint using molecular dynamic studies.

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5:00 PM SB05.09.24
Lactosylated Graphene Oxide—An Strategy For Hepatocellular Carcinoma Targeted Therapy Kevin Ricardo Díaz Gálvez, Alexel J. Burgara-Estrella and Jose A. Sarabia-Sainz; Universidad de Sonora, Mexico

We report the evaluation of lactosylated graphene oxide (GO-AL) as a potential drug carrier targeted at an asialoglycoprotein receptor (ASGPR) from hepatic cancer cells. Structural-modification, safety evaluation, and functional analysis of GO-AL were performed. The structure and morphology of the composite were analyzed by atomic force microscopy (AFM), while Raman and FTIR spectroscopy were used to track the chemical modification. For the safe application of GO-AL, an evaluation of the cytotoxic effect, hemolytic properties, and specific interactions of the glycoconjugate were also studied. SEM and AFM analysis of the GO showed graphene sheets with a layer size of 2–3 nm, though a few of them reached 4 nm. The Raman spectra presented characteristic peaks of graphene oxide at 1608 cm^{-1} and 1350 cm^{-1}, corresponding to G and D bands, respectively. Besides, Si–O peaks for the APTES conjugates of GO were identified by FTIR spectroscopy. No cytotoxic or hemolytic effects were observed for GO samples, thus proving their biocompatibility. The cytotoxicity in cancer cells of GO, GO-A or GO-AL was evaluated at different concentration by MTT (0.25 to 100 ug/mL). The interaction of *Ricinus communis* lectin confirmed that GO-AL has a biorecognition capability and an exposed galactose structure. This biorecognition capability was accompanied by the determination of the specific absorption of lactosylated GO by HepG2 cells mediated through the asialoglycoprotein receptor. The successful conjugation, hemolytic safety, and specific recognition described here for lactosylated GO indicate its promise as an efficient drug-delivery vehicle to hepatic tissue.

5:00 PM SB05.09.26
Temperature-Controlled Gene Expression Using Thermoresponsive Polymer-DNA Conjugates Assala Al Samad and Michael Booth; UCL, United Kingdom

Nucleic acid technologies, including plasmids, ASO, siRNA and mRNA, are a suite of well-studied and emerging tools to study living systems and target genetic disorders *in vivo*. Controlling nucleic acid technologies by external stimulus has become a vital requirement in biotechnology and gene therapy. Among the external stimulus that can be used, temperature is an ideal candidate due to its reversibility and high tissue penetration, when combined with ultrasound[1]. Temperature control can be achieved by using thermoresponsive polymers. Thermoresponsive polymers are “Smart Materials” that can switch between globule and coil states when changing the temperature. They are divided into 2 categories; polymers with a lower critical solution temperature (LCST) aggregate when temperature is above a critical temperature, and polymers exhibiting an upper critical solution temperature (UCST) become soluble above their critical temperature. Poly(N-isopropylacrylamide) (PNIPAM), which exhibits a LCST of 32○C, has been previously coupled to DNA[2] and preliminary studies have shown it can be used to regulate gene expression when polymerized with antisense oligonucleotides (ASOs)[3]. ASOs are short ssDNA that can bind to complementary mRNA then allow their cleavage in the presence of RNAse H enzyme, and have been used to control protein production in cell-free and living systems. In this project, we are exploring the conjugation the LCST and UCST (co)polymers onto DNA template and ASOs to produce a platform for temperature control.
Here, different (co)polymers (PNIPAM and P(NIPAM-co-AAm)) with LCSTs in the range of 32-38○C were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization and conjugated to functional DNA and ASO by click chemistry to produce defined polymer-nucleic acid species. These conjugates aggregated upon heating, as expected, and were used to control cell free protein synthesis (CFPS). In the first instance, we conjugated PNIPAM to a DNA template, encoding a fluorescent protein. The expression from DNA-PNIPAM was significantly decreased upon heating above the LCST, compared to the non-modified DNA template. We have also generated defined conjugates of ASOs with PNIPAM, unlike the previously example that employed free radical polymerisation[3]. In preliminary results, these ASO-PNIPAM conjugates were able to degrade mRNA below the LCST, but exciting, showed no degradation above the LCST.
These results demonstrate that it is possible to use thermoresponsive polymers to control both large (DNA template) and small (ASOs) nucleic acid technologies, using bioconjugation. Creating these bioconjugates, rather than the polydisperse nanoparticle aggregates, allows for the formation of a distinct, single molecular species, which simplifies synthesis, analysis, and pharmacokinetics. Our future aim is to attach LCST and UCST (co)polymers, which can be activated by mild hyperthermia, to many nucleic acid technologies and demonstrate their ultrasound-targeted application in biology and medicine.
ACKNOWLEDGEMENTS
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5:00 PM SB01.03.13
4D Printed Fiber-Reinforced Highly Stretchable Uterine Tissue Engineering Scaffolds with Controlled Release of Hormone Jizhuo Chen, Shangsi Chen and Min Wang; The University of Hong Kong, Hong Kong

Diseases of and injuries to the uterus can have significant effects on functions of the uterus, causing irregular menstruation, dysmenorrhea, or even infertility. These medical problems severely influence the quality of life of millions of females both physically and mentally. Conventional treatments for uterine diseases resort to drug therapy as a conservative treatment, hysteroscopic adhesiolysis as a surgical treatment, and so on. Although these treatments can mitigate the pain and partly restore functions of the uterus to some level, infertility due to uterus disease or injury poses a great challenge in the medical field. Tissue engineering (TE) now offers a promising approach to address the difficult problems in human body tissue/organ repair and regeneration, and it has been successfully used to regenerate body tissues such as skin, blood vessels, bone, tendon and ligament. However, tissue engineering strategies have been rarely adopted to treat uterine defects owing to various difficulties, including matching the highly elastic behavior of myometrium of the uterus. In this study, fiber-reinforced strong and highly stretchable tissue engineering scaffolds with controlled release of a hormone were made via 4D printing and their characteristics were subsequently studied. The fabrication of the new scaffolds involved the following steps: (1) 17β-estradiol (E2)-encapsulated polydopamine (PDA) nanospheres were synthesized; (2) a thermoplastic polyurethane (TPU) was dissolved in an organic solvent and different amounts of E2/PDA nanospheres were added to make E2/PDA/TPU mixtures which were subsequently electrospun into E2/PDA/TPU nanofibers; (3) different amounts of E2/PDA/TPU short fibers were blended homogenously with a poly(D,L-lactide-co-trimethylene carbonate) ("PLATMC", which is a shape memory polymer often used for 4D printing for different applications, including applications in the tissue engineering field) solution to make printing inks; (4) the inks were used in 4D printing to fabricate uterine scaffolds with designed structures. The optimal amounts of both E2/PDA in electrospun TPU fibers and E2/PDA/TPU in printing inks were determined through various experiments. Good printability was achieved through ink optimization. Tensile tests of 4D printed scaffolds showed that with the 30% wt. content of fibers in scaffolds, the Young's modulus and tensile strength of composite scaffolds were 2.5 and 3.6 times, respectively, those of 4D printed pure PLATMC scaffolds, with less than 20% sacrifice in ultimate elongation. *In vitro* E2 release experiments revealed that E2 was released gradually from PDA/TPU fibers during the 8-week test period without apparent burst release. The *in vitro* degradation study showed that PLATMC in composite scaffolds degraded initially causing with the exposure of fibers, and E2/PDA was then released gradually with time. In *in vitro* biological study, rat bone marrow mesenchymal stem cells (rBMSCs) seeded on composite scaffolds were found to attach and proliferate well with the cell survival rate reaching 99.5% at day 2 of culture. All of these results show that the 4D printed highly stretchable scaffolds with controlled release of E2 have high potential for uterine tissue regeneration.

SESSION SB05.10: Nanomaterials and Targeting
Session Chairs: Michelle Bradbury and Gemma-Louise Davies
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2016

8:30 AM SB05.10.02
Aptamer-Functionalized Metal-Organic Frameworks as an Efficient Delivery Vehicle of Antimicrobial Peptides Jon Ostolaza, Anna Scheeder, Ioanna Mela, Clemens Kaminski and David Fairen-Jimenez; University of Cambridge, United Kingdom

Infections caused by bacteria are among the most serious physiological conditions that threaten human health. The swift emergence of resistant bacteria is jeopardizing the efficacy of most antibiotics, highlighting the importance of finding non-invasive theragnostic systems to treat bacterial infections. Currently, different antimicrobial systems used in the field include metal-ion nanoparticles (NPs) (*e.g.*, Ag NPs), semiconductor photocatalytic materials (*e.g.*, TiO_2), and antibacterial-nanocarrier composites. However, these systems face several shortcomings such as very low efficiency, short-term effect, and fast release of the antimicrobial agent. To overcome these issues, metal-organic frameworks (MOFs) have emerged as a promising theragnostic system. MOFs are nanoporous crystalline materials made by the self-assembly of metal clusters and organic linkers. They have shown high biocompatibility, high drug loading capacity, slow release of their cargo, and a surface that is easy to functionalize. Despite the potential of these materials as nanocarriers, hardly any research has been carried out using MOFs for antimicrobial delivery.

In this work, a novel MOF named PCN-222 was functionalized with aptamers (apt@PCN-222), short oligonucleotide sequences that selectively bind to bacteria, to deliver doxorubicin and antimicrobial peptides (apt@dox@PCN-222) to bacterial targets. PCN-222 is a photoluminescent Zr-based nanomaterial that has shown great potential for bio-applications due to its large porosity, high stability, and biocompatibility. Growth assays for Gram-positive (*Bacillus subtilis*) and Gram-negative (*Escherichia coli*) bacteria were used to determine bacteria growth with bare PCN-222, free doxorubicin, apt@PCN-222, and apt@dox@PCN-222. Different characterization techniques were used to assess the physico-chemical properties of the NPs. High resolution transmission electron microscopy (HR-TEM) was used to confirm the crystallinity NPs. Scanning electron microscopy (SEM) and dynamic light scattering (DLS) were carried out to determine the particle size of the NPs and their colloidal stability, respectively. Ultraviolet-visible spectroscopy (UV-vis) was used to determine the drug loading content and inductively coupled plasma mass spectrometry (ICP-MS) was utilized to quantify the binding of aptamers into the surface of PCN-222. Finally, the binding of apt@PCN-222 NPs to the different types of bacteria was assessed by structured illumination microscopy (SIM).

Crystalline PCN-222 NPs with a size of 145 ± 7 nm and a BET area of 1980 m^2/g were successfully synthesized. Doxorubicin was successfully encapsulated into PCN-222, obtaining a drug loading greater than 40%. This result confirms the expected high porosity of this NP. Enhanced binding of PCN-222 to the bacteria was corroborated by measuring the overlapping region by SIM since GFP-expressing *E. coli* are green and the PCN-222 NPs are red. The increase in binding levels was obtained by exploiting the synergistic effect of two binding mechanisms: electrical binding due to the positive charge of PCN-222 and selective binding by the addition of aptamers to the surface of the MOF. The phosphate ions present in PBS destroyed the porous matrix of PCN-222, thus releasing the doxorubicin in a slower manner than the current antibacterial-nanocarrier composites. The slow release of the drug, together with the selective binding of the apt@PCN-222 conjugate to the bacteria resulted in an increased reduction of bacteria growth when compared to free doxorubicin.

PCN-222 has shown promising physico-chemical properties for the effective delivery of antimicrobial agents to bacteria. Further studies will examine the effect of using larger aptamers or cationic polymers to increase its targeting effects. This study represents the first systematic attempt to target bacteria using aptamer-functionalised PCN-222, promoting the use of nanomaterials against antibiotic resistance.

8:45 AM SB05.10.03
Ultrasmall Gold Nanoparticles Decorated with Biomolecules for Specific Interaction with Cells and Proteins Matthias Epple[1], Nataniel Bialas[1], Marc

Heggen[2], Kai Klein[1], Sebastian Kollenda[1], Kathrin Kostka[1], Benedikt Kruse[1], Kateryna Loza[1], Viktoriya Sokolova[1] and Natalie Wolff[1]; [1]University of Duisburg-Essen, Germany; [2]Ernst-Ruska Centre, Forschungszentrum Juelich, Germany

Ultrasmall gold nanoparticles (diameter 1-2 nm) are smaller than most proteins and therefore well suited to elucidate particle-protein interactions after suitable surface functionalization. siRNA and fluorescing dyes (e.g. FAM, Cy5, Alexa647) were attached by copper-catalyzed azide-alkyne cycloaddition (click chemistry) to azide-terminated gold nanoparticles. Peptides of different length were directly attached via cysteine, taking advantage of the strong gold-sulfur bond. The particles were characterized by high-resolution transmission electron microscopy, differential centrifugal sedimentation, and ultraviolet spectroscopy. Extensive NMR spectroscopic investigations of dispersed particles were possible due to the ultrasmall nature of the particles. By combining the results of all these analytical techniques, a full image of the particles was gained, including the number of ligands (typically 5-10 per nanoparticle) and the details of the ligand-gold bond.
The nanoparticles were surface-decorated with biomolecules and synthetic receptor molecules to interact with the surface of model proteins as probed by NMR spectroscopy, isothermal titration calorimetry, and fluorescence polarisation. Such particles are easily taken up by cells as demonstrated in classical two-dimensional cell cultures and in three-dimensional organoids. Notably, the particles were able to enter the cell nucleus and also to cross the blood-brain barrier in brain organoids that exhibit a functional blood-brain barrier in vitro. We also demonstrated how they were taken up by bacteria.
In conclusion, covalently functionalized ultrasmall gold nanoparticles have a strong potential for specific interaction with proteins, for imaging and as drug carrier into cells and organoids.

9:00 AM SB05.10.04
Biomolecular Corona and Mechanisms Involved in Tumor-Targeting and Renal Clearance of Mesoporous Silica Nanoparticles Si-Han Wu; Taipei Medical University, Taiwan

Mesoporous Silica Nanoparticles (MSNs) have been considered promising for in vivo biomedical applications, such as targeted therapy and diagnostic imaging. However, once nanoparticles are exposed to the biological system, biomolecular corona formed around the nanoparticles can result in unexpected outcomes in terms of therapeutic efficiency, biodistribution, and pharmacokinetics. Therefore, understanding the composition and functionality of protein corona is crucial for nanomedicine development. Nowadays, cancer nanomedicines are widely applied to overcome the low tumor-targeting efficiency of the conventional drug, but the elimination processes of nanoparticles are still unclear. Kidneys, with a filtration threshold of 6 nm for metal-based nanoparticles or proteins defined by the previous investigation, are the major excretion organs in metabolism to remove excess waste in the body.
In this study, we employed LC-MS/MS, SDS-PAGE, DLS, and Zeta potential measurements to identify the protein corona after the *in vitro* incubation of 25 nm cationic PEGylated MSNs with human plasma and intravenous injection of nanoparticles into the mice. Additional bioinformatics analyses using ClueGo and Ingenuity Pathway Analysis (IPA) revealed altered regulation in crucial pathways. The biodistribution of MSNs in 4T1 breast tumor-bearing BALB/c mice was investigated using immunofluorescence microscopy and a non-invasive *in vivo* imaging system (IVIS). Our results demonstrated that superior tumor-targeting efficiency could be achieved more simply by reducing protein adsorption but not manipulating protein type on the surface of MSNs. On the other hand, immunofluorescence and TEM visualization showed the localization of PEGylated MSNs in the glomerular basement membrane and mesangial cells. Notably, intact 25 nm cationic PEGylated MSNs were observed in the collective urine. A comprehensive evaluation revealed that the biomolecular mechanisms involved in the excretion of MSNs are through the proximal tubular epithelial cells by caveolae-mediated albumin transcytosis.

9:15 AM SB05.10.05
Synthesis of Silver-Modified Nanoceria Formulations Through Solution-Based Nanoengineering and Their Unique Efficacies Towards (Non-) Enveloped Virus Species Craig J. Neal[1], Candace Fox[1], Elayaraja Kolanthai[1], Yifei Fu[1], Udit Kumar[1], Christina Drake[2], Griffith Parks[1] and Sudipta Seal[1]; [1]University of Central Florida, United States; [2]Kismet Technologies, United States

The utility of noble metal species in catalysis has been further broadened by investigations into their complex substrate interactions (catalyst-substrate/support effects). Such studies highlight the impact of chemical environment on material character as emergent phenomena (*e.g.* varied plasmon character, unique reaction selectivity (reactivity)). In the presented study, noble metal silver's limited solubility in and surface-phase formation on redox-active cerium oxide nanoparticles is overcome by manipulating the unique chemistry of ionic silver in aqueous solution. In particular, the oxidation of silver and, thereby, the final nanomaterial synthesis products, are *nanoengineered* by top-down chemical etching process to remove contaminant silver (oxide) phases post-synthesis (utilizing Tollen's reagent, $[Ag(NH_3)_2]^+$, formation from silver (oxide)) (*AgCNP1*) or selective-oxidation of Ce^{3+} over silver by hydrogen peroxide ($H_2O_2+Ag^0,Ag_2O \rightarrow Ag^++H_2O+$(radical oxygen species)), bottom-up process, to preclude silver (oxide) particle phase formation (*AgCNP2*). Each synthesis produces surface/near-surface silver-phases of varied oxidation states (evidenced by x-ray photoelectron spectroscopy) due to the unique crystal environments evolved by each synthetic route (evidenced by transmission electron microscopy, x-ray diffraction, electroanalysis). Further, synthesis conditions and product silver phase character strongly impact cerium site reduction in each formulation (25.8 and 53.7 %Ce as Ce^{3+} for AgCNP1 and 2, respectively). Biomedically-relevant, reactive oxygen species modulating enzyme-mimetic catalysis assays (peroxide-degrading: catalase, superoxide radical scavenging: superoxide dismutase) were performed for each formulation, which correlate catalytic redox activity with extent of cerium reduction in the formulations. The complex nature of the silver surface phase character and silver/ceria-mediated surface catalysis activity of each formulation were further highlighted in studies demonstrating their unique efficacy towards inactivation of enveloped (OC43 *coronavirus*) and/or non-enveloped (RV14 *rhinovirus*) viruses. Specificity towards virus character is further studied through electroanalytical methods (electrochemical impedance spectroscopy, circuit modeling) and adsorption studies.

9:30 AM *SB05.10.06
Inorganic/Organic Nanocomposite Particles (I/O-NP); A Platform Technology for Future Healthcare Applications Marco Giardiello; University of Liverpool, United Kingdom

Nanomedicine represents one of the fastest growing fields of research in recent years, encompassing both therapeutic and diagnostic medicine. Global impacts across several wide-ranging disease conditions have been achieved, for example Doxil/Caelyx and Myocet for cancer chemotherapy, Macugen for macular degeneration, Fosrenol for renal disease and Endorem for magnetic resonance imaging. Critically, all advances in nanomedicine are driven by material development on the nanoscale, with many applications established through fundamental research and design of novel nanomaterials. Thus, in order to discover next generation technologies, next generation nanomaterials must be developed.
The success of current clinical nanomedicine is borne out of advances in both inorganic and organic nanomaterials. The Inorganic/Organic Nanocomposite Particles (I/O-NP) platform technology is composed of organic, polymeric nanoparticles that incorporate and functionalise various inorganic nanoparticles. The aim is to harness the versatility of both inorganic nanoparticle (I-NP) and organic nanoparticle (O-NP) technologies to develop a highly versatile platform with multiple opportunities in varied healthcare applications possible through variation in nanocomposite structure and composition. Through advanced materials design and collaborative research approaches, the scientific objective is to apply the versatility of the I/O-NP platform across several emerging healthcare applications, both diagnostic and therapeutic. Herein an overview of synthetic approaches towards composite material developments aimed at several healthcare applications will be presented:
1. Superparamagnetic Iron Oxide Nanoparticle based tracers for Magnetic Particle Imaging (MPI)

2. Gold nanoparticle based radiosensitisers for Proton Beam Therapy
3. Lanthanide Upconversion Nanoparticles as Optical Imaging Probes
4. Polymeric nanocomposites as theranostic agents for Magnetic Resonance Imaging (MRI)

10:00 AM BREAK

SESSION SB05.11: Nanomaterials in the Body and Immunomodulation
Session Chairs: Gemma-Louise Davies and Matt Trau
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2016

10:30 AM *SB05.11.01
Ultrasmall Silica Nanoparticle-Intrinsic Therapeutic Solutions for Modulating the Tumor-Immune Microenvironment in Cancer Michelle Bradbury[1], Ulrich Wiesner[2] and Michael Overholtzer[1]; [1]Memorial Sloan Kettering Cancer Center, United States; [2]Cornell University, United States

Considerable strides continue to be made in the design of nanoparticles as highly specialized therapeutics for improving treatment outcomes and overcoming limitations that may be observed with standard pharmacologic agents. Novel emerging paradigms that lead to durable response rates in combination with other classes of therapeutics are also critically needed. One promising strategy exploits the unique self-therapeutic capabilities that may be exhibited by the nanomaterials themselves, which do not require attachment of a cytotoxic drug. These capabilities are governed by the physico-chemical properties of these materials, which can disrupt signal transduction pathways, cell cross-talk or invasion, induce cell death programs, or mediate other biological properties within the melanoma tumor microenvironment (TME), thereby providing unprecedented opportunities for combating disease. We find that an ultrasmall fluorescent core-shell silica nanoparticle, Cornell prime dots (C’ dots), exhibits multiple distinctly separable intrinsic therapeutic properties, including their ability to (1) specifically induce regulated cancer cell death programs, such as the iron-dependent process, ferroptosis; (2) selectively modulate expression profiles with activation of multiple gene classes and proinflammatory cytokines, in addition to their ability to (3) directly activate immune cell populations towards an anti-tumor pro-inflammatory phenotype in syngeneic models. Our future work will continue to explore the nature/type of interactions among TME populations exposed to C' dots, probing mechanisms by which these particles engage pro-inflammatory anti-tumor and cytotoxic responses. Such information, in turn, can be used to develop novel treatment paradigms for clinical cancer care.

11:00 AM DISCUSSION TIME

11:30 AM SB05.11.04
Engineering Immunotherapeutic Exosomes from Dendritic Cells Stimulated by Intracellular Self-Assembled Peptide Networks for Cancer Vaccine Min A. Kang[1], Aloka Paragodaarachchi[1], Takamasa Kawano[2], Kiyotaka Shiba[2], Stefania Gallucci[3] and Hiroshi Matsui[1,4]; [1]Hunter College-CUNY, United States; [2]Japanese Foundation of Cancer Research, Japan; [3]University of Massachusetts Amherst, United States; [4]Cornell University, United States

Here we inrtoduce a new approach for generating immunotherapeutic nanoparticles of dendritic cell (DC)-derived exosomes (DC-Exos) on a large-scale for the clinical translation. Exosomes denote a family of nanoparticles (30–120 nm in a diameter) secreted by most cell types. Secreted exosomes consist of a surrounding lipid bilayer containing various proteins, lipids, and nucleic acids in donor cells. The use of DC-derived exosomes was recognized to address the technical challenges associated with DC-based immunotherapy, leading to multiple clinical trials. However, the workload required to upscale the production of DC-Exos is currently not suitable for their major clinical use. Our lab has been showing that a peptide (NapFFK(NBD)Yp) self-assembles in fiber networks in the cytoplasm of donor cells, catalyzed by alkaline phosphatases (ALPs), and such peptide self-assembly can increase the secretion of exosomes in various cancer cells, reaching in some cases a 10-fold increase. We observed that the peptide self-assembly was triggered by ALP in DCs, in which the expression of required enzyme was induced by specific growth factors, and this assembly stimulated mass production of DC-Exos; the production of exosomes from bone marrow-derived DCs was amplified 7-folds by the self-assembled peptide without inducing major toxicity. We also showed the potential that the self-assembled peptide could activate DCs to become strong stimulators of the immune response by triggering pro-inflammatory recognition mechanisms *via* proteomic analysis and flow cytometry. With proteomics, the heatmap of protein expression of exosomes with the peptide treatment indicates the packaging of exosomes is not affected by self-assembled peptides in parental cells, an important condition for their clinical applications. The proteomics could also suggest possible biogenesis and mechanism of amplified generation of exosomes.
The outcome could advance scientific knowledge for precision medicine as proposed exosomes can be applied as intercellular vectors for personal RNA-based therapy (both miRNAs and siRNAs) with capability of individualized-specific targeting of cancers and suppression of immunogenic response. It will also lay the foundations for future studies implementing DC-Exos as delivery systems in mRNA vaccine, cardiovascular diseases-related RNA therapeutics that can be regulated through exosomes.

11:45 AM SB05.11.05
Virus-Mimetic Vaccine Based on Self-Assembled Antigen-Polymer Conjugates Eliciting Effective Immunity Against Influenza Virus Geunseon Park[1], Woonsung Na[2], Jong-Woo Lim[3], Chaewon Park[1], Hyun-Ouk Kim[4], Daesub Song[3] and Seungjoo Haam[1]; [1]Yonsei University, Korea (the Republic of); [2]Chonnam National University, Korea (the Republic of); [3]Seoul National University, Korea (the Republic of); [4]Kangwon University, Korea (the Republic of)

Vaccines have been providing humankind with the ability to defend against infectious diseases. However, existing vaccines face obstacles such as a risk of adverse effects and limited immunogenicity. In the present work, we developed a self-assembled vaccine (SAV) platform based on antigen conjugated with an amphiphilic block copolymer, mPEG-b-PLA-NHS. To improve subunit vaccine immunity, SAV was designed to be nanoscale for effective antigen transport and to display repetitive antigens on its surface to trigger immune cells via multivalent recognition. SAV demonstrated improved cellular uptake by dendritic cells (DCs), hence promoting an efficient activation of the adaptive immune system. In vivo study revealed that SAV induced high levels of IgG, IgG1, and IgG2, indicating effective B cell activation and T cell-mediated immunological response. In addition, we confirmed that SAV containing hemagglutinin (HA) effectively prevented mice from mortality due to influenza virus infection. These results imply that the self-assembled nanosystem constituted of antigen-polymer conjugate can serve as an effective and versatile vaccine platform.

SESSION SB05.12: Considering the Neural-Nanoparticle Interface
Session Chairs: Gemma-Louise Davies and Jacek Wychowaniec
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2016

1:30 PM SB05.12.02
A NIR-II Bio-Interface for Non-Invasive Deep-Brain Stimulation Xiang Wu and Guosong Hong; Stanford University, United States

Neuromodulation techniques, such as electrical deep-brain stimulation and optogenetics, are capable of selective activation or inhibition of certain subgroup of neurons, thus providing unprecedented opportunities for the dissection of complex neural circuitry and the treatment of neurological disorders such as Parkinson's disease. The electric field or visible light used in the current predominant neuromodulation approaches, however, is strongly attenuated by the brain tissue, thus necessitating invasive implantation of stimulation electrode or optical fiber. Such invasive brain implants inevitably cause acute brain damage, chronic immune response, and physical tethering that interferes with the animal's natural behavior. Therefore, it is desirable to develop new methods that can modulate neural activities with an implant-free and tether-free interface.
To address these challenges, we designed a nanomaterial-based bio-interface in one of the biological transparence windows, the second near-infrared window (NIR-II, 1000-1700 nm), for remote and non-invasive deep-brain stimulation. NIR-II light exhibits reduced scattering than visible light and lower water absorption than longer wavelength NIR light, and is thus the optimal wavelength for deep-brain neuromodulation. Although no existing opsin responses to NIR-II photons, we got inspiration from the findings of Nobel laureate David Julius that rattlesnakes sense infrared irradiation through its thermal effect using transient receptor potential (TRP) channels. We hypothesized that TRP channels can also be used as NIR-II receptors in mammalian neurons. However, to activate deep-brain TRP channels, a high laser power is required, which inevitably leads to a high temperature increase on the brain surface, and as a result, altering the neural behaviors and even causing brain damage. To overcome this challenge, we designed nanotransducers named MINDS (macromolecular infrared nanotransducers for deep-brain stimulation) that strongly interact with NIR-II light. Specifically, MINDS consist of a NIR-II absorbing semiconducting polymer core with a photothermal conversion efficiency of 71% in the NIR-II window, and an FDA-approved amphiphilic polymer shell to facilitate water solubility and biocompatibility. As a result, through-scalp wide-field NIR-II illumination creates a local hotspot around MINDS up to a depth of 5-mm in the brain, while largely sparing the brain surface from heating. Consequently, MINDS act as an NIR-II sensitizer to remotely activate deep-brain TRP-expressing dopaminergic neurons in freely behaving mice without any brain implant or physical tethering, producing significant behavioral changes in a conditioned place preference test.
The utility of this NIR-II neuromodulation technique sits between optogenetics and chemogenetics: it eliminates the chronic brain implants and fiber tethering required for optogenetics and features a more precise temporal control of activation and inactivation than chemogenetics. Therefore, the NIR-II neuromodulation approach reported here allows timely behavioral modulation of freely moving subjects with minimal chronic gliosis in the neural tissue and no interference to natural animal behaviors. With complete elimination of any brain implant and head tethering, our approach could afford wide applications in dissecting the complex neural circuits of normally behaving animals in a natural interaction environment, such as in the IntelliCage, in the future. **This work was recently published in *Nat. Biomed. Eng.* (Wu, X. *et al.* Tether-free photothermal deep-brain stimulation in freely behaving mice via wide-field illumination in the near-infrared-II window. *Nat. Biomed. Eng.* 6, 754-770 (2022)).**

1:45 PM SB05.12.03
On the Coupling Mechanism Occurring at the Neuron-Nanoparticle Interface Greta Chiaravalli[1,2], Jasnoor Jasnoor[2,3], Tiziana Ravasenga[2,3], Elisabetta Colombo[2,3], Simona Francia[2,3], Stefano Di Marco[2,3], Fabio Benfenati[2,3], Riccardo Sacco[1] and Guglielmo Lanzani[1,2]; [1]Politecnico di Milano, Italy; [2]Istituto Italiano di Tecnologia, Italy; [3]Ospedale Policlinico San Martino, Italy

The injection of organic photo-responsive nanoparticles (NPs) of poly(3-hexyltiophene) (P3HT) into rat models of retinitis pigmentosa was proposed as a "*liquid retina device*" to treat degenerative blindness, inducing a light evoked retinal neuron response (Maya-Vetencourt et al., 2020; Francia et al., 2022). Although the efficiency of organic polymer-based retinal devices in vivo has been proven, the interpretation of the working mechanisms that grant photostimulation at the polymer/neuron interface is still a matter of debate.

In our work, we focus on understanding the mechanisms which may play a role at the bio-hybrid interface, decoupling them into: (i) a photochemical effect, which in our case consists in the photocathodic behavior of P3HT in watery oxygenated environment; (ii) an electrostatic effect, due to light induced capacitive charging of the NP, known as Photo-Dember effect. With mathematical modeling and electrochemical studies, we are able to identify the relative importance of each mechanism as a function of light intensity impinging onto the substrate, cleft size and cleft resistive properties.

The photo-chemical mechanism, connected to the production of O_2^- in the cleft, appears to be relevant solely when light intensity increases above the physiological ranges and under conditions of strict proximity to the neuron membrane (<50 nm). The capacitive effect induced by the electrostatic charging of the nanoparticle is instead appreciable only in the presence of a highly resistive medium, where ionic screening can be assumed as negligible (Debye Length>>cleft thickness): if this condition is verified by the system, even physiological light intensities (0.2 W/m^2) are able to induce appreciable depolarization of the neurons. The highly resistive medium in the model is accounted for by the presence of adhesion proteins in the cleft. Therefore, the formation of *"proteic islands"* is suggested by the model as a fundamental ingredient to ensure the coupling among neuron and nanoparticle at reduced light intensity.

A preliminary confirmation of our simulation results comes from ex vivo experiments on retinal explants that received P3HT-NPs in the subretinal space either acutely after the explantation or that were taken from rats which had been subretinally injected in vivo with P3HT-NPs one month before. The recordings of retinal ganglion cell firing on acutely injected explants displayed a significantly reduced response with respect to the retinas which experiences a prolonged in vivo contact with the NPs before explantation.
The combined use of modeling and physiological experiments suggests that, in vivo, NPs are engulfed by the neuronal membrane with a highly resistive medium which ensures an efficient electrostatic coupling. While at the high light intensities used in in vitro experiments both phenomena may take place, at the lower light intensities used in vivo the sole electrostatic effect is responsible for the photostimulation. The results also suggest that in vitro experiments do not faithfully reproduce the in vivo condition and that a prolonged in vivo contact between NPs and the neurons, occurring in vivo, is necessary to fully elicit the physiological effects.

2:00 PM SB05.12.04
Ultrasound Triggered Liposome Light Source for Noninvasive Optogenetics Huiliang Wang; The University of Texas at Austin, United States

Optogenetics has revolutionized neuroscience understanding by allowing spatiotemporal control over cell-type specific neurons in neural circuits. However, visible light cannot be directly delivered to deep brain tissue, due to the severe dissipation and scattering of photons. As a result, invasive craniotomy is usually required to implant optical fibers in the brain for in vivo optogenetic stimulation, resulting in permanent damage and chronic gliosis in brain tissue. To achieve non-invasive optogenetics with high temporal resolution and excellent biocompatibility, we have developed focused ultrasound triggered liposome-based light sources (Lipo@IR780/L012 nanoparticles) for deep brain photon delivery. Synchronized and stable blue light emission was generated under ultrasound irradiation due to the activation of chemiluminescent L012 via nearby reactive oxygen species generated by IR780. In vitro tests revealed that Lipo@IR780/L012 nanoparticles could be triggered by ultrasound for light emission at different frequencies and hence activate opsin-expressing spiking HEK cells under the ultrasound irradiation. In vivo optogenetic stimulation further demonstrated that motor cortex neurons could be noninvasively and reversibly activated under the repetitive ultrasound stimulation after i.v. injection of Lipo@IR780/L012 nanoparticles to achieve limb motions control.

2:15 PM BREAK

SESSION SB05.13: Sensing/Diagnostics
Session Chairs: Gemma-Louise Davies and Marco Giardiello
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2016

3:30 PM SB05.13.02
Nanoparticle-Based Surface Localized Nucleic Acid Amplification for Rapid and Ultrasensitive Electrochemical Detection Jeong Ook Soh[1], Young Keun Kim[2] and Ju Hun Lee[1]; [1]Hanyang University, Korea (the Republic of); [2]Korea University, Korea (the Republic of)

Of various methods that have been developed for the diagnosis of diseases, molecular diagnostic approaches have proven to be of great significance and thus have been developed to a great extent. Of these approaches, nanoparticle-based systems for nucleic acid detection have gained much attention due to the remarkable features of the nanoparticle platform (large surface area, electrochemical catalysis, biocompatibility, etc.). These methods produced notable results for detection of disease-related genetic material, which suggested the potential to overcome the critical drawbacks of conventional PCR-based diagnosis. However, the acquisition of both high sensitivity and short detection runtime in a single method remain a challenge as methods with high sensitivity demand lengthy procedures while faster methods require higher concentrations of genetic material for detection. In response to this matter, we propose an innovative nanoparticle-based system composed of a nucleic acid amplification method paired with electrochemical assay for rapid and ultrasensitive detection of genetic biomarkers. Termed “nanoparticle surface localized amplification (nSLAM)”, the method uses DNA functionalized Fe_3O_4−Au core−shell nanoparticles as a platform for nucleic acid amplification and accumulation. The surface-anchored DNA act as primers that bind and amplify target DNA directly on the nanoparticle surfaces using conventional PCR procedures. The surface-accumulated amplicons are subsequently subjected to electrochemical detection, which induces significantly amplified current signals that identify the presence of the target material. The nanoparticles function as dispersible nanometer-sized electrodes that significantly improve the biochemical contact efficiency between the primers and target gene of interest, further enabling amplification and collection of extremely low concentrations of target material. Furthermore, multiple measurements of electrochemical detection induce rearrangement of the dispersible nanoparticles, substantially enhancing the current signals for both ultrasensitive and rapid detection of target genes. The detection performance was tested using the COVID-19 model, which produced a remarkable sensitivity of ~1 RNA copy/µL using 35 PCR cycles. This ultrasensitivity enabled the reduction of amplification cycles to as low as 4 cycles (~7 min runtime) using 1 fM COVID-19 cDNA, which demonstrated the system’s capacity for rapid detection. These results suggest the potential for the system to overcome critical drawbacks of conventional COVID-19 molecular diagnosis by speeding up the detection process to enable expeditious treatment-related measures taken by medical personnel during emergency situations. The nSLAM system was also tested using the estrogen receptor 1 (ESR1) gene model, a ctDNA biomarker from metastatic breast cancer, which resulted in a successful detection of as low as ~1 aM concentration using 40 PCR cycles and reduction to 10 PCR cycles (~18 min runtime) for 1 fM ESR1 detection. The detection results provide a solution to the crucial shortcomings of detecting ctDNA for liquid biopsy, as the short half-life and extremely low abundance of ctDNA in blood are supplemented by the rapid and ultrasensitive detection properties of the system. The system is a promising platform that can be used to detect cancer- and infectious disease-related genetic material in an ultrasensitive and rapid manner. The system also demonstrates great versatility that can be tailored to specific diseases by designing and substituting the primers used for amplification. We plan to further develop the system as a multiplex platform for simultaneous detection of various diseases.

3:45 PM SB05.13.04
Hybrid Bio-Electronic Memristive Neuromodulation Interface for Real-Time Adaptive Coupling Between Neuronal Populations Catarina Dias[1], Domingos Castro[2], Miguel Aroso[2], Joao Ventura[1] and Paulo Aguiar[2]; [1]University of Porto - Faculty of Sciences, Portugal; [2]i3S, Portugal

Significant efforts are being made to develop nanoscale electronic devices integrated into neuromorphic circuits capable of emulating the dynamics of natural synapses. The coupling between neuronal populations via artificial synapses bears great potential for therapeutic strategies focused on the monitoring and control of neuronal electrical activity. Such hybrid systems, effectively coupling biological and electrical components, are important milestones for the development of a new generation of neuroprosthetic devices aimed to address a number of challenging neurologic disorders [1]. Consequently, therapeutic strategies based on the direct modulation of neuronal electrical activity have been producing remarkable results, with successful examples ranging from cochlear implants to deep brain stimulation. Developments in these implantable devices are hindered, however, by important challenges such as power requirements, size factor, signal transduction, and adaptability/computational capabilities. Memristors, neuromorphic nanoscale electronic components able to emulate natural synapses, have gained attention as a core component is these hybrid systems, mainly because of their neuromorphic properties, small size and low power signature [2]. They are nanoscale two-terminal electrical components whose present conduction state depends on the electrical stimulus that has been previously applied to them. The dynamics of a memristor’s response to stimulation is analogous to that of synapses, presenting learned transitions from low to high conductivity states, and vice versa. Importantly, the timescale of these transitions can be made analogous to the plasticity timescale of learning mechanisms in the brain, such as synaptic short-term plasticity (STP), which acts on the range from seconds to minutes. Relevant proofs of concept have already been presented in the literature [3], but we argue that crucial aspects have not yet been demonstrated on how these memristor-based hybrid systems can effectively operate in a meaningful way. Here we show, for the first time, how biological *in vitro* hippocampal neuronal populations can be dynamically coupled with a memristive device acting as a synapstor, forming a hybrid bio-electronic system [4]. We demonstrate that the conductance state of a memristor can be changed by the electrical activity of biological neurons and mediate a dynamic connection between isolated spiking neuronal populations. Our system connects biological neurons to microelectrodes, amplifier, memristor, stimulator, microelectrodes, and back to biological neurons, in an effective real-time configuration that does not use software nor simulations. Using our system, we can have neuronal population B being effectively activated if, and only if, there is a consistent firing pattern of activity in population A (network bursting activity). Importantly, we demonstrate that our artificial synapse is capable of short-term plasticity, dynamically changing its conductance level in both directions. Our results pave the way for further implementation of elements able to perform more complex modulatory operations in neuronal populations. We envision very similar systems being used for the automatic detection and suppression of seizures in epileptic patients.

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4:00 PM SB05.13.05
Extended Functionality of Spherical Nucleic Acid for Biosensing Applications Eunhye Park and Jwa-Min Nam; Seoul National University, Korea (the Republic of)

Spherical nucleic acids (SNAs) are composed of inorganic core materials in cooperation with nucleic acids shell as soft material. The nucleic acid can be densely conjugated to the surface of the core material depending on the type of the core material. Polyvalent SNAs help in biosensing development because they provide a higher opportunity to recognize target strands. However, despite the widely applicable potential of DNA sequences on SNA, the function of nucleic acids has been limited in very simple operations. For example, colorimetric detection using gold nanoparticle assemblies triggered by target analytes is a common method in nanostructured biosensing applications. Previously, nucleic acid sequences worked simply to capture target strands or form DNA-mediated hybridization for core material assemblies.
To extend the functionality of the SNA nanoprobe, DNA nanotechnology can be combined with the SNA nanostructure. Accordingly, the way to exploit SNA for biosensors is to define a new role of nucleic acids layer on it. Nucleic acids can perform well-defined functions such as signal conversion or target amplification itself as far as the sequence-specific operating role is concerned. Target sequence conversions are useful when the target strands require high selectivity. For example, single nucleotide polymorphisms (SNPs) are challenging as target nucleic acids because there is only one single base mismatch between the analytes to distinguish specific targets, and the concentration of SNPs in biological samples is low. Consequently, converting sequences in high-density SNA nanoprobes allows similar target sequences to be transmitted to noticeably different sequences via encoding strand amplification. According to the experimental results, one target strand was encoded about 1000 strands in a distinctly different sequence. To distinguish four multiple targets of SNPs i.e., wild and mutant types, toehold-mediated strands displacement reaction on hydrogel microstructure has been designed as following detection process. Target sequence converting SNAs are enzyme-free amplification of targets and increased selectivity.
Furthermore, massively target strands hybridized SNA nanoprobe can be employed for the target amplification probe itself. To increase the target strand amplification efficiency, the nanoparticle-mediated cycle reaction has been developed under enzyme-free conditions with naked-eye detection. In each cycle, target amplifying SNA can exponentially increase the number of target DNA strands by up to 174^n folds during n cycles. The cycles can be repeated as enough strands are amplified. SNA-based target amplification showed four times higher detection efficiency than polymerase chain reaction (PCR), which is widely used for nucleic acid amplification with 2^n folds for n cycles. In addition, it was possible to detect the target strands up to 100 zM of target strands with a convenient detection process.

SESSION SB05.15/SB06.14: Virtual Joint Session: Probing NanoBio Interactions
Session Chairs: Gemma-Louise Davies, Mohamed Elsawy, Sahitya Movva, Deborah Sementa and Jacek Wychowaniec
Thursday Morning, April 27, 2023
SB05-virtual

8:00 AM *SB05.15/SB06.14.01
Engineering Peptide-Based Synthetic Condensates Lorraine Leon; University of Central Florida, United States

Biological condensates (membraneless organelles) are liquid droplets consisting of proteins and nucleic acids that form within cells via liquid-liquid phase separation. These droplets are dynamic, have been shown to coalesce within cells, and can form and dissipate in response to biological and environmental signals. Many condensates have multiphase structure where different cellular components are sequestered into different layers, each with their own function. Here we discuss designing synthetic condensates to understand the role of diverse molecular interactions within proteins on biological phase separation, investigate the encapsulation of small molecules and enzymes, and establish design rules for multiphase formation. The synthetic condensates are formed via complex coacervation of oppositely charged polypeptides. Complex coacervation is a liquid-liquid phase separation that occurs via enthalpic charge interactions and entropic effects from the release of counterions and hydration water. We have created a library of different polypeptide sequences that incorporate various charge patterns, hydrophobic amino acids, and aromatic amino acids in the sequence. In addition, our sequences incorporate different chiral patterns of amino acids that bias the formation of liquid complex coacervates by preventing hydrogen bonding between the polypeptides know to form solid polyelectrolyte complexes. With this library we aim to explore the effects on the stability, encapsulation selectivity, and materials properties of the coacervate phase. Moreover, we mix coacervate phases with different interfacial tensions to create multiphase droplets.

8:30 AM SB05.15/SB06.14.02
Apoptosis Cell Classification Using Phase Contrast Images Yuki Kikuchi, Yuki Okuhashi, Hiroaki Ishihata, Misato Kashiba and Satoshi Sasaki; Tokyo Univ of Technology, Japan

Materials that cause apoptosis of cancer cells should potentially be candidates for future anti-cancer drug. Apoptosis cell classification using AI will be an effective method to evaluate the effect. Characteristics of apoptosis cells are effectively identified from the fluorescence-stained images. The effectiveness will increase if the classification could be performed without stains.
γ secretase inhibitor (GSI) is reported to cause apoptosis of K562, a human chronic myelogenous leukemia cell line. We found that AI-based classification results of phase-contrast images of the cells were quite similar to those of fluorescence images. Factors that AI identified, but naked eyes could not identify, were examined. Biochemical change inside cells were studied in connection with morphological characteristics.

8:45 AM SB05.15/SB06.14.03
Recognition Functionality Mapping at a Single Molecular Level by Frequency-Modulation AFM Imaging Ryosuke Izumi, Masayuki Morimoto and Hitoshi Asakawa; Kanazawa University, Japan

Molecular recognition is an essential function in developing advanced materials, including biomaterials. The precise design of molecular recognition functionalities, such as selectivity, affinity, and stimuli-responsibility, is the most important challenge in this research field. There are many studies on the design of molecular recognition elements using macrocyclic molecules, metal-organic complexes, and biomolecules. The designed recognition elements can capture guest molecules based on specific interactions. In addition, developing characterization tools is equally important to understand molecular-recognition functionalities and apply the advanced materials to various fields. Depending on their application, the designed recognition elements are often fixed on material surfaces. We easily imagine that the functionalities of the fixed recognition elements are influenced by their orientation and distribution on the material surfaces. However, a molecular scale understanding of the functionalities of the fixed recognition elements is still challenging due to the lack of analytical methods. Although the functionalities, such as the amount of capturing guest molecules, can be investigated with conventional analytical techniques, understanding the functionalities of each recognition element at a single molecular scale is difficult due to the averaging over numerous elements in conventional methods.

To overcome the limitation of conventional analytical methods, a method based on frequency modulation atomic force microscopy (FM-AFM). The FM-AFM technique is known to have the capability to visualize subnanometer-scale structures of various molecules and materials in liquid. The subnanometer resolution of the FM-AFM technique in liquid is based on the high sensitivity for interaction forces acting on the tip apex (the detectable theoretical limit is four pN). Moreover, conservative and non-conservative (dissipative) forces are measured separately in FM-AFM imaging. The characteristics of the FM-AFM technique suggest establishing a novel analytical method to investigate the recognition functionalities at a single molecular level based on the FM-AFM.

In this study, molecular-scale investigation of recognition events was demonstrated by FM-AFM imaging with a guest molecule-modified tip. Metal-salen complexes were fixed on a Si substrate as a model of molecular recognition elements. Amino-terminated AFM tips were prepared in this study because the metal-salen complexes have reported the capture of amino-containing molecules through the formation of coordination bonds. The FM-AFM experiments were performed with the amino-terminated AFM tips and the metal-salen complex fixed substrate. As a result, the fixed metal-salen complexes were visualized in the height images constructed by the measured signal of conservative forces. In contrast, energy dissipation images showed that dissipative interactions occurred in only a part of the fixed metal-salen complexes visualized in the height images. The results indicate that only a part of the fixed metal-salen complexes can recognize the amino group at the tip apex. The difference in the recognition function between the fixed metal-salen complexes is most likely caused by their orientation and dynamics. Our results demonstrate that the proposed analytical method based on the FM-AFM techniques with guest molecule-modified tips has the potential to investigate the recognition functionalities of the fixed recognition elements at the single molecular level, indicating future contributions to the development of advanced materials with recognition functions.

8:50 AM SB05.15/SB06.14.04
Development of Injectable Silk Hydrogel for Nanoprodrugs Control Release Mengheng Yang, Anh T. Dao, Ryuju Suzuki, Yoshitaka Koseki and Hitoshi Kasai; Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan

In traditional drug delivery systems, nanoparticles tend to accumulate at tumor sites due to the enhanced permeability and retention (EPR) effect, resulting in therapeutic efficacy. However, in the process of transporting through the blood, there is inevitable diffusion of drug to the normal tissue, causing side effects and reducing efficacy at the tumor site. An approach for such problems is to selectively release the drug at the tumor site through localized drug administration.

Silk protein hydrogels are inherently suitable for biological applications due to their permeability, high water content, and structural properties compatible with cell membranes. Its biodegradability can also be modified and subsequently utilized to control the drug release behavior, making silk hydrogel a potential drug-loading material. In vivo, hydrogels can be broken down by proteases. By changing the properties of the hydrogel, the degradation rate of the silk hydrogel can be tuned, therefore achieving controllability over the drug release. The study of injectable silk protein hydrogels as drug delivery systems has achieved good results in research for breast and liver cancers, but the research focus of controlling water-insoluble drug loading and drug release properties of hydrogels has not yet been realized. The aim of this study is to fabricate silk protein hydrogels that could be used as nano-prodrug carriers.

To this end, systematic changes in silk hydrogel preparation conditions were screened, and the obtained hydrogels were then used to load and release various types of drugs. Changes in dissolution conditions and gel parameters such as temperature, sonication time, shaking, stirring time, etc., during the preparation of hydrogels are considered to be factors that affect the performance of hydrogels. The properties of silk protein hydrogels were analyzed by gel fraction, swelling ratio, degradation rate, FT-IR, XRD, rheometer and so on.

In this report, calcium chloride solution was used to dissolve fibroin to obtain hydrogels with gelation times ranging from 1 to 4 days. By changing the gelation conditions, hydrogels with different properties were obtained. In addition, the loading of nano-prodrugs (NPDs) has been preliminary investigated. The in vitro drug release behavior of drug-loaded hydrogels will be studied. We expect to create an injectable hydrogel in which degradability can be controlled in vivo. This means that drug release can be manually controlled.

8:55 AM *SB05.15/SB06.14.07
Cyclic Peptide/Polymer Conjugates for Therapeutic Applications Sebastien Perrier; University of Warwick, United Kingdom

We describe the synthesis, characterisation and therapeutic applications of bioconjugate based on cyclic peptides covalently attached to well-controlled polymeric chains. The conjugates assemble into short nanotubes (20 to 200nm) through the stacking of the cyclic peptide motives, with functionality imparted by the polymeric chains. The resulting constructs show remarkable properties in terms of cell penetration, and *in vivo* biodistribution.

9:25 AM SB05.15/SB06.14.06
Graphene-Conductive Ink Coated Laser Engraved Kapton Electrochemical Biosensor for the Detection of Dopamine and Interleukin 6 Dipannita Ghosh[1], Md Ashiqur Rahman[2], Javier Becerril[2], Melanie Suarez[2], Robert Freeman[2], Ali Ashraf[2] and Nazmul Islam[1]; [1]The University of Texas at Rio Grande Valley, United States; [2]University of Texas at Rio Grande Valley, United States

A novel electrochemical biosensor platform based on graphene conductive polyaniline ink and laser-engraved Kapton sensor has been developed for the detection of dopamine and IL-6. Dopamine is an important catecholamine neurotransmitter, and the abnormal concentration of dopamine has been linked to several neurological diseases. IL-6 acts as an important biomarker for prostate cancer detection. We have developed graphene-conductive Polyaniline ink (G-PANI) and laser-engraved Kapton sensor in this work. For the fabrication of the laser engraved sensor, CAD design has been utilized and the parameter of the laser system has been modified. We have used silver ink as contact pads and Autolab Potentiostat for the electrochemical analysis. Due to the superior electrical conductivity, graphene is an appealing sensing material. Conductive Polymers coupled with graphene exhibit better conductivity, tunable surface properties, superior biocompatibility, and stability. Polyaniline incorporated in graphene improves solubility in aqueous solutions and shows improved conductivity and stability. Doping with acids enhances and improves the electroactive behavior of Polyaniline, and so we have created a homogenous mixture of phytic acid, polyaniline, and graphene with a planetary mixer. The SEM images depict that the surface of G-PANI is smoother with the nanoporous structure with around 1 μm diameter. To evaluate the effectiveness of the developed electrode in detecting dopamine and IL-6, we have investigated electrochemical techniques (Cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS)) with Fe^{2+}/Fe^{3+} redox pair. The Nyquist plots obtained from EIS are almost perfect semicircles (a characteristic of non-diffusion-limited electrochemical processes), with the diameter substantially dependent on charge transfer resistance(R_{ct}). The diameter of the Nyquist semicircle decreases with the increase of conductivity of the electrode surface and a shift to lower R_{ct} values. From the obtained equivalent circuit, G-PANI ink has a very low Rct value (13.5Ω), compared to the unmodified one (58.7 kΩ). We have analyzed the sensitivity of our proposed inks by using Cyclic Voltammetry with 3 μM dopamine in a basic medium (pH 7.4) with a scan rate of 0.08 V s^{-1}. The anodic peak current of the cyclic voltammograms (CVs) is 22.17 times higher than the unmodified laser-engraved Kapton sensor. The limit of detection (LOD) of the unmodified and modified sensor has been calculated over the range from 0.5 µM to 5µM dopamine. The G-PANI modified sensor has a much lower LOD (0.4084 µM) compared to the unmodified one (1.441 µM). The calibration curve shows a linear relationship (R^2 =0.99832 for G-PANI modified Kapton sensor) between the anodic peak current (I_{PA}) and dopamine concentrations. The sensor has been mildly oxidized by ozonolysis for about 30 sec to introduce -COO- groups for the immobilization. The equivalent circuit obtained from the EIS spectra has a higher Rct (1.87 kΩ) after ozonolysis, due to the inhibition of the electron transfer between the modified electrode and the negatively charged redox species. After IL-6 antibody immobilization, R_{ct} increased (12.5 kΩ) because IL-6 antibody film acts as a kinetic barrier for the electron transfer of the redox marker. Under optimal analysis settings, the analytical performance of the G-PANI modified Kapton sensor is tested in the presence of varying amounts of IL- 6 antigens utilizing EIS methods (frequency range 10 kHz to 10^6 kHz). The limit of detection for IL-6 antigen detection was 62.1283 pg/ml. In the future, we will be working on developing flexible paper-based electrochemical sensors for environmental estrogen detection.

SESSION SB05.14/SB06.13: Virtual Joint Session: Tuning Nano Properties
Session Chairs: Gemma-Louise Davies, Anna Salvati and Rein Ulijn
Wednesday Morning, April 26, 2023
SB05-virtual

10:30 AM *SB05.14/SB06.13.01
Designing Bioinspired Materials for Therapeutics and Biosensin Molly Stevens; Imperial College London, United Kingdom

This talk will provide an overview of our work in the design of self-assembled, functionalised peptide and protein nanoparticles, hydrogels and bio-interfaces for applications in healthcare. These hybrid materials are of growing importance with potential applications including drug delivery and disease detection. We are developing high-throughput synthesis techniques to diversify peptide libraries and quickly survey properties of interest such as fluorescence and supramolecular behaviour [1]. Using molecular dynamics simulation, we can rationalise the different self-assembly behaviours across length scales and to understand the interplay of membrane-curvature and nanotopography at the biointerfaces to aid in the development of cell-active substrates [2]. With the design of peptide-polymer hybrid hydrogels, we are incorporating tailorable mechanical properties to self-healing injectable scaffolds with exciting applications in regenerative medicine [3]. We are exploiting the sensing capabilities of functionalised nanoparticles to engineer nanoprobes for in vivo disease diagnostics that produce a colorimetric response ideal for naked eye read-out [4] and for CRISPR-based preamplification free detection of ncRNAs (CrisprZyme) [5]. I will talk about how we integrate our portfolio of nanoparticle-based sensing probes for diagnosing and monitoring infectious and non-communicable diseases with integration to smartphone technology for mHealth approaches [6]. This talk will also provide an overview of our recent advances in Raman spectroscopy-based characterisation techniques for tracking the functionalisation in single nanoparticles [7]. Finally, I will discuss how we are actively engaging in efforts towards the democratisation of healthcare innovations [8].

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11:00 AM SB05.14/SB06.13.02
Culturing and Characterization of Primary Corneal Epithelial Cells on PGS Films for Cornea Tissue Engineering Sevilay Sahin[1,2], Ebru Demir[1,2], Kamal Asadipakdel[1,2] and Sibel Cetinel[1,2,3]; [1]Sabanci University Nanotechnology Research and Application Center, Turkey; [2]TUBITAK, Turkey; [3]Sabanci University, Turkey

The cornea is the transparent, avascular, watch-glass-shaped tissue at the outermost part of the eye. It is effective in good vision as it allows the light coming into the eye to be transmitted to the lens. The cornea consists of five distinct layers, which are the epithelium, Bowman's membrane, stroma, Descemet's membrane, and endothelium. The epithelium layer is the outermost layer of the cornea and is in direct contact with the outer environment. It has important functions such as water intake from tear and protection of the cornea from external factors. The corneal epithelium layer consists of 5-7 layers of corneal epithelial cells connected by tight junctions. Thus, selectivity is ensured in the intake of water and minerals from outside. The limbal epithelial stem cells in the limbus layer, which are located next to the cornea differentiate, and form corneal epithelium. By this stem cell source, corneal epithelium layer can be regenerated. The corneal epithelium is located on a thin layer consisted of collagen fibrils called Bowman's membrane. Bowman's membrane is a cell-free corneal layer and does not regenerate. Due to reasons such as keratoplasty being the only treatment method for corneal diseases, limited donor for transplantation and high donor age, corneal tissue engineering studies are of great importance.
In this study, it was aimed to mimic the corneal epithelium layer. Accordingly, corneal epithelial cells immortalized after being isolated from the human donor cornea were cultured on PGS films. The most suitable PGS films produced by different length pre-polymers were selected and the ability of the cells to show their properties on Bowman's membrane was examined. According to the MTS assay results, PGS membrane with longer pre-polymer chains provided better corneal epithelial viability. In addition to this, cytokeratin-3, which is the main corneal epithelial marker, was expressed in higher amounts in the cells cultured on PGS membrane produced with longer pre-polymers. This study presents a recent innovation for cornea tissue engineering and makes a significant contribution to the literature.

This work is funded by 2232 International Fellowship for Outstanding Researchers Program of TUBITAK (Grant number 118C371). The funder had no role in study design, data collection or analysis, the decision to publish, or the preparation of this abstract.

11:05 AM *SB05.14/SB06.13.03
Plasmonic and Magnetic Nanoparticles for Biomedical Application Nguyen T. Thanh; Univ College London, United Kingdom

The development of new chemical methods for the next generation of nanoparticles with very high magnetic moment, fine tuning Au nanorods and novel hybrid and multifunctional nanostructure is presented.
Detailed mechanistic studies of their formation by sophisticated and advanced analysis of the nanostructure allows tuning of the physical properties at the nanoscale; these can subsequently be exploited for diagnosis and treatment of various diseases. The studies are conducted to provide insight for future material design approaches. It will also help to identify the critical process parameters that can be manipulated in order to obtain the suitable physical properties for the intended applications.

Ref:

Storozhuk, L., Besenhard M. O., Mourdikoudis, S., LaGrow, A. P., Lees, M.R., Tung, L. D., Gavriilidis, A., **Thanh, N. T. K*** (2021) Simple and Fast Polyol Synthesis of Stable Iron Oxide Nanoflowers with Exceptional Heating Efficiency. *Journal of Applied Materials and Interface.* **13:** 45870−45880)
See more publicaiton here: https://scholar.google.com/citations?user=pK_qvc0AAAAJ

11:35 AM SB05.11.03
Commercializing Nano Implants—Real Human Clinical Evidence of Success in the Spine Tom Webster[1,2,3]; [1]Hebei University of Technology, China; [2]Saveetha University, India; [3]UFPI, Brazil

The incorporation of nanotechnology into medicine (termed nanomedicine) has often been criticized for a lack of human clinical translation. While numerous studies have shown the ability of nanomaterials to improve tissue growth (such as bone, cartilage, nervous system tissue, etc.), fight infection, limit inflammation, and kill tumors in in vitro or animal studies, it has been largely speculated that few nanomaterials have been commercialized into real products helping human health. This talk will show for the first time human data in which spinal implants were modified to possess nanotextures and have been implanted into humans over the past 5 years. Impressively, out of approximately 14,000 patients, there have been no cases of implant failure including no cases on implant infection. Mechanistic studies have demonstrated that nanotextured implants not only mimic the natural roughness of bone itself but also possess altered surface energy to adsorb endogenous proteins known to promote osteoblast (bone forming cell) functions while inihibiting bacteria functions. Such results represent some of the only results available demonstrating the successful use of nanotextured spinal implants in humans and further demonstrate that bacteria infection can be stopped through the use of nanotextures alone, and not antibiotics which are causing the emergence of harmful antibiotic resistance bacteria.

SYMPOSIUM

April 11 - April 27, 2023

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SESSION SB05.16/SB06.15: Virtual Joint Session: Design and Function of Peptide and Protein-Based Materials
Session Chairs: Gemma-Louise Davies, Lorraine Leon, Deborah Sementa and Jacek Wychowaniec
Thursday Morning, April 27, 2023
SB06-virtual

10:30 AM *SB05.16/SB06.15.01
The Coming of Age of De Novo Protein Design David Baker; University of Washington, United States

Proteins mediate the critical processes of life and beautifully solve the challenges faced during evolution. Our goal is to design a new generation of proteins that address current-day problems not faced during evolution. In contrast to traditional protein engineering efforts, which have focused on modifying naturally occurring proteins, we design new proteins from scratch to optimally solve the problem at hand. We now use two approaches. First, guided by Anfinsen's principle that proteins fold to their global free energy minimum, we use the physically based Rosetta method to compute sequences for which the desired target structure has the lowest energy. Second, we use deep learning methods to design sequences predicted to fold to the desired structures. In both cases, we produce synthetic genes encoding these novel protein sequences and characterize them experimentally. In this talk, I will describe recent achievements in de novo protein design, including the development of novel self-assembling protein nanomaterials. I will also highlight RFdiffusion, a powerful new guided diffusion model that generates proteins in a manner similar to the popular image-generating tool DALL-E.

11:00 AM SB05.16/SB06.15.02
Effect of Charge on Molecular Self-Assembly, Nanoscopic and Bulk Material Properties of Ultra-Short Peptides Mohamed A. Soliman[1], Abdulwahhab Khedr[1], Charlotte J. Edwards-Gayle[2], Jacek K. Wychowaniec[3] and Mohamed Elsawy[1]; [1]De Montfort University, United Kingdom; [2]Diamond Light Source, United Kingdom; [3]AO Research Institute Davos, Switzerland

Bioinspired *de novo* self-assembling peptides have been widely used for the development of soft biomaterials for a wide variety of biomedical and pharmaceutical applications, such as cell scaffolding for tissue engineering[1], controlled and localised drug delivery[2], biosensing[3], and many others. The meticulous control of peptide-based nanomaterial properties over the length scale, by molecular design, remains the main challenge for tailoring biomaterials properties to meet the application needs. In our group, we have recently adopted a minimalistic molecular engineering approach for the development of Ultrashort Ionic-complementary Constrained Peptides (UICPs), which were rationally designed to self-assemble into amphiphilic β-sheet nanofibers with unique hydrogelation properties and surface activity.[4] We have previously demonstrated the crucial role played by aromatic stacking for the formation and thermodynamic stabilisation of UICP β-sheet structures. Herein, we will show how charge interactions can be manipulated for fine tuning molecular self-assembly, morphology and size of nanofibrous structures formation and viscoelasticity of UICP hydrogels.

A library of 18 peptide sequences (4-5 residues long) was developed to study the effect of the sequence net charge, charge density distribution, reversal of charge order and ionic self-complementarity on their propensity towards self-assembly and gelation. Interestingly, 12 of these peptides self-assembled into β-sheet nanofibrous structures forming hydrogels at pH 4.5-5, as confirmed by ATR-FTIR, SEM, TEM, SAXS and oscillatory rheology. Full control over β-sheet content (ranging from ~30-80%), fibre morphology (thin fibrils, thick straight fibre bundles, twisted helical nanofibres, flat nanoribbons and nanotubes) and sizes (~4-67 nm in diameter), as well as gelation (critical gelation concentrations ranging from ≤7.5 to ≥100 mM) and viscoelastic properties (storage moduli G' ~0.1-100 KPa) was achieved by the careful positioning of both Glu and Lys residues at both C- and N-termini, in the sequence core and on both the hydrophilic and hydrophobic faces of the peptide chain. In essence, this design approach enabled/disabled lateral growth along the β-sheet ladder via electrostatic attraction (counter charge, anion-pi and cation-pi)/repulsion, hence controlling fibre thickness, morphology, entanglement, and the resulting viscoelasticity of the system. Our UICPs platform thus provides the flexibility in peptide molecular design for the manufacturing of soft biomaterials with versatile properties that can be in future tailored to the relevant biomedical application.

Acknowledgements

The authors would like to thank Rachel Armitage at De Montfort University for her assistance with SEM experiments and Natalie Allcock at University of Leicester for helping with TEM imaging. This work was funded by the Newton-Mosharafa fund awarded to A.K. and M.E. and the Egyptian Government missions' sector scholarship awarded to M.S. The authors are also grateful to Diamond Light Source for awarding beamtimes (SM28806 and SM28287) to this project.

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11:15 AM SB05.16/SB06.15.03
Co-Assembling Ultra-Short Ionic Complementary Peptide Emulgels for Controlled Delivery of Combination Anticancer Therapy for Glioblastoma Abdulwahhab Khedr[1,2], Mohamed A. Soliman[1,3] and Mohamed Elsawy[1]; [1]De Montfort University, United Kingdom; [2]Zagazig University, Egypt; [3]Cairo University, Egypt

INTRODUCTION

Assembling peptides represent a versatile chemical toolbox for the development of soft shear thinning nanomaterials exploited for a variety of biomedical applications. Herein, we developed two *de novo* ultra-short ionic co-complementary peptide sequences (5 amino acids long, each) capable of co-assembly into β-sheet nanofibers, immediately forming hydrogels upon mixing the countercharge peptide solutions. These peptides were designed based on the tetrapeptide Phg4.[1] These are the cationic peptide KPhg4 and the anionic counterpart $E(Phg4)^{Rev}$, in which the charged residues are alternating with phenylglycine (Phg) and distributed in a pattern conferring a charge co-complementarity between both sequences. Both peptides were characterized for molecular assembly and hydrogelation at the physiological pH 7.4, both individually and in combination where co-assembly into nanofibres is induced through counter charge interaction. Also, these biomaterials were used for emulsifying pharmaceutical oils, forming O/W emulsion hydrogels (emulgels). These dual-phase systems were used for loading both hydrophilic and hydrophobic anticancer drugs for sustained localised drug delivery against human malignant glioblastoma U87 MG cells.

EXPERIMENTAL METHODS

1. Emulgel formation: Peptide solutions were mixed at different molar ratios, pH and total peptide concentrations and at different O:W ratios. **2. ATR-FTIR spectroscopy:** Characterisation of peptides' secondary structures. **3. Thioflavin T assay:** Quantification of β-sheet secondary structures and for co-assembly kinetics. **4. Oscillatory rheology:** Characterisation of gels viscoelastic properties. **5. Scanning electron microscopy (SEM):** Characterisation of the emulgel's network and vesicular structures. **6. Transmission electron microscopy (TEM):** Characterisation of nanostructures morphology. **7. *In vitro* drug release. 8. Cell culture and cell viability assay:** Cytotoxicity assay of emulgels and drug-loaded emulgels against U87 cells.

RESULTS & DISCUSSION

Individual peptides neither self-assembled into β-sheet structures nor formed hydrogels at the physiological pH over a wide range of peptide concentrations. Mixing counter charge peptide solutions at pH 7.4 spontaneously formed self-supported hydrogels over a wide range of peptides molar ratios (1:9-9:1) of total peptide concentrations 10-50 mg/mL. The highest abundance of β-sheets was observed for mixtures prepared at and around the equimolar ratio with fast rate of co-assembly (equilibrium within 1 hour after mixing). Also, these peptide mixtures showed a unique surface activity, forming O/W emulsions when mixed with oily phase at 5-50 mg/mL peptide concentration and different O:W ratios (2:8-8:2). Oscillatory rheology showed that gel stiffness is controllable by fine-tuning molar ratios of peptide components. SEM showed the formation of microspheres (15-60 µm diameter) within the gel nanofibrous network for all formulations, with fibres diameter estimated using TEM. Plain gels with a net positive charge (high cationic to anionic peptide molar ratio) showed significant cytotoxicity against U87 cells. In addition, the hydrophilic anticancer drug; vincristine sulfate, loaded into the emulgel aqueous phase showed sustained drug release profiles over 96 hours with improved cytotoxicity against U87 cells. These results suggest that the physico-mechanical properties, drug loading capacity and cytotoxicity of these systems are dependent on pH, peptides molar ratio, total peptide concentration and O:W ratio, which in turn will have a direct effect on emulgel's anticancer activity.

CONCLUSIONS

In conclusion, these emulgels showed that the mesoscopic and bulk mechanical properties and cytotoxicity can be tuned by molecular design, pH, peptide concentration, and molar ratio and O:W ratio control, to develop biomaterials that can satisfy the needs of combination anticancer therapy.

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11:20 AM SB05.16/SB06.15.04

Self-Assembling Peptide Nanofiber Hydrogel as 3D Scaffolds for Corneal Stromal Cells Ebru Demir, Sevilay Sahin and Sibel Cetinel; Sabanci University, Turkey

The leading causes of corneal damage are keratoconus, Fuchs endothelial dystrophy, keratoconus, and corneal ulceration. Once corneal damage causes visual impairment or blindness, cornea transplantation is the best treatment option to restore vision. Corneal tissue engineering provides an alternative to corneal transplantation to overcome limited donor tissue availability and drawbacks of transplantation. However, the complex mechanical, structural, and optical properties of the cornea make tissue engineering a challenging application. The expected properties of a corneal tissue-engineered scaffold include water permeability, optical transparency, and mechanical strength along with biodegradability, biocompatibility, and porosity. Some of these properties such as superior optical transparency and biocompatibility can be provided by peptide-based hydrogels. In this study, two different self-assembled peptide hydrogels are investigated for corneal stromal tissue engineering. Both MAX8 and RADA16-I peptides convert into β-sheet-forming hydrogels at high ionic strength and physiological pH. <div>Additionally, MAX8 peptides are modified with three different peptide ligands to enhance cell adhesion and inhibit neovascularization in the scaffold during stromal regeneration. The peptide hydrogels demonstrated proper optical transparency between %90 and %100 and refractivity of 1,337 mimicking natural corneas while maintaining 3D structure for corneal stromal cell proliferation. Hydrogels made up of MAX8 exhibited 40 ±1 Pa, 35,68 Pa, and 78,20 Pa average crossover modulus with different biomarker ligands and RADA8 showed similar results. The gel recovery was also observed after 10 µN constant shear stresses were applied to both hydrogels. On the other hand, human stromal keratocytes continued expressing cell-specific markers, collagen-I and keratocan, in both hydrogel formulations indicating their potential applicability.

This work is funded by 2232 International Fellowship for Outstanding Researchers Program of TÜBITAK (Grant number 118C371). The funder had no role in study design, data collection or analysis, the decision to publish, or the preparation of this abstract.

11:25 AM SB05.16/SB06.15.05

Antimicrobial Activity of β-Sheet Forming Ultra-Short *De Novo* Ionic-Complementary Peptides Towards Wound Infections Mohamed A. Soliman[1,2], Abdulwahhab Khedr[1,3], Raymond Allan[1], Katie Laird[1] and Mohamed Elsawy[1]; [1]De Montfort University, United Kingdom; [2]Faculty of Pharmacy, Cairo University, Egypt; [3]Faculty of Pharmacy, Zagazig University, Egypt

Bacterial resistance is currently compromising the antibiotics activity that saved millions of people in the last 8 decades[1]. Recently, peptide-based hydrogels were introduced as soft, versatile, shear-thinning and thixotropic materials that can be sprayed for topical applications. Thanks to their biocompatibility, biodegradability and physicochemical tunability, peptide hydrogels have a great potential to be used as sprayable antimicrobial biomaterials for treatment of infected wounds. They might also overcome the antibiotic resistance through multi-mechanisms of bacterial killing. So, this work aimed to utilise ultra-short *de novo* ionic-complementary peptide sequences (4 – 5 amino acids) for the development of antimicrobial bionanomaterials based on the peptide self-assembly into β-sheet nanofibers and building networks of hydrogel in response to pH change.

Based on this, Phg4 peptide, previously reported by our group[2] was compared to 2 other Phg4 derivatives (EPhg4 and KPhg4) to investigate the role of charge type and distribution on the self-assembly into β-sheet fibers and hydrogel and whether such modifications could impart antimicrobial activity for the hydrogel. Interestingly, the three peptides self-assembled into β-sheet fibrillar assemblies and entangled to form hydrogels in response to pH change, as revealed from molecular (FTIR) and mesoscopic (SEM and TEM) characterisation. Critical gelation concentration (CGC) was significantly affected by peptide modifications, where it decreased from 37 mM for Phg4 to 15 mM for EPhg4, while KPhg4 showed to have the highest CGC at 75 mM concentration. Oscillatory rheology revealed viscoelasticity of hydrogels formed by the three peptides and ability to recover from shear stress i.e. thixotropic materials implying their sprayability. Hydrogel stiffness varied for the three peptides, with a storage moduli G' of 10 and 93 KPa for Phg4 and EPhg4 at 75 mM, respectively, however KPhg4 appeared as viscous weak gel that did not show linear viscoelasticity.

To investigate the inherent antibacterial activity of the three developed hydrogels, time killing point assays were carried out against the 2 bacterial species commonly responsible for causing wound infections (Methicillin-resistant *S. aureus*, gram positive and *P. aeruginosa*, gram negative). Strikingly, all hydrogels exhibited *in vitro* bactericidal behaviour against planktonic *P. aeruginosa MPAO1* (10^5 CFU/mL) within 2 hours (hrs) besides their ability to prevent *P. aeruginosa* biofilm formation in a concentration dependent killing manner where the higher the peptide concentration, the shorter the time needed for eradication that ranged from 2--8hrs. On the other hand, hydrogels of the three peptides did not show any antimicrobial activity against *MRSA NCTC 10442*, which was also confirmed by observation of bacterial cell morphology using SEM and confocal laser scanning microscopy (CLSM). Phg4-based hydrogel (92 mM) was then selected for further investigations and showed antibacterial activity towards both planktonic and surface population of four different clinical *P. aeruginosa* strains obtained from University Hospital Southampton NHS Foundation Trust in addition to other ESKAPE pathogens (*A. baumannii* 18X50606 and *E. coli* NCTC 8003, *K. Pneumoniae* ATCC 700831).

In conclusion, these ultrashort constrained ionic complementary peptides based on their stable self-assembly could be considered as a promising approach for treating wound infections as well as tackling the bacterial resistance and might be used as biomimetic ECM scaffolds for tissue regeneration at the wound site.

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11:30 AM SB05.16/SB06.15.06

Improving the Efficacy of Neovascular AMD Therapy with Long-Term Drug Delivery Systems Saliha Durak[1,2], Özlem Kutlu[1,2] and Sibel Cetinel[1,2]; [1]Nanotechnology Research and Application Center (SUNUM), Sabanci University, Turkey; [2]Faculty of Engineering and Natural Sciences, Sabanci University, Turkey

Neovascular age-related macular degeneration (nAMD) is a progressive condition that is common in individuals over 50 years of age and cannot be cured in 90% of patients, and is one of the most common causes of blindness affecting more than 200 million people worldwide. Current therapeutic approaches include periodic intravitreal injections of monoclonal antibody-based anti-VEGF (anti-Vascular Endothelial Growth Factor) drugs. In spite of successful progress in neovascular AMD therapy in recent years, anti-VEGF therapies have some limitations such as the high cost and limited half-lives of protein drugs, need for frequent intravitreal injections, intravitreal injection-related complications and inadequate response to some anti-VEGF drugs. Because of these drawbacks, new approaches need to be developed for long-lasting anti-VEGF drug delivery. Peptide drugs offer ease of production and storage,

extended drug shelf life and reduced costs. Currently, a drug using anti-VEGF peptides in the treatment of nAMD is not available and several anti-VEGF peptides in the literature are waiting to be evaluated for their efficacy in nAMD therapy. This project aimed to develop a composite drug delivery system consisting of poly(glycerol sebacate) (PGS) nanoparticles and cross-linked hyaluronic acid hydrogel that reduces the frequency of intravitreal administration by providing sustained release (up to 6 months) of anti-VEGF peptide drugs as a new generation treatment method.
In this study, PGS nanoparticles obtained by solvent evaporation method have high encapsulation efficiency (93,7%) and their size was around 200 nm. HA-DVS crosslinked hydrogel was synthesized by Oxa-Michael addition reaction and successful crosslinking was confirmed by FTIR spectroscopy. Drug delivery system was formed by incubating anti-VEGF peptide loaded PGS nanoparticle solutions with crosslinked HA-DVS hydrogel to have 25% (v/v). The *in-vitro* drug release from drug delivery system was less than 20% in the first month, consistent with the targeted long-term release profile. It was demonstrated by calculating cell viability that the anti-VEGF peptide loaded drug delivery system does not cause cytotoxic effects on human retinal pigmented epithelial (ARPE-19) cells for up to 72 hours. The inhibition effect of anti-VEGF peptide on angiogenesis was determined by calculating cell viability and examining tube formation by incubating human umbilical vein endothelial cells (HUVEC) with anti-VEGF peptide-loaded drug delivery system.
Developing new generation biomaterials for the storage and preservation of therapeutic peptides and improving their bioavailability with prolonged release will significantly improve the efficiency of long-term treatment strategies for neovascular AMD.

11:45 AM SB05.11.02
Versatile Use of Tyramine-Modified Self-Assembling β-Sheet Peptides and Hyaluronic Acid Hydrogels—From Design and 3D Printing to Immunomodulation Jacek K. Wychowaniec[1], Ezgi I. Bektas[1], Andrea J. Vernengo[1], Charlotte J. Edwards-Gayle[2], Marcia Mürner[1,3], David Eglin[4] and Matteo D'Este[1]; [1]AO Research Institute Davos (ARI) | AO Foundation, Switzerland; [2]Diamond Light Source, United Kingdom; [3]ETH Zürich, Switzerland; [4]Mines Saint-Étienne, France

Multifunctional biomaterials which exhibit well-defined physicochemical properties and encode spatiotemporally controlled biological signals have the potential to act as next generation advanced systems modulating cellular behaviour. Within tissue regeneration field one of the commonly arising themes is impaired regeneration associated with the compromised immune system.[1] One solution to tackle this issue is to design immunomodulatory biomaterials that temporally control the overall level of inflammation.[1] For example, it has been shown that molecular weight of hyaluronic acid (HA) directly influences the polarization state of macrophages.[2] Designing functional materials that incorporate immunomodulatory effects, biocompatibility and that allow stable long-term polarization of macrophages is therefore of high interest in tissue engineering and 3D bioprinting.[1]
Self-assembling β-sheet forming peptides and tyramine-modified HA (THA) are two examples of biopolymers that have been shown as vital biomaterials spanning advanced cell culture systems up to effective minimally complex microenvironments for the generation of organoids.[3, 4] The role of these materials interfacing immune cells is not yet fully uncovered, therefore here we designed a selection of hydrogels built from self-assembling β-sheet forming peptides[5] and THA,[6] that can be processed by 3D micro-extrusion printing. A selection of peptide sequences was based on the alternation of hydrophobic and hydrophilic amino acids: **DABACABACD** (**A**: hydrophobic residue: **F** phenylalanine or **Y** tyrosine, **B**/**C**: hydrophilic residue e.g.: **K** lysine or **E** glutamic acid). THA of two molecular weights (280 kDa and 1640 kDa) were synthesized as previously described.[6]
A parametric study was carried out on the designed selection of **DABACABACD** peptides to verify the effect of rational peptide sequence modification on final physicochemical properties of peptide alone and peptide-THA composite hydrogels. **D** residues were rationally varied between hydrophobic (**Y**) or hydrophilic (**E**) amino acids to modulate the interactions' ability of formed β-sheet edges and shell with other peptide fibres and THA. All parental peptides self-assembled into semi-flexible networks and hydrogels above critical gelation concentration in the region of 2.5-5 mM and display characteristic high β-sheet content. Self-assembly, rheological properties and printability of both peptide and peptide-THA hydrogels can be controlled by the choice of primary peptide sequence, fabrication technique and final crosslinking mechanisms including enzymatic (horseradish peroxidase, H_2O_2) and visible green light crosslinking using Eosin. For the first time we also demonstrate the polarization effects of the supplemented THA on macrophages differentiated from human peripheral blood mononuclear cells over 5 days. M1 and M2 polarization modulated by the supplementation with low and high molecular weight THA were unravelled by the semi-automated image analysis from confocal microscopy, gene expression analysis and ELISA.
In summary here we uncover the link between basic molecular interactions driving self-assembly of functional tyramine modified peptide-based and hyualuronic acid-based biomaterials and demonstrate their capabilities as extrudable platforms for immunomodulatory tissue engineering.

Acknowledgements
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SESSION SB06.01: Design Rules for Peptide and Protein-Based Materials I
Session Chair: Joel Schneider
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2020

10:30 AM *SB06.01.01
Peptide-Enabled Design of Therapeutic Supramolecular Polymers Honggang Cui; Johns Hopkins University, United States

The physicochemical, biological, and responsive features of supramolecular polymers (SPs) enable their unique applications in many biomedical settings. By leveraging the assembling and biological features of short peptides, we have developed a class of therapeutic supramolecular polymers that are formed by self-assembly of rationally designed peptide-drug conjugates. Depending upon the drug's intrinsic assembling potential and its water solubility, various peptide designs were adopted to promote the drug's association into discrete supramolecular polymers that could further entangle into hydrogels. Our results suggest that the critical micellization concentration of an individual SP has a significant impact on their biodistribution and pharmacological behavior for systemic delivery, which is reflected in the maximum tolerated dose, tumor accumulation, toxicity, and eventually the therapeutic efficacy in suppressing tumor growth. On the other hand, the drug-based supramolecular hydrogel can be used for the local delivery and sustainable release of immune-modulating agents, and this localized chemoimmunotherapy hydrogel offers great potential to augment antitumor immune response and to sensitize tumors to immunotherapies in a safe and effective manner.

11:00 AM SB06.01.02
3D Printed Hydrogels: Engineering the Properties and Performance via Side Chain Design of Block Co-Polypeptides Stars Ronnie V. Garcia, Elizabeth Murphy, Nairiti Sinha, Yoichi Okayama, Robert Murphy, Matthew E. Helgeson, Javier Read de Alaniz and Craig Hawker; University of California, Santa Barbara, United States

Polypeptide-based hydrogels are of increasing importance due to their intrinsic biodegradability and tunable functionality that make them desirable for biological applications. While mechanical stability and shear processing properties has been demonstrated in many extrusion-based applications, ranging from injectable therapeutic carriers to recent 3D printing of living materials, probing the relationship between polypeptide structure and self-assembly has not been well studied. Herein we describe the synthesis and properties of a library of amphiphilic block-co-polypeptide stars with various canonical and non-canonical amino acid building blocks. Structure-function relationships were characterized using various rheological and scattering techniques to elucidate design rules for 3D printing. Significantly, non-natural amino acid building blocks were observed to form more stable networks with superior material properties compared to their natural analogs. The rational design of these materials provides a novel strategy for accessing tunable material properties based on molecular design that further expand the palette of 3D printable biomaterials.

11:15 AM *SB06.01.03
Controlled Assembly of Sequence-Defined Peptoids into Hierarchical Materials Chun-Long Chen; Pacific Northwest National Laboratory, United States

As one of the most common and well-developed peptidomimetics, peptoids have recently received increasing attention for the design and synthesis of functional materials with hierarchical structures.[1] Due to the unique proteinase-resistance, chemical and thermal stabilities of peptoids, peptoid-based nanomaterials are promising candidates for applications in photonics,[2, 3] flexible electronics,[4] and biological systems.[2, 3, 5] Recently, by designing amphiphilic peptoids that contain aromatic hydrophobic domains, our team recently reported their self-assembly into highly crystalline membrane-mimetic 2D nanosheets[2, 6] and 1D nanotubes,[7] we demonstrated that these peptoid materials are highly stable and a wide range of functional groups can be precisely placed within these materials to achieve programmable functions. To gain a better understanding of their formation mechanisms of these biomimetic materials, herein, I will report our recent discovery of designing short peptoid oligomers for controlled assembly into twisted nanoribbons, helices, along with nanosheets and nanotubes. Mechanistic studies using X-ray diffraction, AFM, TEM combined with computational simulations indicate the asymmetric packing of amphiphilic peptoids is the main driving force that leads to the formation of twisted nanoribbons and nanohelices. Tuning hydrophilic side chain chemistry, the number of hydrophobic side chains, and the solution pH can significantly influence the peptoid assembly pathways and dynamics for the formation of hierarchical materials with designed morphologies.

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11:45 AM SB06.04.03
Spontaneous Alignment of Self-Assembled Cationic and Amphiphilic β-Sheet Peptides Gal Yosefi, Hanna Rapaport and Ronit Bitton; Ben-Gurion University of the Negev, Israel

Many of the bio-functionalities in living systems rely upon the alignment of the tissue (e.g., bones, heart, and spinal cord); hence aligned materials are very attractive for biomedical applications such as scaffold creation for tissue engineering. Scaffolds composed of self-assembling peptides offer biocompatibility and the versatility necessary to create tailor-made materials. Yet, utilizing the material's ability to self-assemble to create an aligned material without the application of external stimuli is still a challenge.
Here we present a novel material based on amphiphilic and charged β-sheet peptide (Pro-Lys-(Phe-Lys)$_5$-Pro) that undergoes a spontaneous time-dependent isotropic–nematic phase transition in an aqueous solution without the need for any external force.
This natural, timely orientation of the peptide fibrils in an aqueous solution, confirmed by small angle x-ray scattering and cryo-transmission electron microscopy, creates a highly dynamic system, for which the degree of alignment and the time required to achieve a complete isotropic–nematic phase transition is found to be concentration dependent and can be predicted by a model based on Onsager's excluded volume theory. Remarkably, the nematic phases remain aligned over the course of several months without the application of any external stimuli and can be cross-linked to form aligned gels by mild shearing through a salty medium.
This spontaneously aligned peptide-based material offers a novel platform for various biomedical applications such as bio-sensors, tissue engineering scaffolds, or drug delivery vehicles.

SESSION SB06.02: Biomedical Applications of Peptide and Protein-Based Materials I
Session Chairs: Mibel Aguilar and Rein Ulijn
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2020

1:30 PM *SB06.02.01
Peptide-Based Functional Coatings and Assemblies That Resist Bacteria, Viruses and Fungi Meital Reches; The Hebrew University, Israel

The lecture will present bio-inspired functional coatings and assemblies that are spontaneously formed by short peptides. These peptide-based coatings self-assemble on either biotic or abiotic surfaces under mild conditions without any need for a curing step. The coating can serve many functions. One application is preventing biofouling - the undesirable adhesion of biomolecules and organisms to surfaces. This process leads to numerous adverse phenomena including hospital-acquired infection, blockage of water desalination facilities, and food contamination. We showed that this coating prevents the first step of biofouling, which involves the adsorption of bioorganic molecules to the substrate. Moreover, the coating significantly reduces the attachment of various organisms to surfaces. Another function that these peptide-based coatings can mediate is the adhesion of mammalian cells to implants. This function is important for the integration of implants into the human body. Finally, we showed that these peptides self-assemble in solution into particles that can be incorporated into polymeric films by co-extrusion and act to reduce the number of bacteria, fungi, and viruses on the surface.

2:00 PM SB06.02.02
Ultrashort Peptides as Versatile Materials for Biomedical Applications—From Scaffolds for 3D Cell Culture to Strong Adhesives. Panagiotis Bilalis, Abdulelah Alrashoudi, Hepi Susapto, Manola Moretti, Salwa Alshehri, Sherin Abdelrahman and Charlotte A.E. Hauser; King Abdullah University of Science and Technology (KAUST), Saudi Arabia

Ultrashort amphiphilic peptides with a characteristic sequence motif and containing up to seven natural amino acids exhibit self-assembling dynamic behaviours under physiological conditions. Despite their small size, they can form α-helical, β-sheet and β-turn secondary structures in aqueous solutions. At higher concentrations, they form nanofibers, leading to hydrogels with a very high content of water (>99%w/w). These hydrogels are biocompatible, biodegradable, and generally non-immunogenic and can find applications as 3D cell culture substrates, bioinks for 3D bioprinting, hemostatic agents, drug delivery systems, materials for soft tissue repair and others. Inspired by nature and particularly by the mussel's foot proteins that consist of a high content of a modified amino acid, 3,4-dihydroxy-L-phenylalanine (L-DOPA) and by introducing L-DOPA to the ultrashort peptide sequence, we successfully developed hydrogels with adhesive properties for wet environments, while keeping the characteristics of self-assembly. Moving a step forward by introducing a polymerizable group to the peptide sequence, we were able to crosslink the peptide-derived supramolecular structures to covalent polymeric networks. Toward this direction, we synthesized a peptide with catechol moieties and more than one vinyl group to act as a crosslinker. An aqueous mixture of our polymerizable peptide, the crosslinker and a water-soluble photoinitiator can be polymerized instantly under a LED light source to give a strong adhesive. This peptide-based glue cannot only glue objects that weigh more than two kilos but, most importantly can be applied under water. This type of adhesive peptide materials can be used for wound healing, as surgical adhesive glues, and in today's ecological challenges like coral reef restoration.

2:15 PM SB06.03.03
3D Bioprinting of Graphene Oxide-Incorporated Hydrogels for Neural Tissue Regeneration Jiahui Lai and Min Wang; The University of Hong Kong, Hong Kong

Hydrogels, especially natural hydrogels, have often been used for 3D bioprinting due to their numerous advantages, including excellent biocompatibility, biodegradability and similarity to natural extracellular matrix. However, natural hydrogels have shortcomings for 3D bioprinting, such as poor printability and very weak mechanical strength of printed structures. The incorporation of an additive (e.g., cellulose nanofibers, nanoclay particles, etc.) is an effective strategy to improve the performance (including mechanical performance) of natural hydrogels and may expand their potential applications in tissue engineering. The nervous system in human bodies is important as it regulates physiological functions and controls body activities. The native neural tissue is relatively soft and is sensitive to electrical stimulation. Therefore, materials used for neural tissue engineering should be soft and preferably have certain electrical conductivity. Owing to its good electron mobility and high surface-to-volume ratio, graphene oxidase (GO) is a promising material for creating electroactive hydrogels. Gelatin is a natural hydrogel obtained by denaturalization of collagen. It has intrinsic Arg-Gly-Asp (RGD) motifs and accessible active groups, which is desirable for tissue regeneration applications. However, gelatin alone is rarely used for 3D bioprinting because it is in the liquid state at 37 °C and hence cannot maintain the shape of a printed structure during its use in the body. Gelatin methacryloyl (GelMA) is a photocrosslinkable hydrogel that is derived from gelatin with the methacryloyl modification. After crosslinking, GelMA can maintain the shape of the printed structure. In this study, a natural hydrogel-based bioink (GO/Gelatin/GelMA) was developed by combining GO, gelatin, and GelMA, with the aim of obtaining a hydrogel with photocrosslinking ability, relatively soft nature, and improved electroactive properties. The performance of GO/Gelatin/GelMA composite hydrogels with different GO contents [0 ~ 0.1% (w/v)] was investigated in terms of microstructure, mechanical properties, degradation behavior, and water absorption properties. It was found that a low concentration of GO in the composite hydrogel had little effect on the microstructure of hydrogels, improved the mechanical strength slightly (but still at a kPa level), reduced the degradation rate, and increased water absorption. The electrical conductivity of GO/Gelatin/GelMA composite hydrogels was enhanced with the increasing GO contents. The printability of GO/Gelatin/GelMA composite hydrogels was studied by printing out multi-layered grid structures using a pneumatic extrusion-type 3D printer. It was observed that GO/Gelatin/GelMA hydrogels formed smooth filaments after extrusion and could be printed into 10-layer grids with good shape fidelity. After crosslinking, the printed grid structures could maintain their shapes and be held by hand without collapsing. Finally, neural cells (i.e., astrocytes) were added into GO/Gelatin/GelMA hydrogels to form bioinks for 3D bioprinting. It was found that astrocytes maintained high cell viability after bioprinting and grew well after culturing of the scaffolds for several days. The GO-incorporated gelatin/GelMA hydrogels have shown good biocompatibility, biodegradability, good printability, balanced softness and improved electroactivity, suggesting their high potential for 3D bioprinting, as well as applications in neural tissue regeneration.

2:30 PM SB06.02.04
DNA Origami Directed Virus Capsid Polymorphism Mauri Kostiainen; Aalto University, Finland

Most known viruses protect their genome by encapsulating it inside a protein capsid. Viral capsids can adopt various geometries, most iconically characterized by icosahedral or helical symmetries. The assembly process of native capsids is highly cooperative and governed by the protein geometry, protein-protein as well as protein-nucleic acid interactions. Importantly, the absolute control over the size and shape of virus capsids would have imminent advantages in the development of new vaccines and delivery systems. However, tools to direct the assembly process in a programmable manner are exceedingly elusive or strictly limited to specific structures. Here, we introduce a modular approach by demonstrating DNA origami directed polymorphism of single protein subunit capsids. We achieve control over the capsid shape, size, and topology by employing user-defined DNA origami nanostructures as binding and assembly platforms for the capsid proteins. Binding assays and single-particle cryo-electron microscopy reconstruction show that the DNA origami nanoshapes are efficiently encapsulated within the capsid. Further, we observe that helical arrangement of hexameric capsomers is the preferred mode of packing, while a negative curvature of the origami structure is not well tolerated. The capsid proteins assemble on DNA origami in single or double layer configurations depending on the applied stoichiometry. In addition, the obtained viral capsid coatings are able to efficiently shield the encapsulated DNA origami from nuclease degradation and prevent the structures from aggregation. Therefore, these findings may in addition find direct implementations in DNA nanotechnology-based bioengineering by paving the way for the next-generation cargo protection and targeting strategies.

2:45 PM BREAK

SESSION SB06.03: Additive Manufacturing of Peptide and Protein-Based Materials—From Design to Applications
Session Chair: Honggang Cui

Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2020

3:30 PM *SB06.03.01
Protein-Engineered, Dynamic Hydrogel Bioinks for 3D Bioprinting Sarah C. Heilshorn and Lucia G. Brunel; Stanford University, United States

3D bioprinting has emerged as a promising tool for spatially patterning cells to fabricate models of human tissue. To date, most bioinks have been formulated with a focus on printability, while often overlooking the cell-interactive properties of the material. Here, we present a protein-engineered bioink material designed to have viscoelastic mechanical behavior, similar to living tissue. This viscoelastic bioink is composed of an engineered protein and a recombinant polysaccharide that are crosslinked through dynamic covalent bonds, a reversible bond type that allows for cellular remodeling over time. Viscoelastic materials are challenging to use as inks, as one must tune the kinetics of the dynamic crosslinks to allow for both extrudability and long-term stability of the printed structure. We overcome this challenge through the temporary use of small molecule catalysts and competitors that modulate the crosslinking kinetics and degree of network formation. These inks are used to print a model of breast cancer cell invasion, where the inclusion of dynamic crosslinks was required to allow cell invasion. Altogether, we demonstrate the power of protein-engineered, dynamic bioinks to recapitulate the native cellular microenvironment.

4:00 PM SB06.03.02
3D-Printing Biopolymer Gels with an Electric Field—A Simple Route that Avoids Nozzles, Heat and UV Light Wenhao Xu and Srinivasa R. Raghavan; University of Maryland, College Park, United States

3D-printing of hydrogels has attracted great interest in recent years. In particular, gels of biopolymers such as proteins (e.g., gelatin) or polysaccharides (e.g., alginate) are used to encapsulate cells, and these can serve as scaffolds for tissue engineering. The promise of 3D-bioprinting lies in custom-printing a body part, potentially using a patient's own cells. However, current 3D-bioprinting is a cumbersome operation that requires a large 'printer' and expensive 'inks'. The inks, i.e., suspensions of cells in a pre-polymer, are typically pumped through fine nozzles in the printer. As soon as drops of this suspension emerge out of the nozzle, they are converted into gels by heat or UV light. By rastering the nozzle in 3D, a solid gel is built from the ground up (in layer-by-layer fashion) in a desired shape. Issues with this approach include the fact that the use of high shear (in the nozzle) or UV light can damage sensitive cells. Moreover, conventional 3D-bioprinting is slow and requires hours to create a custom part.

Here, we introduce an alternative method for 3D-printing gels of biopolymers such as alginate. Our method uses moderate electric fields (DC voltages around 5 to 15 V) and a solution of the above biopolymer. The central idea is that the biopolymer is gelled at a precise location by applying the electric field through fine metal electrodes. By moving the electrode(s) in 3D space using an externally controlled XYZ stage, we can build a gel in a specific shape. A gel that is 2 to 3 cm tall can be formed in a matter of minutes with our technique. The gel is also highly robust and it can be lifted out of the solution and manipulated by hand within seconds after the printing is complete. Layered gels with different internal contents can be readily created by this technique. Thus, this electro-gelation strategy could serve as a rapid, inexpensive, and powerful alternative to conventional 3D-printing of hydrogels.

4:15 PM *SB06.03.04
Bioinspired 3D-Hydrogels for Bone-Tissue Regeneration Lihi Abramovich; Tel Aviv University, Israel

Bone is a highly regenerative tissue, thus in young individuals, most fractures are spontaneously healed. Yet, in cases of large bone defects, as observed after bone tumor resections, severe fractures, or inflammatory diseases, the template for orchestrated regeneration is lacking. Therefore, reconstruction of bone defects continues to be an enormous clinical challenge. Although autogenic, allogeneic, and xenogeneic bone materials have been widely applied to treat such defects, they possess potential limitations, including limited availability and donor site morbidity, potential immunogenicity, and risk for disease transmission. Biomimetic materials that can stimulate and accelerate bone formation represent a promising alternative. The implementation of such matrices for bone regeneration is hampered by several requirements, including a 3D porous architecture, biological activity, biocompatibility, and immunomodulation.

Here, we applied a co-assembly approach using hydrogel-forming peptides, resulting in a synergistic modulation of their mechanical properties to form extraordinarily rigid hydrogels which supported osteogenic differentiation based on cells-mechanosensing. Furthermore, we designed a multi-component scaffold composed of polysaccharides, short self-assembling peptides, and bone minerals. We demonstrate the formation of a rigid, yet injectable, and 3D printable hydrogel without the addition of cross-linking agents. The formed composite hydrogel displays a nanofibrous structure, which mimics the extracellular matrix and exhibits thixotropic behavior and a high storage modulus. This composite scaffold induces osteogenic differentiation and facilitates calcium mineralization.

This work provides a conceptual framework for the utilization of co-assembly strategies to push the limits of nanostructure physical properties obtained through self-assembly for the design of new biomaterials for tissue engineering applications.

4:45 PM SB06.03.05
3D-Printed Dipeptides with Programmed Crystallinity for Multilevel Anticounterfeiting Ji Tae Kim; The University of Hong Kong, Hong Kong

The self-assembly of peptides into ordered supramolecular structures is of great interest in the field of materials chemistry [1]. The existing self-assembly pathways, however, have not been able to achieve the spatial programmability in shape, position, and crystallinity required for micro-circuit integration, due to their dynamics with stochastic nature.

Here, we present an additive manufacturing method that enables hierarchical structuring of diphenylalanine (FF) dipeptides from molecular to sub-micrometer scales [2,3]. This method exploits a femtoliter ink meniscus to guide the self-assembly of FF in three dimensions, thereby enabling the printing of a freeform, crystalline FF microarchitecture. Importantly, the extent of crystallization can be controlled in situ by solvent engineering. We have demonstrated that one can turn the crystallization "on" and "off" at will during the printing process, enabling the spatio-selective programming of crystalline/amorphous phase distribution in a single printed body. This capability offers a single-step route to integrate dipeptide's functionalities – e.g., piezoelectricity, optical nonlinearity/anisotropy – into the body of complex structural parts. Successful demonstration of 3D digital polarization-encoded anticounterfeit micro-labels has proven the practicality of the developed method. In this talk, we will further discuss the prospects of our work for potential applications in bioelectronics and photonics.

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SESSION SB06.04: Biomedical Applications of Peptide and Protein-Based Materials II
Session Chairs: Aline Miller, Samuel Stupp and Rein Ulijn
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2020

8:45 AM *SB06.04.01
A Target-Oriented Approach for Materials Design Joel Schneider; National Cancer Inst, United States

Many drugs bind their biological targets selectively and reversibly with characteristic binding constants and on/off-rates. These same targets can serve as depots for drug loading, and be used as building blocks for the construction of new drug delivery materials. For example, self-assembling a given biological target should afford a material with a tunable copy number of selective binding sites that can house and subsequently release drug at predictable rates. We demonstrate feasibility of this approach by preparing gel networks by self-assembling amphiphiles containing the drug target of the antibiotic vancomycin. This drug kills bacteria by reversibly binding to the dAla-dAla dipeptide found within bacteria, inhibiting cell wall biosynthesis. Gel networks formed by dAla-dAla assembly serve as selective depots for vancomycin and provide sustained release of drug over months *in vivo*. Biophysical experiments and release simulations using mathematical models of mass transport dynamics indicate that drug release is largely dependent on the on/off-rates defining the reversible binding event between drug and target. Lastly, we demonstrate that the gel can be reloaded multiple times by simple tail-vein injection after releasing its cargo.

9:15 AM SB06.04.02
Transcytotic Intercellular Gelation Enables Cell Spheroids Jiaqi Guo[1], Fengbin Wang[2], Yimeng Huang[1], Hongjian He[1], Weiyi Tan[1], Meihui Yi[1], Edward Egelman[2] and Bing Xu[1]; [1]Brandeis University, United States; [2]University of Virginia, United States

Cell spheroids bridge the discontinuity between *in vitro* systems and *in vivo* animal models, but inducing cell spheroids by nanomaterials remains an inefficient and poorly understood process. We used cryo-EM to determine the atomic structure of helical nanofibers self-assembled from D-peptides, and used fluorescent imaging to show that endo/exocytosis of enzyme-responsive D-peptide assemblies results in intercellular gels that enable cell spheroids. Specifically, D-phosphopeptides self-assemble to form nanoparticles to undergo endocytosis. The nanoparticles, being resistant to proteolysis and partially dephosphorylated, go through exocytosis to the cell surface and turn into helical nanofibers, which act as the artificial matrices of intercellular gels to induce cell spheroids from either suspended or adherent cells. No cell spheroids form without the endo- or exocytosis, the phosphate triggers, or the shape-switching of the peptide assemblies. This study, coupling transcytosis and morphological transformation of peptide assemblies to form intercellular gels in situ, mimics biogenesis to form intercellular matrices, and demonstrates a biomimetic approach for regenerative medicine and tissue engineering.

9:30 AM SB06.04.04
Contactless Magnetically Responsive Injectable Hydrogel to Guide Aligned Tissue Regeneration Arianna Rossi[1,2], Franco Furlani[1], Giada Bassi[1,3], Catarina Correia[4,5], Carla Cunha[4], Anna Piperno[2], Monica Montesi[1] and Silvia Panseri[1]; [1]National Research Council, Italy; [2]University of Messina, Italy; [3]University of G. D'Annunzio, Italy; [4]i3S - Instituto de Investigação e Inovação em Saúde, Portugal; [5]ISEP - Instituto Superior de Engenharia do Porto, Portugal

INTRODUCTION
Human tissues have well-defined architectures and mechanical properties that play a crucial role in their functionality. Specifically, cellular alignment is fundamental in several tissues and organs such as spinal cord, muscle, tendon, and cartilage. Several well-oriented scaffolds, able to reproduce the crucial tissue microarchitecture and to sustain regenerative process, have been produced by various tecniques (e.g. bioprinting, electospinning, freeze-drying), but very few have shown translational applications also due to the invasive surgery necessary to be implanted. Injectable hydrogels can be transplanted *via* minimally invasive injection, but usually without displaying any aligned structure. In the present work, we developed an injectable hydrogel with anisotropic architecture by applying a static magnetic field (SMF), based on gellan gum (GG), a biocompatible and biodegradable polysaccharide, hyaluronic acid (HA) and magnetic collagen fibers (MagC) for skeletal muscle regeneration.
METHODOLOGY
GG (1%) hydrosol added of sodium citrate (0.1%) and HA (0-0.6%) can be injected at 37°C. The gelation occurs in the presence of cations (e.g. PBS, cell culture media, biological fluids) in few minutes. MagC are prepared by mixing the 1mg/mL magnetic nanoparticles to collagen type I at pH 7.4 in different ratios (1:1, 1:3), then they are added to the hydrosol. Mechanical properties were investigated by rheometer and dynamic mechanical analysis. An extensive 3D in vitro cell culture was performed to study cell muscle behavior (viability, differentiation, elongation) and immunomodulation of human and murine macrophage response by ELISA and flow cytometry analysis. Then the hydrogels were subcutaneously implanted and aligned in Wistar-Han rats. At 1, 3 and 7 days, the hydrogels and the surrounding tissue were processed for histological and immunohistochemical analyses. Potential toxicity was evaluated by analysing the spleen, liver, kidney, and lymph nodes.
RESULTS
The hydrogel could be easily extruded by a 30G needle. MagC embedded into the hydrogels were easily aligned by a short (<10 min) application of an external SMF (400mT, distance of ≈4cm) and, once gelated, it showed mechanical properties comparable to muscle tissue (12-19 kPa), and stress relaxation behavior was similar to human tissues when 0.3% HA was added. Additionally, the hydrogel did not negatively affected muscle cells viability and morphology, it enhanced their elongation on the magnetic fibers, and modulated macrophage polarization. Even in vivo, the hydrogel was easily injected and aligned, and no local or systemic immune reaction was detected.
CONCLUSION
In the present work, we developed a contactless magnetically responsive injectable hydrogel to direct aligned musculoskeletal tissue regeneration. *In vitro* analysis pointed out the system biocompatibility that was confirmed during the *in vivo* test, in which also was highlighted its ability to achieve an aligned architecture by a remote SMF application during the gelation.
The versatility of the proposed system can be expected to find application to several different minimally-invasive or endoscopic surgical interventions on different body parts that might benefit from the injection of anisotropic and bioactive materials, such as the heart, cartilage, brain, spinal cord.
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9:45 AM SB06.04.05
Nanoscale Infrared Spectroscopy Reveals Non-Specific Binding Mechanism of Edaravone—The Next Possible Drug to Cure Alzheimers Suman Paul[1], Tobias Gokus[1], Elina Berntsson[2], Sebastian Wärmländer[2] and Andreas Barth[2]; [1]Attocube Systems AG, Germany; [2]Stockholm University, Sweden

The research on Alzheimer is one of the most popular topics across the labs worldwide where much time is spent to test candidate drugs. Edaravone is one such inorganic salt insoluble in water sold under the brand name Radicava. In our research, Edaravone was incubated with Amyloid-β_{40} in four different ratios and samples were collected at different times. The results clearly demonstrated lesser fibrils when an increased amount of Edaravone was present. Further, we were able to study the interaction between Amyloid-β_{40} and Edaravone using neaspec's popular nano-FTIR method. We found that Edaravone uniformly and non-specifically binds to Amyloid-β fibrils.

10:00 AM BREAK

10:30 AM *SB06.04.06
Novel Functions in Peptide Supramolecular Materials Samuel I. Stupp; Northwestern University, United States

Over the past two decades our laboratory has investigated the supramolecular polymerization of molecularly modified peptides in water known as peptide amphiphiles. In media of high ionic strength, these systems form highly hydrated networks of nanoscale filaments with diverse architectures and peptide sequence dependent degrees of internal order. A very exciting platform of bioactive materials has emerged from these systems with unprecedented ability to signal cells and drive regeneration of tissues. The lecture will report on a recent breakthrough in this area identifying supramolecular motion in peptide materials as an important feature in their ability to signal cells. Another topic to be discussed is recent work on the integration of peptide supramolecular polymers with covalent polymers, which generates a wide variety of stimuli-responsive materials. These novel materials respond to light as well as magnetic and electric fields, and exhibit the ability to emulate behaviors expected from living creatures. These materials can mechanically actuate, exhibit locomotion on surfaces, swim in water, and exhibit phototactic movements. In these emerging robotic materials, the presence of supramolecular assemblies of peptides plays a key role. This lecture will also discuss a new emerging frontier in the area of peptide materials, namely the design of systems capable of self organizing into electro-active structures such as ferroelectric phases and of generating ionically conducting structures for devices.

11:00 AM SB06.04.07
Development of Bioadhesive Microcapsules as a New Cellular Treatment for the Diffuse Cartilage Lesions Desiré Venegas Bustos, Matilde Alonso and Jose Carlos Rodriguez Cabello; Bioforge, University of Valladolid, Spain

Introduction: Cartilage structures can be damaged causing two types of injuries: focal; the lesion is restricted to a concrete zone or diffuse; the lesion affects a broad area of the articular cartilage. This type of lesions appears due to the reduced self-healing capacity of articular cartilage. Diffuse damage is much more difficult to treat, usually restricted to palliative care or systemic anti-inflammatory treatments. This type of diffuse lesions have a high prevalence as the common type of degenerative processes.
More recently, cell-based approaches using autologous chondrocytes or mesenchymal stem cells (MSCs)[1] have been tested and it can even be found in some clinics. However, the efficacy of such cell-based treatment is controversial[2]. In general terms, the applied cells stay in the injection site only for short periods of time, so their regenerative potential is greatly reduced. The most promising approach is the combination of such cells with a biomaterial-based carrier that can play that role.
The general objective of the project, in order to resolve the previous task, is the development of bioadhesive and injectable cell microcarriers with the ability to regenerate the articular cartilage. This aim is materialized in the fabrication of multibiofunctional capsules that are able to promote the cell cargo with selective adhesion and location on the articular surface. To do so, special attention is paid to the cell-material interaction on both the inner and outer surface of the capsule by means of the inclusion of specific cell adhesion domains and sequences that promote the adhesiveness to collagen II and chondroitin sulfate.
The microcapsules are based on a novel kind of biomaterials, named Recombinamers that are polypeptide materials obtained by recombinant DNA technology. In particular, the core composition of the microcarrier is the Elastin-like Recombinamers (ELRs)[3].
Experimental methods: Recombinant DNA techniques have proven to be very powerful tools for the development of novel protein-based biomaterials. This class includes ELRs, which are protein-based polypeptides that comprise repetitive units of the Val−Pro−Gly−X−Gly (VPGXG)n pentapeptide, in which X (guest residue) could be any amino acid except
L-proline. ELRs are inspired by elastin, showing excellent biocompatibility, and they exhibit thermo-responsiveness in aqueous media.
The cloning and molecular biology for gene construction were performed using standard genetic-engineering methods. Production was carried out by recombinant techniques using Escherichia coli as the cell system. Purification was performed by several cooling and heating purification cycles (Inverse Transition Cycling) following centrifugation; the ELRs obtained in this manner were dialyzed against MilliQ water and lyophilized.
Results and discussion: Genetic engineering methods allowed the synthesis of the genetic construct capable of synthesizing the desired biomaterial. Biopolymer adhesion to the hyaline-cartilage matrix was demonstrated measuring the adhesion forces between our biomaterial and surfaces with collagen II and chondroitin-sulfate versus control surfaces and quartz-microbalance.
Tailored layer-by-layer (LbL) approaches allowed the encapsulation of cell spheroids of autologous chondrocytes and MSCs.
In vitro and ex vivo assays were performed using cartilage explants from patients surgically intervened, this type of analysis showed the derivatized ELR adhesion efficacy to the articular surface and the final liberation of cell spheroids encapsulated hoping to demonstrate the cartilage regeneration.
Conclusion: In conclusion, a novel protein-based biomaterial with adhesion to the hyaline-cartilage matrix was synthetized. Besides, cell spheroids were encapsulated by the polymer.
Hence, in this study could be possible overcome the limitations of the current treatments used in diffuse cartilage lesions and suppose an advance in regenerative medicine.

11:15 AM *SB06.04.09
Biomolecules for Non-Biological Things: Peptide 'Bundlemer' Design for Polymerizatoin and Hierarchical Solution Assembly Darrin J. Pochan; University of Delaware, United States

Self-assembly of molecules is an attractive materials construction strategy due to its simplicity in application. By considering peptidic molecules in the bottom-up materials self-assembly design process, one can take advantage of inherently biomolecular attributes; intramolecular folding events, secondary structure, and electrostatic interactions; in addition to more traditional self-assembling molecular attributes such as amphiphilicty and kinetic assembly pathway dependence, to define hierarchical material structure and consequent properties. A new solution assembled system comprised of theoretically designed coiled coil bundle motifs, also known as 'bundlemers', will be introduced. The molecules and nanostructures are not natural sequences and provide opportunity for arbitrary nanostructure creation with peptides. With control of the display of all amino acid side chains (both natural and non-natural) throughout the peptide bundles, desired physical and covalent (through appropriate 'click' chemistry) interactions have been designed to produce polymer nanostructures. One-dimensional nanostructures span exotically rigid rod molecules that produce a wide variety of liquid crystal phases to semi-flexible chains, the flexibility of which are controlled by the interbundle linking chemistry. The assemblies can be responsive to temperature since the individual bundle building blocks are physically stabilized coiled coil bundles that can be melted and reformed with temperature. Computational design is used to design bundlemers with different net charged character in order to manipulate their interactions in solution. Finally, rigid rod polymer chains can be processed into liquid crystals and fiber materials with a completely peptidic molecular foundation. Included in the discussion will be molecule design, hierarchical assembly pathway design and control, click chemistry reactions, and the characterization of nanostructure via electron microscopy, neutron and x-ray scattering, and rheological measurements, as well as inherent material properties (e.g. extreme stiffness, responsiveness to temperature and pH, stability in aqueous and organic solvents).

SESSION SB06.05: Complex and Dynamic Peptide Matter
Session Chair: Rein Ulijn
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2020

1:30 PM *SB06.05.02
Photocontrol of Peptide Self-Assembly and Catalytic Activity Alexander Kros; Leiden University, Netherlands

Coiled-coil peptides can be designed to self-assemble with high affinity and selectivity, leading to them being widely employed for the de novo design of synthetic biomaterials. Active control of coiled-coil peptide formation allows spatiotemporal control of their binding interactions, a property which has proven useful in synthetic materials and biological applications. Previous studies showed the ability of the hydrophobic core to adapt to different amino acids with different sizes and polarities. In particular, the use of light to reversibly control peptide structure has been investigated because of the high resolution and biocompatibility of this strategy. Previous efforts to reversibly photocontrol coiled-coil peptides relied on intramolecular cyclization to control peptide structure, or the intermolecular connection of two separate coiled coil strands with a photoswitchable linker. The incorporation of photoswitches in the binding interface of coiled coils has not yet been attempted, and provide a more direct route for control over their activity. Therefore the incorporation of photoswitchable azobenzene-based amino acids, which change structure and polarity through cis/trans isomerization, allow for photocontrol over coiled-coil assembly.

In a second example, we incorporated phenylazo-phenylalanine in betasheet formning peptides to obtain photocontrol in the mode of assembly. With the azobenzene units in a trans-form, betasheets were obtained while upon irradiation these were transformed in micellar structures. Introduction of histidines in the peptide design resulted in catalytic active betasheets, which could be reversibly switched upon irradiation of the azobenzen units. Both examples show that the introduction of azobenzene-derived amino acids in peptides yields photocontrol over the assembly and catalytic activity in various supramolecular assemblies.

2:00 PM SB06.05.03
Self-Sorting in Supramolecular Peptide Amphiphile Nanostructures Si Eun Lee, M H. Sangji, Liam C. Palmer and Samuel I. Stupp; Northwestern University, United States

Soft materials in nature, such as the extracellular matrix and the actin filaments and microtubules found in the cytoskeleton, are often composed of mixtures of molecules that co-assemble into functional multicomponent networks through precise control of supramolecular interactions. Creating synthetic materials with ordered structures which mimic complex natural fibrous networks that self-sort into individual populations offers a valuable approach to designing novel multi-functional tissue scaffolds for regenerative medicine. We recently reported that supramolecular twisted nanostructures formed from peptide amphiphile (PA) molecules exhibit different supramolecular chirality depending on the intermolecular hydrogen bonding, which is determined by the amino acid sequences used. Here, we demonstrate that PAs can be designed to self-sort into either separate nanostructures or co-assemble within the same nanostructures by mixing PAs of different peptide sequences that vary in their β-sheet strength but have the same electrostatics. We use atomic force microscopy (AFM) to reveal the nanoscale morphology of the assemblies, and confocal laser scanning microscopy (CLSM) to determine the distribution of fluorescently labelled PA monomers between nanostructures. By correlating the two imaging modalities on the same region of the samples, we show that the multicomponent PA mixtures can co-assemble or self-sort based on the supramolecular twist of the assemblies: when PAs that form left-handed nanostructures are mixed with PAs that form right-handed nanostructures, the two components self-sort. However, a PA that forms both left- and right-handed nanostructures can co-assemble with either PA to different extents. Our results demonstrate that the driving force for the self-sorting reported here is determined by the enthalpic penalty of the torsion required to change the twist of a peptide in a β-sheet and is controlled by the internal hydrogen bonding sequence.

2:15 PM SB06.05.04
Supramolecular Peptide Crystals with Hydrophilic and Hydrophobic Pores for Chemo-Mechanical and Mechano-Chemical Actuation Vignesh Athiyarath, Elma E. Naranjo, Xi Chen and Rein Ulijn; Advanced Science Research Center, United States

Water-responsive (WR) materials generate mechanical energy by drastically changing their dimensions with respect to changes in relative humidity.[1]
Peptides are versatile building blocks for supramolecular materials with tunable properties and functionalities. We recently started to explore supramolecular peptide crystals with aqueous pores as candidates for systematic understanding of water-bonding triggered actuation, and recently demonstrated the first examples.[2]
Based on these previous results, we hypothesized that, peptides self-assembling into hydrated crystals with flexible hydrophobic and hydrophilic pores can be developed as multifunctional chemo-mechanical actuators. We explore two main features: (i) development of addressable crystals that can access multiple phases with different porosity and mechanical properties through controlled environments; (ii) addressable porous crystals that control chemical reactions.
First, we demonstrate that WR crystals of peptides with aliphatic and aromatic side-chains can be utilized to develop crystals with tunable mechanical properties. A number of di- and tri-peptides with aromatic and aliphatic side chains were studied, giving rise to crystals with water pores that are interspersed with hydrophobic (aromatic or aliphatic) pores. We will provide our progress in establishing systematic understanding of how peptide sequence dictates crystal packing and porosity.
Second, we will discuss one example, dipeptide Leu-Ile, that shows remarkable multifunctional behavior. This peptide crystallizes from water at room temperature to form a 2.5 hydrate and under heating as 0.75 hydrate. Both the forms have hydrophilic and hydrophobic channels and are interconvertible, resulting in switchable porosity. Remarkably, we found that changes in heating and hydration allows us to access three additional polymorphs, with

different properties and porosities. All five forms are interconverted reversibly by controlling relative humidity or temperature accordingly. The changes in the H-bonding pattern of water channel in each structure influenced the porosity, mechanical and solid-state fluorescence properties. Thus, a single crystal of the dipeptide can be tuned reversibly for different mechanical strengths with the aid of relative humidity and temperature.

Due to the controlled mechanical actuation in response to water bonding, we reasoned that peptide crystals may be promising to control hydrolysis or condensation reactions. In order to study this aspect, WR crystals of the tripeptide His-Tyr-Phe, was investigated. These crystals have nanometer sized pores that allow for easy diffusion of various esters of *p*-nitrophenol. We observed that by applying changes in the relative humidity on these guest-included crystals, the crystals can be actuated (reversible pore closure) and esters can be hydrolyzed. LCMS measurements showed the presence of transesterification of ester-substrates with the tyrosyl -OH group of the peptide molecule, thus leaving the free nitrophenol. The mass corresponding to trans-esterified intermediate and *p*-nitrophenol were also observed in TOF-SIMS technique recorded in the solid-state. Thus, we show proof-of-concept of mechano-chemical actuation and reactivity of peptide crystals.

In summary, we demonstrate that short peptide crystals are highly versatile materials with tunable porosity and responsiveness to humidity and temperature. These materials can be designed for multifunctional chemo-mechanical actuation by choosing suitable sequence of amino acid components. These structures are based on short peptides and are therefore scalable and hold much promise as sustainable and biodegradable materials.

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2:30 PM SB06.05.05

Plant-Based Amyloids from Food Waste for Removal of Heavy Metals from Contaminated Water Wei Long Soon[1], Mohammad Peydayesh[2], Raffaele Mezzenga[2] and Ali G. Miserez[1]; [1]Nanyang Technological University, Singapore; [2]ETH Zürich, Switzerland

Water pollution is one of the major global threats brought about by industrial, agricultural, and any other anthropogenic activity. Heavy metals represent a large group of water pollutants that can accumulate in the human body, causing cancer and mutagenic diseases. Technologies currently used to treat polluted wastewaters of heavy metals employ chemical, ion-exchange, and membrane purification methods. However, high pressure and power requirements of membrane-based technologies require large energy input, making drinking water expensive and thus less affordable in developing countries. In this study, plant amyloid-carbon membranes consisting of sunflower and peanut amyloid fibrils were fabricated through a green and sustainable process and were used to remove toxic heavy metal pollutants to drinkable standards with negligible energy consumption. Protein-rich sunflower and peanut meals serve as low-cost raw materials obtainable from industrial oil production, from which proteins were extracted, isolated, and self-assembled into functional amyloid fibrils for heavy metal removal. These amyloid fibrils were incorporated into a carbon matrix to produce hybrid amyloid-carbon membranes, and were used to filter Pt-, Cr-, and Pb-containing water to produce water of drinkable standards containing < 10 ppb heavy metals with minimal energy input. This process can easily be upscaled due to its simplicity and minimal use of chemical reagents, pointing towards the future of low-cost yet efficient water treatment technologies.

2:45 PM BREAK

SESSION SB06.06: Design Rules for Peptide and Protein-Based Materials II and Bioelectronics
Session Chairs: Daniela Kalafatovic and Rein Ulijn
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2020

3:30 PM *SB06.06.01

Complex Morphogenesis out of Self-Organizing Polypeptide Recombinamers with High Intrinsic Disorder—From Bioinks to Biomorphs Jose Carlos Rodriguez Cabello; University of Valladolid, Spain

Natural structures are the result of complex hierarchical self-assembling processes. The complexity in those arrives from many fronts. First, the self-assembling molecules are already very complex in composition. Second, most, if not all, the organized structures correspond to far-from-equilibrium states. Third, in many cases they involve the concurrent self-assembling processes of different macromolecules. Fourth, dynamic interactions, environmental responsiveness and adaptability are common properties in those systems. In addition to all that, self-assembly of biological molecules seems to be the result of an order-disorder interplay in which intrinsically disordered molecules, or notable domains in them, play an essential role. Therefore, if one wants to understand and mimic such extraordinary processes, it is necessary to design model systems in which complexity, intrinsic disorder, dynamic behavior, and far-from-equilibrium states are preeminent. This draws a totally different paradigm to the one existing for the more conventional approach in designing most of the present self-assembling systems.

Recombinant technology is a powerful tool to fabricate such complex, but well-defined, and multifunctional macromolecules. Its polypeptide nature permits to include in their molecular design any peptide domain existing on natural proteins that can be of interest. On the other hand, as recombinamers are based in a totally synthetic DNA, the combination of peptide domains is essentially not restricted by any factor and, practically any composition of interest can be produced. Those may include even peptide domains that are not found in natural prote ins but they could be of interest.

During those last years, different recombinamers have been designed and tested in our lab. Some of the molecular designs have proven to be, for example excellent 3D bioinks [1]. In those, superior printability is obtained by an adequate programing, at molecular level, of a sequence of self-organizing events with different strengths and dynamics while showing excellent bioactivity and biocompatibility. In other cases, the combination of competing and independent self-organizing interactions some of them generating out of equilibrium stable arrangements has lead to the generation of complex 3D structures after a process of spinodal decomposition of T-sensitive high MW recombinamers with LCST behavior.

References

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4:00 PM SB06.06.02

Programmable Order-Disorder Transitions Triggering Supramolecular Assembly of Peptides Zachary Urbach, Adam Grosvirt-Dramen and Allon Hochbaum; University of California, Irvine, United States

Many critical biological processes rely on dynamic and biochemically responsive protein assemblies. But mimicking these features in synthetic materials is challenging due to the complexities of protein-protein supramolecular interactions and the specificity of ligand binding sites. To address this challenge, we have developed a platform for the programmable assembly of *de novo* peptides by balancing a disorder inducing sequence motif with structure-stabilizing, bioinspired intramolecular bonding. The assembly platform is based on coiled-coil interactions between peptide monomers and the subsequent supramolecular assembly of coiled-coil oligomer building blocks. pH and charge screening-dependent electrostatic repulsion within the peptide sequence provide a tunable driving force for disorder that disrupts specific peptide-peptide interaction interfaces, precluding assembly. Gating the assembly in this way provides control over the hierarchical assembly of complex supramolecular peptide nanostructures through control of a-helical secondary structure of the monomer. Combining this tunable disorder motif with structure-stabilizing and stimuli responsive disulfide bond staples results in a monomer sequence that assembles in response to either redox or enzymatic signals. The gating of supramolecular interactions in response to these stimuli represent key advances towards the interconversion of biological signals across bionic interfaces and the integration of synthetic biology with a synthetic materials toolkit.

4:15 PM SB06.06.03
Self-Assembled Peptides for Electronic and Piezoelectric Applications Sharon Gilead, Gal Finkelstein and Ehud Gazit; Tel Aviv University, Israel

In recent years, a key direction in the field of electronics and electro-optics involves the transition from inorganic to organic components, thus paving the way towards flexible and wearable electronic devices. Bio-inspired organic materials may be the next-generation of organic optoelectronic devices, based on self-organization principles, which allow facile synthesis, eco-friendliness, resistance to oxidation and no need for heavy metal doping. Recent advances in bioorganic nanotechnology have established the notion that very simple building blocks, such as dipeptides, can form regular nanostructures with distinct mechanical, optical, piezoelectric and electronic properties. In particular, members of the diphenylalanine (FF) peptide archetypical family have been shown to form various morphologies and ordered nanostructures such as tubes, rods, fibrils, spheres, plates and macroscopic hydrogels with nano-scale order. These unique self-assembled peptide materials may be useful in the emerging field of implantable medical devices, which requires biocompatible power solutions to enable continuous and wireless operation.
The abundant mechanical energy stored in our body, ranging from body motion, walking, breathing to internal movement of organs, heartbeats and blood pressure, can be converted into electrical energy by the piezoelectric effect to serve as an autonomic electrical source. Currently, the field of piezoelectric materials mainly relies on lead-based ceramic materials such as lead zirconate titanate (PZT). However, as lead is toxic and entirely non-biocompatible, there is an emerging need for alternative materials with strong piezoelectric performance, especially in the field of bio-applications. Piezoelectric bio-inspired materials have attracted significant attention in recent years as promising alternatives for currently used poisonous piezoelectric materials owing to their strong piezoelectricity along with their biocompatibility. Specifically, several studies have explored the piezoelectric properties of the FF peptide. Although significant progress has been made toward the functionalization of piezoelectric biomaterials, challenges in the formation of well-ordered nanostructures limit their application. Controlling the organization of such assemblies is a crucial milestone in engineering applicable piezoelectric materials since the magnitude of the piezoelectric response is dictated by the molecular organization at the nanoscale. Here, we demonstrate the functionalization of piezoelectric FF derivatives by nano-structural alignment. We have developed a custom-made measurement system for piezoelectric performance evaluation, calibrated using a commercially available piezoelectric material. Utilizing this system, we show the realization of self-assembled peptides as a promising piezoelectric alternative for bio-compatible energy solutions.

4:30 PM SB06.06.06
Dynamic Optical Systems Inspired by Cephalopods Nikhil Kaimal, Georgii Bogdanov, Aleeza Farrukh, Atrouli Chatterjee and Alon Gorodetsky; University of California Irvine, United States

Cephalopods (e.g., squids, octopuses, and cuttlefish) have captivated the imagination of both the general public and scientists alike due to their sophisticated nervous systems, complex behavioral patterns, and visually stunning coloration changes. By drawing inspiration from the structures and functionalities of tunable cephalopod skin cells, we have designed and engineered human cells that contain reconfigurable protein-based photonic architectures and, as a result, possess tunable transparency-changing and light scattering capabilities (1). In turn, we have visualized the refractive index distributions of analogous engineered cells with three-dimensional label-free holotomographic microscopy techniques, and as a consequence, we have developed a detailed understanding of the relationship between their global optical characteristics and subcellular ultrastructures (2). We have moreover extended these efforts to the predictive engineering of the refractive indices and light-scattering properties of multiple self-assembled protein-based platforms, both in vitro and in vivo (2,3). Finally, we have developed improved chemical and genetic strategies for manipulating the sizes, numbers, and refractive indices of our subcellular structures (4). Our combined findings may facilitate an improved understanding of cephalopod camouflage mechanisms and lead to the development of unique tools for applications in biophotonics and bioengineering.

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4:45 PM SB06.06.05
The Pyroelectricity in M13 Bacteriophage Han Kim, Kento Okada, Inseok Chae, Butaek Lim, Seungwook Ji, Yoonji Kwon and Seung-Wuk Lee; University of California, Berkeley, United States

Pyroelectricity serves important biological functions to sense the temperature of living organisms. However, the molecular mechanisms of pyroelectricity in biomaterials are not fully understood. Here we exploit the M13 bacteriophage (phage) as a model system to investigate the structure-and-function relationship of biological pyroelectricity. M13 phage possesses intrinsically aligned dipole structures originating from α-helical structures of the major coat protein (pVIII) arranged in a five-fold helical symmetry without an inversion center. We genetically engineer the tail part of the phage with six-histidine to fabricate vertically standing unidirectionally polarized phage structures on gold substrates. Through additional major coat protein engineering with different numbers of negatively charged glutamate, we investigate the chemical structure-dependent pyroelectric properties of the phage. M13 phage exhibits a pyroelectric coefficient of $0.058\ \mu\mathrm{C}\ \mathrm{m}^{-2}\ \mathrm{K}^{-1}$ upon heating. We also genetically modify the phage to sense different chemical environments based on pyroelectric sensing modality. Computation modeling and circular dichroism spectroscopy analysis verify that the unfolding of the α-helices of pVIII proteins can induce the phage protein polarization changes upon heating. Our phage-based approach to investigating bio-pyroelectricity will enhance our understanding of the thermos-electric behaviors of biomaterials and develop novel biomaterials that can be used for biosensors and electric energy generators in the future.

SESSION SB06.07: Poster Session I: Design Rules for Peptide and Protein-Based Materials
Session Chairs: Aline Miller, Jose Carlos Rodriguez Cabello and Rein Ulijn
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SB06.07.01
***In Vivo* Self-Assembly of Chimeric Ferritin for Multi-Functional Nanoparticle** KoungHee Kim[1], Mi-Ran Ki[1,2], Ki Ha Min[1,2], Sung Ho Kim[1], Jin Woo Shin[1] and Seung Pil Pack[1]; [1]Korea university, Korea (the Republic of); [2]Korea University, Korea (the Republic of)

Protein-based nanoparticles are attractive materials as carriers or templates in various fields because of several advantages: high biocompatibility and stability, uniform size, easy surface modification, and low immunogenicity. In particular, ferritin, one of the valuable nanoparticles, is an iron storage protein with a hollow form of a diameter of inner 8nm and outer 12nm. In ferritin, 24 monomers are arranged with 4-3-2 axial symmetry to form eight three-fold channels (N-terminal interface) and six four-fold channels (C-terminal interface), the diameter of 3~5 Å, which can make material diffusion between the outside and the inside. This structure formation is self-assembly and reversible assembly so that various materials such as drugs, dye, or metals can load inside. In addition, it can manufacture mixed forms with diversely modified monomers or control the number of functional monomers for a degree of activity. However, methods of reversible assembly-disassembly are often harsh enough to cause damage or incomplete assembly by applying extreme pH. Although most studies induce disassembly in pH 2 or 11 conditions, some researchers reported that it could not form intact at reassembly. This study produced a chimeric form without damage by simultaneously expressing two monomers using a dual expression vector. This method can make the chimeric form more easily without an additional purification process and loss of protein yield during manufacture. In order to check the ratio of each monomer and the difference in function according to it, silica forming peptide (SFP)-fused human ferritin monomer was used. The double expression confirmed that ferritin and SFP fusion ferritin were expressed at a constant ratio and gathered to form chimeric ferritin. The chimeric protein showed different sizes and functional properties than ferritins (non or SFP-fused form) composed of single monomers. This study showed that the form with two different monomers could be expressed intact in vivo to confer different functionalities on ferritin. Also, intact fabrication of protein-based nanoparticles combined with various functional tags will be applied more actively in nanotechnology.

5:00 PM SB06.07.02
Bioinspired Stiffness-Controlled Protein Filaments Based on Understanding Hydrodynamics and Molecular Self-Assembly of Constitutive Proteins Young Hyun Noh[1,2], Yong Ho Kim[2,2,2] and Minkyu Kim[1,1,1]; [1]The University of Arizona, United States; [2]Sungkyunkwan University, Korea (the Republic of)

Natural materials like collagen, microtubules, and muscle fibers feature ultralong, tough, and robust mechanical properties. This is induced by complex hierarchical structures formed by the self-assembly of stiffness-controlled filaments and fibrils. As a result, understanding dynamic mechanical properties and the self-assembly of filaments and fibrils has become the focus of studies aimed to better understand the hierarchical structures of natural fibers. Moreover, synthetic polymer-based filaments and fibrils with controlled stiffness have been developed for drug delivery and tissue engineering applications. Recently, protein-based filaments have received attention as synthetic counterparts for healthcare applications due to their biocompatibility and biodegradability. In addition, proteins have highly controllable monomers and diverse functionalities, and they can be genetically fused to yield versatile protein polymers that form exquisitely designed bioinspired filaments. It is reported that crosslinking self-assembled protein nanostructures allows for the preparation of the protein filaments, and modulating crosslinking density enables the control of the filament stiffness. However, methods to tailor the stiffness of protein filaments remains unclear due to the delicate processing required, including the complexity of the self-assembly processes involved with sophisticated molecular interactions.
Herein, we report bioinspired stiffness-controlled protein filaments via the molecular self-assembly of designed protein polymers with constitutive coil-like and rod-like proteins. Using molecular dynamics simulations, biosynthesis, and characterization methods, we found that the hydrodynamics of the coil-like protein component showed high flexibility such that curvature was generated in the filament structures, while the rod-like protein component enhanced the stiffness. This finding leads to the investigation of the fundamental relationship between chain topology for designed protein polymers and their composition, structure, length, symmetry, as well as their interdependence. Our work provides insights into the scientific principles of protein filaments toward constructing biomimicking hierarchically structured protein fibers, which can open new avenues for healthcare applications in drug delivery, tissue engineering, and regenerative medicines.

5:00 PM SB06.07.03
Injectable Hydrogels of Stimuli-Responsive and Surface-Adhesive Multi-Block Copolypeptides JaeHee Lee, Jae Sang Lee, Min Jeong Kang and Dong Woo Lim; Hanyang University, Korea (the Republic of)

Surface adhesive proteins biomimicked from mussel foot proteins (MFPs) have been of interest for tissue engineering and regenerative medicine. Especially, 3, 4-dihydroxyphenylalanine (DOPA) residues of MFPs play a major role in controlled adhesion on the various surfaces under wet conditions. In addition, stimuli-responsive multi-block copolypeptides composed of elastin- or resilin-based blocks are applied as injectable hydrogels for facile administration of various biomedical applications. In this study, ABA type tri-block copolypeptides composed of MFP and elastin-based polypeptide (EBP) with thermal responsiveness were genetically engineered, over-expressed in *E. coli* and non-chromatographically purified. Hydroxylation of Tyr residues of MFP middle block was executed by either mushroom tyrosinase or bacterial co-expression to finely control the degree of modification. Hydroxylated EBP-MFP-EBP (hEME) triblock copolypeptides showed different lower critical solution temperature (LCST) behaviors depending on concentration and hydroxylation as compared to those of unmodified ones. Especially, the hEME triblock copolypeptides under concentrated conditions showed thermally triggered hydrogelation within several minutes because of physical cross-linking of the aggregated EBP blocks above LCST and oxidation of DOPAs into dopaquinones with sodium periodate. Furthermore, the hEME triblock copolypeptide hydrogels exhibited controlled surface adhesion properties on the metal surface as well as porcine skin under wet conditions due to DOPA-mediated intermolecular cross-linking via oxidation. Moreover, to finely tune the surface adhesiveness on the various surface, concentration of sodium periodate, incubation time, and temperature were optimized so that the hEME triblock hydrogels showed maximum adhesive strength of approximately 0.7 MPa. In conclusion, the injectable hydrogels of stimuli-responsive block copolypeptides with surface adhesive properties would be potential as tissue adhesives or hemostasis biomaterials for tissue engineering and regenerative medicine.

5:00 PM SB06.07.04

Synthesis and NMR-Spectroscopic Investigation of Peptide-Coated Ultrasmall Gold Nanoparticles (1-2 nm) Lisa-Sofie Wagner[1], Kai Klein[1], Torsten Schaller[1], Felix Niemeyer[1], Christine Beuck[1], Kateryna Loza[1], Peter Bayer[1], Marc Heggen[2] and Matthias Epple[1]; [1]Universität Duisburg-Essen, Germany; [2]Forschungszentrum Juelich GmbH, Germany

Ultrasmall gold nanoparticles (diameter 1-2 nm) have become increasingly important in biomedicine in recent years. If they are functionalized with biomolecules, they can be used in cancer therapy or for targeted drug release. The nature and size of the biomolecule determined the interaction with the gold surface and the number of attached ligands, including their molecular footprint.
We have attached cysteine-terminated peptides of variable length to ultrasmall gold nanoparticles. Besides model peptides consisting of a terminal cysteine and a chain of alanine, bioactive peptides were attached. The nanoparticle size was determined by differential centrifugal sedimentation (DCS), diffusion ordered NMR spectroscopy (DOSY), and transmission electron microscopy (TEM). By taking advantage of the fact that NMR spectroscopy is possible for ultrasmall nanoparticles, we have extensively characterized the ligand shell on the nanoparticles, including the binding state, by NMR spectroscopy. We have also determined the number of ligands on each nanoparticle by NMR spectroscopy and determined the change of molecular footprint as a function of peptide size. The ligand exchange studies at different temperature and pH as followed by NMR indicated the stability of the nanoparticle-peptide assembly which is important for its biomedical application.

5:00 PM SB06.07.05
High-Strength Spider Silk Composite Fibers with Photocatalytic Functionality Yi Ting Chen[1], Li-Sheng Chiang[1], Bo-Chun Chen[1], I-Hsiang Tseng[2] and Ta-I Yang[1]; [1]Chung Yuan Christian Univ, Taiwan; [2]Feng Chia University, Taiwan

The dragline silk of the giant wood spider (Nephila pilipes) was utilized to develop titanium dioxide (TiO_2)/spider silk composite fibers for photocatalytic applications. The surface of the silk fibers was modified with TiO_2 nanoparticles using hydrothermal method. The reaction procedure was optimized in order to obtain TiO_2 nanoparticles well-attached on the surface of silk fibers without damaging their integrity. The developed spider silk composite fibers remain the high mechanical strength (0.9 GPa) and fracture strain of 20%. The methylene blue dye served as a model to evaluate the photocatalytic performance of the developed composite fibers. The experimental results show that the TiO2/spider silk composite fibers have great ability to degrade the methylene blue and also exhibited appreciable reusability. This study demonstrated the feasibility of using sustainable and mechanically robust spider silk fibers to obtain TiO_2 composite fibers for use in photocatalytic applications.

5:00 PM SB06.07.06
Probing Sequence-Dependent Orientation in VOC Binding Peptides During IPA Exposure Using Near-Edge X-Ray Absorption Fine Structure Spectroscopy Gustavo Sant'Anna[1], Nicholas Bedford[1], Daniel Sim[2] and Steve Kim[2]; [1]University of New South Wales, Australia; [2]Air Force Research Laboratory, United States

Human psychological stress and fatigue levels can be monitored in real-time through performance-related biomarkers such as volatile organic compounds (VOCs) present in the exhaled breath using peptide-based graphene field effect transistors (GFETs). Ultimately, the biotic/abiotic interface is responsible for VOC recognition and subsequent sensor. During VOC exposure, perturbations to the biotic/abiotic interface results in changes to the electronic structure of the graphene, triggering a measurable electronic response. Aromatic residues in the peptides are considered the strongest driving force for noncovalent peptide functionalization of the graphene surfaces. As such, π–π interactions are predicted to play an essential role in sensor performance and thus provide an opportunity for directed sequence design for sensor optimization.
In this work, we determined the overall orientation on various 7-mer VOC binding peptides with different aromatic content on the graphene surface using near-edge X-Ray absorption fine structure (NEXAFS) spectroscopy. Two set of peptides were studied, the first set of sequences was generated via AI and MD simulations for optimal IPA binding. The second set of peptides were modifications of the first set, where key aromatic binding residues were substituted with non-binding functionalities. Peptide orientation was determined on functionalized graphene surfaces before and after dosing with IPA within the NEXAFS chamber to monitor perturbations to peptide morphology under simulated sensors conditions. Overall, clear differences in orientation were determined with NEXAFS, showcasing clear sequence dependence on peptide surface morphology and their interactions with IPA during dosing. This understanding can assist with knowledge-driven development of new sequences for device optimization, which can be further extended beyond VOC GFETs and into various fields of biosensing.

5:00 PM SB06.07.08
Effects of Nanoconfined Water and Heavy Water on the Mechanical Properties of Supramolecular Crystals Janel J. Rivera-Cancel[1,2,3], Nicolas Giovambattista[1,2], Gustavo Lopez[2,4], Xi Chen[3,5] and Rein Ulijn[3,2]; [1]Brooklyn College, United States; [2]The City University of New York Graduate Center, United States; [3]Advanced Science Research Center, United States; [4]Lehman College of the City University of New York, United States; [5]The City College of New York, United States

Water responsive (WR) materials, which can undergo reversible changes in their conformation in response to a change in the relative humidity (RH), have recently gained attention due to the opportunities for them to be used as an energy source. For example, evaporation-driven engines can be powered by WR materials to directly harvest energy from the natural evaporation of water and convert it into mechanical work and electricity. However, little is known about the mechanisms involved in these WR materials or the role of water in these systems. In particular, the effects of deuterium oxide (D_2O) on the mechanical properties of WR materials and the interactions between water and biomolecules is still an open question. In this study, we compared the responsiveness of histidine-tyrosine-phenylalanine (HYF) peptide crystals to H_2O and D_2O and the role of nanoconfined water in the water-peptide interactions. We investigated the changes in the mechanical properties of HYF due to isotope substitution (H_2O and D_2O). We performed experiments using powder x-ray diffraction (PXRD), atomic force microscopy (AFM), and Fourier-transform infrared spectroscopy (FTIR) in a humidity-controlled environment with both, H_2O and D_2O vapor to study its RH responsiveness. We plan to complement our experiments by performing classical and path-integral molecular dynamics simulations.

5:00 PM SB06.07.10
Elastic Modulus of Engineered Polymeric Hydrogel Materials Modulated by Sequence-Controlled Protein Polymers Christopher Camp and Minkyu Kim; University of Arizona, United States

The mechanical properties of polymeric materials are affected by diverse factors such as the compositions and arrangements within individual polymers as well as the overall chain length. However, precise control of those parameters in polymers is not trivial while a heterogeneous distribution of polymer compositions and sizes are common. Such inconsistencies can cause issues with reproducibility of mechanical properties. As such, studies that focus on precise monomer arrangements are difficult without a well-controlled system with uniform chain length and reproducible polymer composition. We developed thermoresponsive artificial protein polymers that can be photo-crosslinked to construct hydrogels, and we used the polymeric hydrogel system as a tool to investigate how changing the arrangement of the monomers can affect the elastic modulus of crosslinked materials. The artificial protein polymer technology offers precise control of the sequences through genetic engineering, and biosynthesis techniques ensure homogeneous chain length.

We found that two protein homopolymers of different sizes showed no significant difference in their elastic modulus when the monomer repeats and crosslinking number were well-controlled in our system. Then, we rearranged the monomer sequences of the homopolymer to investigate a protein block copolymer such that within the block copolymer, the more hydrophobic monomers that can be used for crosslinking were moved closer together on one side with the overall chain length held constant. We found the elastic modulus was dramatically reduced compared to the homopolymer with the same total chemical composition due to the formation of self-assembled structures. The elastic modulus recovered in a protein polymer blend containing the block copolymer and the homopolymer with the same chain length. Therefore, we identified a polymer blend method to overcome some of the loss of the mechanical properties. Our findings can be used to advance the design and control the mechanical properties of polymeric materials for biomedical applications such as tissue engineering, regenerative medicine, and drug delivery.

5:00 PM SB06.07.11
Understanding the Role of Aromatic Architecture in Tuning Water-Responsive Behavior of Peptide Crystals Fahmeed K. Sheehan[1,2,3], Haozhen Wang[4], Darjan Podbevsek[2], Rein Ulijn[2,1,3] and Xi Chen[2,1,5]; [1]The Graduate Center at the City University of New York, United States; [2]The Advanced Science Research Center at the Graduate Center, United States; [3]Hunter College, United States; [4]Stanford University, United States; [5]The City College of New York, United States

Water-responsive (WR) materials that reversibly change structure in response to changes in humidity are increasingly recognized for their potential in energy-harvesting and actuation applications. These materials translate the chemical potential of water into a defined mechanical actuation. Examples in nature include pinecones which expand and release seeds when the local environment is dry. Peptides are versatile designed supramolecular materials[1] and we recently started to explore them as WR responsive materials. Specifically, we previously developed WR peptide crystals with aqueous pores and deformable aromatic regions to understand the fundamental actuation mechanism of WR materials and found that a strong H-bonding network to bind with water was crucial to water-responsiveness[2].

In here we systematically study the architecture and deformability of the aromatic regions and their influence on WR behavior. We selected three aromatic peptide crystals that each contain aromatic regions and aqueous pores, but distinct aromatic topologies: Phenylalanine (F), diphenylalanine (FF), and histidyl-tyrosyl-phenylalanine (HYF). Based on architecture alone, we expected FF, which is composed of a network of water pores connected through aromatic zippers, to be a strong WR material owing to its large aqueous pore and H-bonding network. Surprisingly, we found that the structural rigidity offered by its aromatic zipper structure prevented any shape change in response to changing humidity. On the other hand, F emerged as an extremely strong WR material with an energy density of 19.8 MJ/m^3, exceeding that of HYF at 6.5 MJ/m^3. Results from powder X-ray diffraction (PXRD) and Fourier-transform infrared spectroscopy (FTIR) confirm that F undergoes a crystal phase change between 60-70% relative humidity that results in its WR actuation. This contrasts with HYF which reversibly loses its lattice structure upon dehydration. Our observations suggest that FF, which is too rigid, cannot deform in response to humidity, whereas HYF, which is more flexible, does not respond efficiently. These findings show that water-responsiveness requires a fine balance between water-bonding and aromatic stacking domains, and they can inform the design of responsive aromatic peptide crystals and provide further insight into the WR mechanism of supramolecular materials.

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5:00 PM SB06.07.13
Fabrication, Structural Characteristics and Properties of a New Wool Based Non-Woven Fabric Hye Gyeoung Lee and In Chul Um; Kyungpook National University, Korea (the Republic of)

Silk sericin has a good biocompatibility, wound healing effect, and high water retention. Owing to the unique properties, it has been extensively studied to apply it to cosmetic and biomedical fields. Recently, a silk natural nonwoven fabric was successfully fabricated by using the adhesion character of sericin. In this study, a sericin was coated to wool fiber to provide a binding character of wool fiber and to improve the biocompatibility of wool. Also, the sericin coated wool nonwoven fabric was fabricated by carding, wetting, and hot press processes and the effect of the sericin amount on the structural characteristics and properties of the fabrics was investigated. It was found by FE-SEM observation that more sericin was well coated in wool fibers of the nonwoven fabric with increase of sericin addition. As the addition amount of sericin increased until a certain point, the breaking strength of the nonwoven fabric was increased, and then kept unchanged with further increase of sericin addition. Regardless of sericin content, all sericin coated wool non-woven fabrics showed a good cell viability.

5:00 PM SB06.07.14
Effect of Sericin Content on the Structural Characteristics and Properties of Silk Non-Woven Fabric Ye Eun Kim, Yu Jeong Bae and In Chul Um; Kyungpook National University, Korea (the Republic of)

Silk is composed of two biopolymers (fibroin and sericin) and a biomaterial with excellent blood compatibility, biodegradable and low inflammatory reactions in a body. Recently, a new natural silk non-woven fabric was successfully fabricated with simple treatment (wet and hot press treatment) attracting researcher's attention in medical and cosmetic applications. Although the mass production of new natural silk non-woven fabric was successfully done using an electric winder system, it is still necessary to reduce the production cost for various applications. In the present study, new silk non-woven fabrics were fabricated with new methods. Furthermore, the effect of sericin content on structural characteristics and mechanical properties of silk non-woven fabrics was examined. The sericin content in silk was diversely controlled by altering the degumming condition. As the sericin content in silk increased, the porosity, thickness, crystallinity, and elongation of the silk non-woven fabric decreased. On the other hand, the moisture regain and maximum stress increased as the sericin content increased. In addition, regardless of the sericin content, all silk non-woven fabrics showed an excellent cell viability.

5:00 PM SB06.07.15
Fabrication, Structural Characteristics and Properties of Silk Non-Woven Fabrics from Different Silkworm Varieties Yeon Jin Kim and In Chul Um; Kyungpook National University, Korea (the Republic of)

Since silk has good blood compatibility, excellent cyto-compatibility and minimal inflammatory reaction in a body, silk has been studied to apply it to biomedical and cosmetic applications including bone substitute, wound dressing, and mask pack. Recently, silk non-woven fabric has attracted researcher's attention because the mass production is possible using conventional facilities and good mechanical properties can be obtained. It was reported that various properties of silk can be obtained by using various silkworm varieties. Although a few silk non-woven fabric was prepared using the silkworm varieties previously, the related study has not been extensively. Therefore, in this study, the effects of different silkworm variety on structure and properties of silk non-woven fabrics were examined. Kumokjam resuled in white silk nonwoven fabric, whereas other silkworm varieties leaded to yellow colored nonwoven fabric. The weight distribution of the silk cocoons was different depending on the silkworm variety affecting reeling distance of cocoon. Daehwangjam showed the highest cocoon weight (0.88 g) and N74 exhibited the lowest (0.35 g). Interestingly, the reel-ability of the silk cocoons was strongly affected by the silkworm variety indicating the productivity of silk nonwoven fabric was determined by the silkworm variety.

5:00 PM SB06.07.16
Preparation, Structure and Properties of Silk Non-Woven Fabric with Different Cocoon Layers Yun Yeong Choi and In Chul Um; Kyungpook National University, Korea (the Republic of)

Silk is a natural composite material composed of continuous silk filaments and has been used as textile material for a long time. Thanks to the unique properties of silk including blood compatibility and cyto-compatibility, it has been studied as biomedical and cosmetic materials. Recently, a natural silk non-woven fabric was successfully fabricated using electric winder and hot press increasing its applicability to biomedical and cosmetic applications. In the present study, new silk non-woven fabrics were fabricated using electric winder. Silk fiber in different silkworm cocoon layers were used in the fabrication and the effect of the layer on the structural characteristics and properties of silk non-woven fabric was examined. As the silk in the outer layer was used, the crystallinity index of silk non-woven fabric was decreased and the moisture regain was increased. In case of mechanical properties, the breaking strength, elongation at break, and work of rupture of silk non-woven fabric were increased with using the silk in outer layer. All silk non-woven fabrics showed excellent cell-viability.

5:00 PM SB06.07.17
Biopolymer Design that Translates Single-Molecule Protein Nanomechanics to Macroscale Mechanical Properties of Polymer-Network Materials Samuel Kim[1], Marcus V. Cathey[1], Brandon C. Bounds[1], Piotr Marszalek[2] and Minkyu Kim[1,3,1]; [1]University of Arizona, United States; [2]Duke University, United States; [3]The University of Arizona, United States

Natural materials are a great blueprint for the development of next-generation biomaterials because of their exceptional physical, chemical, and biological properties. To mimic the unique properties of natural materials, protein-based polymer networks are utilized to develop well-characterized functional proteins that can be engineered into artificial protein polymers. However, it is still unclear how these artificial proteins can be incorporated into polymer networks that can properly translate protein nanomechanics. To translate protein nanomechanics to bulk mechanical properties, strong and specific cross-linkers is necessary to form stable polymer networks with reduced topological defects. Our recent work has shown that streptavidin tetramers fulfill the requirements and can be used to form protein-based polymer networks, potentially allowing the translation of protein nanomechanics to bulk hydrogel materials.

In this study, we investigated a novel mechanism involving streptavidin cross-linkers to determine optimal design components for producing protein polymer networks that can translate the single-molecule behavior into bulk mechanical properties. To properly mimic the reversible deformability of red blood cells and develop functional biomaterials for cardiovascular tissue engineering applications, ankyrin, a cytoskeleton protein from red blood cells were designed as artificial protein building blocks for fabricating polymer networks that can translate ankyrin nanomechanics to macroscale functional biomaterials.

SESSION SB06.08: Biomedical Applications of Peptide and Protein-Based Materials III
Session Chair: Meital Reches
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2020

8:15 AM *SB06.08.01
Self-Assembling Peptide Hydrogel Materials—From Lab to Commercialization Aline F. Miller[1,2]; [1]Manchester BIOGEL, United Kingdom; [2]University of Manchester, United Kingdom

Progressive efforts are been made to develop increasingly complex soft materials, driven by both fundamental curiosity and by urgent unmet clinical needs of an increasingly aging population. Self-assembling peptides have captivated attention as a key building block for the design of soft matter as they are inherently biocompatible and allow the design of stable, versatile hydrogels for use in a variety of biomedical applications. Here, I will discuss our platform technology for the design of hydrogels exploiting the self-assembly of short (8-12 amino acids) β-sheet forming peptides, and emerging themes in understanding and controlling their self-assembly and processability to create unique nanostructures and with tunable functionality, at scale. I will go onto exemplify how they are being translated from the lab into the clinic and finding application as supports for tissue regeneration, drug discovery, scaffolds for organoid manufacture and as vehicles for targeted drug delivery through commercial venture.

8:45 AM SB06.08.02
Design of Artificial Protein Polymers for Healthcare Materials Minkyu Kim; The University of Arizona, United States

Natural materials can serve as great inspirational sources to develop next-generation polymeric materials for healthcare applications, attributed to their exceptional physical, chemical and biological properties including biocompatibility, biodegradability and potential nontoxicity. Typically, the unique properties of natural materials are related to their biopolymer components, particularly multi-functional proteins and peptides, and the structural organization of biopolymers in materials. To mimic the superior properties of natural materials, well-characterized functional protein and peptide building blocks can be engineered into artificial protein polymers, which can then be hierarchically assembled into nanostructured polymeric materials, in contrast to fundamentally constructing the entire complex natural system. Based on this bioinspired approach, my research group is focusing on the development of (i) erythrocyte-mimicking microparticles with constitutive polymer networks that contain proteins with exceptional mechanical properties for effective and long-term drug delivery, (ii) protein polymers as a material platform to promote the use of numerous antimicrobial peptides as next-generation antimicrobial therapeutics to treat various (emerging) infectious diseases, and (iii) a self-assembled protein coating on metallic biomaterials to mimic human skin-fingernail interface for an enhanced skin-implant interface. In this presentation, I will discuss our current progress in developing erythrocyte-mimicking microparticles and antimicrobial peptide-incorporated self-assembled materials, which we expect to advance a wide variety of healthcare applications, including but not limited to tissue engineering, drug delivery, and combating the antibiotic resistance crisis.

9:00 AM SB06.08.03

Genetic Fusion of Thermoresponsive Polypeptides Mediates 1D Assembly of Coiled Coil Bundlemers Sai Patkar, Yao Tang, Arriana Bisram, Darrin J. Pochan and Kristi Kiick; University of Delaware, United States

Design of stimuli-responsive nanofibrillar assemblies is of interest for generating controllable nanomaterial motion for actuation in simple machines. Protein-engineering approaches provide excellent opportunities for the design and production of extremely well-defined biomimetic materials capable of organizing different types of molecular building blocks at multiple size scales. In this study, we genetically fused thermoresponsive resilin-like polypeptides (RLPs) of various lengths to two differnt computationally designed coiled coil-forming peptides with distinct thermal stability, to develop strategies to control the assembly of the coiled coil peptides on the basis of the temperature-triggered phase separation of the RLP units. This library of RLP-functionalized coiled coils was recombinantly produced in bacterial expression hosts and purified via immobilized metal affinity chromatography. Their composition and purity were confirmed via gel electrophoresis, mass spectrometry, and amino acid analysis. Ultraviolet-Visible turbidimetry measurements at 350 nm were used to validate that the thermosensitive phase behavior of the RLPs was preserved in the genetically fused hybrid polypeptides. An increase in scattering intensity upon cooling below the transition temperature was indicative of an onset of assembly. Circular dichroism spectra showed strong helicity characteristic of the coiled coil state remaining stable in the hybrid polypeptides below their transition temperature. Cryogenic-transmission electron microscopy revealed that genetic fusion of RLPs to both coiled coil-forming peptides resulted in nanofibrillar assembly of coiled coil peptide bundlemers. Our study provides opportunities for the fabrication of thermoresponsive 1D assemblies which can be used as fundamental subunits in simple molecular machines.

9:15 AM SB06.08.04

3D Scaffold-Based Cellular Model Mimicking the Heterogeneity of Osteosarcoma Microenvironment Giada Bassi[1,2], Silvia Panseri[1], Arianna Rossi[1,3], Denis Cochonneau[4,5], Elisabetta Campodoni[1], Monica Sandri[1], Dominique Heymann[4,5] and Monica Montesi[1]; [1]Institute of Science, Technology and Sustainability for Ceramics (ISSMC)_ National Research Council, Italy; [2]University of Studies "G. D'Annunzio", Italy; [3]University of Studies of Messina, Italy; [4]Institut de Cancérologie de l'Ouest (ICO), Tumor Heterogeneity and Precision Medicine Lab, France; [5]CNRS, Nantes Université, France

INTRODUCTION

Capturing and reproducing the biological complexity of cancer *in vitro* is an exciting challenge for scientists. Osteosarcoma (OS) constituted the main entity among primary bone sarcomas with a poor prognosis due to chemoresistance and early metastasis. Following the tumor engineering approach, we developed a more predictive 3D scaffold-based *in vitro* model reproducing the OS microenvironment heterogeneity. Promising results were obtained by our group in 2020, confirming the higher predictivity of in vitro 3D bone-like scaffold-based models of enriched-CSCs compared to scaffold-free conditions[1]. Using a biomimetic hybrid scaffold, that recapitulates the bone extracellular matrix (ECM)[2], 3D cell cultures of OS enriched-Cancer Stem Cells (CSCs)[3] and co-culture of RGB human MNNG-HOS OS (HOS) cells with mesenchymal stem cells (MSCs) or HUVEC cells, will be developed and characterized.

EXPERIMENTAL METHODS

The MgHA/Coll scaffolds derive from a bio-inspired biomineralization process[2]. The enriched-CSCs were obtained by sarcosphere-forming culture[3] and RGB human MNNG-HOS OS (HOS) were kindly provided by Nantes University. The cell seeding conditions have been defined and the cell/biomaterial interaction was studied by looking at the scaffold colonization by fluorescence analysis, the cell viability and morphology (live&dead assay, histology), the expression of cell-specific markers (immunohistochemistry, Western blot analysis and qPCR), the Sarcosphere-Forming Efficiency, the Stem Cell Frequency, the migration and invasion ability (transwell inserts 8 µm pores), and looking in detail at the mechanism of cell-cell and cell-ECM crosstalk.

RESULTS AND DISCUSSION

The results demonstrate that cells can grow and colonize the surface of the scaffold; CSCs, seeded by injection onto the core of the scaffold, expressed a higher level of stemness marker compared to the 2D in vitro culture. The mimetic structure of the scaffold allows to creation a bioactive environment stimulating HOS-MSCs and HOS-HUVEC crosstalk.

CONCLUSION

Overall, the results demonstrate that the proposed 3D scaffold-based in vitro model creates a permissive and inductive microenvironment able to mimic more in detail the OS complexity.

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9:30 AM *SB06.08.05

Chondroinductive and Chondroprotective Biomaterials for Cartilage Engineering Julie C. Liu; Purdue University, United States

Despite the promise of cartilage engineering, decades of research have not yielded a long-term cartilage-engineered therapy. Traditionally, research has focused either on generating new cartilage or reducing inflammation that degrades cartilage. A significant gap exists in understanding how biomaterial properties contribute to cartilage regeneration within the inflammatory environment found in damaged joints. Our group is developing biomaterials that both promote new cartilage formation from mesenchymal stromal cells (i.e., chondroinductive) and protect cartilage matrix from degradation in a pro-inflammatory environment. To do so, we developed a hydrogel consisting of a blend of collagen I and II that harnesses the chondroinductive activity of collagen II and the superior gelation properties of collagen I gels. Incorporating collagen II into collagen I gels promotes the in vitro differentiation of mesenchymal stromal cells to cartilage and improves cartilage repair and regeneration in a rabbit defect model. Building on that work, we incorporated peptide-modified chondroitin sulfate to increase in vitro cartilage matrix formation. Furthermore, inclusion of hyaluronic acid within the scaffolds conferred protective properties to the cartilage matrix by decreasing the degradative enzymes (e.g., MMP-13) secreted by cells in the presence of pro-inflammatory cytokines.

10:00 AM BREAK

SESSION SB06.09: Design Rules for Peptide and Protein-Based Materials III
Session Chairs: Jose Carlos Rodriguez Cabello and Rein Ulijn
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2020

10:30 AM *SB06.09.01
Tailoring Multifunctional Peptide-Based Biomaterials Mibel Aguilar; Monash University, Australia

Peptide self-assembled systems offer significant advantages including biological compatibility, ease of synthesis, low toxicity and functionalisability. However, the control over essential features such as chemical, structural and metabolic stability, the scale and relatively slow rate of self-assembly remain significant challenges. We have designed helical *N*-acetyl-β^3-peptides that spontaneously undergo supramolecular self-assembly to form a new class of biomaterials [1-4]. The unique helical structure of the peptide monomer offers the opportunity to introduce a wide variety of functions to the new fibres based on straightforward modification of the side chains of the component amino acids. These materials are also resistant to proteolytic degradation further adding to their potential as novel biomaterials. We have exploited this high symmetry to design lateral supramolecular self-assembly motifs to link the fibres in a controlled manner. The bioactivity of the resulting materials can be tailored to control cell adherence and function or targeted delivery of bioactive compounds, opening up a new generation of metabolically stable and biocompatible biomaterials [5-7].

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11:00 AM SB06.09.02
Truncated Coiled-Coil Peptides as a Building Block for Hierarchical Material Synthesis Joshua Meisenhelter[1], Matthew Langenstein[1], Jeffery G. Saven[2], Darrin J. Pochan[1] and Chris Kloxin[1,1]; [1]University of Delaware, United States; [2]University of Pennsylvania, United States

Proteins are capable of incredibly complex tasks enabled by their structure and exact display of chemical functional groups. Non-native materials applications of proteins are often limited owing to their sensitivity to denaturation upon chemical modification. Unlike most proteins, shorter peptide sequences are able to undergo denaturing and refolding cycles. This work investigated use of a peptide-based material that possesses the exact display of chemistry and self-assembling properties of proteins but is readily modified without negatively impacting the hierarchical structure. In previous work, 29-amino acid sequence peptides were computationally designed to form four-peptide coiled-coil assemblies or bundlemers. The bundlemers were stable over a range of temperatures and pH as an individual unit and were modified with maleimide and thiol functional groups to polymerize through a thiol-Michael reaction to form rigid-rods. Here, we investigate the effect of truncating the 29-amino acid coiled-coil sequence to 15-amino acids. Circular dichroism revealed that the 15-amino acid sequence only forms random-coils; however, subsequent bioconjugation of two 15-amino acid peptides at their N-termini resulted in extraordinarily long rigid-rods (2nm wide by multiple microns long), as observed by cryo-TEM. The observed polymerization is hypothesized to follow a chain-growth assembly mechanism that relies on the transient formation of unstable 15-amino acid coiled-coils that initiate/nucleate stable rigid-rod formation via overhanging 15 amino-acid random-coils. This pathway is unique from the previous 29-amino acid sequences, which form through a step-growth assembly pathway. The newly developed 15-amino acid peptide sequence accesses new assembly pathways for the creation of extraordinarily rigid polymers for broad applications ranging from nanowires to ultra-strong and ultra-light fibers.

11:15 AM *SB06.09.04
Soft Computing Guided Discovery of Short Peptides and Peptide Assemblies Daniela Kalafatovic; University of Rijeka, Croatia

The discovery of new active peptides (i.e., antimicrobial, antiviral, catalytic) is challenging, as they are part of a very large search space and the correlation between the peptide sequence and the desired activities and/or functions is not yet fully understood. To avoid expensive and time-consuming guesswork and experimental failure, our strategy is to apply soft computing techniques to accelerate peptide discovery. Soft computing is a set of probabilistic algorithms, which are robust to imprecision and tolerant to uncertainty, that enable us to grapple with analytically intractable problems and make up for the lack of theoretical knowledge. In our project we apply a wide range of soft computing models to predict peptide activity, construct novel peptides and cover the chemical search space (Kalafatovic et al., J. Cheminform, 2019). More in detail, we tackle the problems of (1) sensitivity of highly accurate predictive models, (2) building predictive models with low amount of available data, (3) interpretability of neural network-based classifiers, (4) ability to generate new peptide sequences, and (5) coverage-based parallel exploration of chemical space.
Focusing on therapeutic peptides, we addressed the issue of sensitivity of highly accurate predictive models (Erjavac et al., AI Life Sciences, 2022) and proposed the sequential properties representation scheme to improve their predictive power (Otovic et al., J. Chem. Inf. Model, 2022). This provided the foundations to employ deep learning models improved by transfer learning for the prediction of underrepresented categories or poorly researched peptide functions, such as their predisposition towards self-assembly or catalysis. To gain insight into the decision process of black-box neural network models we employ the Grad-Cam technique, which enables us to pinpoint the properties and residues important for the prediction results and analyze their behavior. We envision that these strategies will maximize the chance of successful identification of functional peptides, partly reducing the environmental impact of failed experimental attempts.

SESSION SB06.10: Clinical and Translational Aspects of Peptide and Protein-Based Materials

Session Chairs: Lihi Abramovich, Silvia Marchesan and Rein Ulijn
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2020

1:30 PM SB06.10.01

Volumetric Imaging and Analysis of Tissues for Clinical Research through *De Novo* Formation of Citrate-Based Fluorophores Jinyoung Pac[1], Dong-Jun Koo[1], Bohyun Kim[2], Ji-Ung Park[3,1], Sung-Yon Kim[1,1] and Yan Lee[1]; [1]Seoul National University, Korea (the Republic of); [2]Konkuk University Medical Center, Korea (the Republic of); [3]Seoul National University Boramae Hospital, Korea (the Republic of)

Two-dimensional (2D) slide-based histopathology is the current paradigm in diagnosis and prognosis. However, loss of volumetric information accompanied by slide preparation provides limited information about the spatial progression of diseases that may lead to an incorrect diagnosis. Recent technological advances, especially tissue-clearing techniques, have enabled three-dimensional (3D) imaging of pathological samples to overcome these limitations. However, affinity-based labeling strategies such as small molecule dyes and fluorescently-labeled antibodies show limited compatibility with tissue-clearing techniques. Moreover, the nonspecific binding of small fluorescent probes and slow penetration of antibodies into large-scale tissues due to their high molecular weight hinder the uniform staining of biological samples and may produce misleading results. Until now, effective labeling and imaging techniques for thick tissues have not been achieved despite the demand for accurate volumetric analyses of pathological samples.
Here, we present an imaging technique, 3DNFC ("3D tissue imaging through *de Novo* Formation of Citrate-based fluorophores"), for 3D reconstruction of thick tissues through the integration of tissue clearing techniques and citrate-based fluorogenic reaction. 3DNFC provides the anatomical morphology of tissues by generating fluorophores on non-fluorescent amino-terminal cysteine and visualizes the 3D structure of the tissues. Furthermore, 3DNFC can unbiasedly analyze various features from pathological tissues in their natural context based on the 3D reconstructed images. We believe that 3DNFC overcomes many limitations of conventional histopathology and may be a suitable 3D analog for the microscopic examination of pathological samples.

1:45 PM SB06.10.02
Development of Wet Adhesive Hydrogels to Correct Tracheomalacia Ece Uslu[1], Vijay Kumar Rana[1], Sokratis Anagnostopoulos[1], Peyman Karami[1], François Gorostidi[2], Kishore Sandu[2], Nikolaos Stergiopulos[1] and Dominique Pioletti[1]; [1]École Polytechnique Fédérale de Lausanne, Switzerland; [2]University Hospital, CHUV, Switzerland

Tracheomalacia (TM) is a congenital disease seen commonly in infants. It is characterized as collapse, or narrowing of airway lumen during respiration, resulting from softness or weakness of cartilage rings and/or abnormality in tracheal muscle. The main clinical approach to solve TM is to correct the geometry of the malacic trachea and to prevent the airway collapse. Surgical interventions and stenting are commonly used treatment methods for TM. However, they have certain limitations. For example, surgical interventions are time consuming and require extensive surgical skills. On the other hand, stenting can cause stenosis, migration, erosion, and the rigidity of stents could prevent natural and dynamic neck movements in infants. Moreover, extraluminal stents needs to be fixed outside of the trachea with pexy sutures which causes trauma to the surrounding tissues. Therefore, current treatment options are not well-suited and there is no well-established method to treat TM effectively.

To overcome these limitations, a numerical model was developed to prove the hypothesis that airway collapse can be hindered by correcting the geometry of malacic trachea with the external mechanical support of an adhesive hydrogel patch. This *in silico* model showed that the application of an adhesive hydrogel patch helped to preserve the physiological shape of the trachea by constraining the tracheal membrane folding. Based on this study, we formulated a new adhesive hydrogel employing hydroxyethyl acrylamide (HEAam) and Polyethylene glycol dimethacrylate (PEGDM). We found that HEAam-based hydrogels provided robust wet adhesion on the tracheal surface thanks to the two-step polymerization approach, bonding firmly to the tissue surface much better than currently known adhesive hydrogels. We further used micro-CT and *ex vivo* measurements to prove the potential of the hydrogel patch to restrain the luminal collapse when it is wrapped to a malacic trachea extraluminally. Finally, we examined the durability and stability of the hydrogel with and without corporation of PEG-NHS in enzymatic and oxidative mediums. We observed that PEG-NHS increased adhesion performance, and decrease swelling and degradation behavior, which are key aspects to consider for biomaterials in long term. Therefore, this study, to be confirmed by in vivo studies, can overcome the current limitations and open the possibility of a new treatment in the difficult clinical situation of tracheomalacia in newborn.

2:00 PM SB06.10.03
NIR Light-Responsive Proteinaceous Ag_2S Nanodots as a Biocompatible Nanotheranosis Platform for Imaging-Guided Photodynamic Anticancer Therapy Mou Seung Kim[1], Yong J. Jeong[2] and Yun Kee Jo[1,1]; [1]Kyungpook National University, Korea (the Republic of); [2]Korea National University of Transportation, Korea (the Republic of)

Light-responsive nanotheranostics are highly desirable for cancer theranostics because they can make it possible to visualize and treat the cancer specifically through precise external modulation of the site *via* a single injection. Quantum dots (QDs) have been extensively considered to construct light-responsive nanotheranostics due to excellent optical properties and rich surface chemistry. However, the clinical application of QDs-based nanotheranositcs is still elusive due to the potential toxicity of contrast agents and the poor retention at the target site. Here, a sticky protein-based nanodots platform that simultaneously allows near-infrared (NIR)-responsive photodynamic therapy (PDT) treatment and real-time tracking in a highly biocompatible, site-specific manner. A suite of proteinic nanoparticles decorated with silver sulfide (Ag_2S) QDs were fabricated through electrospraying and subsequent biomineralization of a bioengineered mussel adhesive protein fused with a silver-binding AgP35 peptide (MAP-AgP35) under mild condition. The light-activatable proteinic Ag_2S nanodots exhibited excellent anticancer therapeutic effects through intensive release of reactive oxygen species (ROS) as well as effective *in vivo* imaging ability under irradiation of NIR light (808 nm), while showing a good biocompatibility towards normal cells. Thus, our mussel protein-based Ag_2S nanodots have a great potential as a externally controllable nanotheranostics to realize imaging-guided therapeutic implications for the complete ablation of cancer.

2:15 PM SB06.10.04
Heterofunctional polYmeric DegRAding Chimeras (HYDRACs)—A Novel Class of Compounds Capable of Targeted Protein Degradation Max M. Wang, Mihai Truica, Brayley Gattis, Sarki Abdulkadir and Nathan C. Gianneschi; Northwestern, United States

ackground
The proto-oncogene Myc is known to play critical roles in tumorigenesis and therapeutic resistance, being dysregulated in >70% of human cancers. Heterodimerization with its binding partner Max is known to be required for oncogenic transformation, yet the development of small molecule inhibitors has been hampered due to the lack of suitable binding pockets. Myc inhibitory peptides derived from the first helix (H1) of the bHLH-LZ region have been generated in efforts to address this limitation. However, poor pharmacokinetic profiles have precluded their clinical translation. Here, we use a novel modular platform technology referred to as the Heterofunctional polYmeric DegRAding Chimera (HYDRAC) for the development of dual-functional Myc inhibitors/degraders.
Methods
HYDRACs were generated using ring-opening metathesis polymerization (ROMP) wherein peptides occupy every side chain, resulting in structures highly resistant to proteolysis. Characterization was done using HPLC, ESI, NMR, and GPC. Taking advantage of the platform's ability to multiplex different payloads in a sequence-controlled manner, heterofunctional constructs were designed incorporating secondary sequences in addition to Myc-targeting H1. Specifically, a degron sequence (RRRG) was incorporated to engage endogenous cellular machinery for targeted protein degradation. For biological

studies, immunofluorescence and confocal microscopy were used to assess cellular penetration; cellular viability assays coupled with use of both cellular (isogenic pairs, Myc-dependent and independent lines) and biochemical (scrambled H1 sequence, homopolymers, monomeric peptides) controls were used to assess tumor antiproliferative effects and Myc-specific responses. Myc target engagement was assessed via immunoprecipitation assays, NMR, circular dichroism, and fluorescence polarization with protein degradation monitored by Western blot. A CRISPR knockdown library screen of all known E3 ligases and mass spec was used to identify pathways responsible for HYDRAC-induced protein degradation.
Results
A library of HYDRACs with narrow polydispersity and predetermined degrees of polymerization were generated. These heterobifunctional compounds were shown to be cell-penetrating with antiproliferative effects at sub-micromolar IC50 values in a formulation- and Myc-dependent manner. HYDRAC treatment resulted in significant decreases in Myc protein levels, which was rescued by proteasomal inhibition with MG132, without changes in mRNA levels. RNAseq showed selective overexpression of Myc pathway genes, suggesting on-target effects. Biophysical analysis showed strong HYDRAC-Myc interactions, which was further supported by the presence of Myc protein following pull-down of biotin-terminated HYDRACs. Selectivity studies revealed that the antiproliferative effects and Myc engagement of HYDRACs require an intact H1 targeting sequence. Identification of E3 ligases implicated in the degradation pathway using a combination of a CRISPR knock down library and mass spectrometry are ongoing. Mice bearing transplanted Myc-CaP tumors, mimicking the clinical course of human castration resistant prostate cancer, showed delayed tumor growth following IP administration of Myc-degrading HYDRACs. Studies exploring the biodistribution and pharmacokinetic profile of the compound, as well as the ability to degrade other proteins of interest using combinations of degron sequences are ongoing.
Conclusion
We present a novel platform technology that addresses the challenges inherent to peptide delivery approaches. The presented work demonstrates the feasibility of HYDRACs for targeted Myc inhibition and degradation, providing rationale for further studies in Myc-driven tumor models. This successful demonstration of a first-in-class compound also opens the door for the development of HYDRACs targeting other proteins of interest and incorporation of different E3 ligase recruiters for tissue or disease-specific activity.

2:30 PM BREAK

SESSION SB06.11: Protein and Peptide Based Coacervates
Session Chair: Rein Ulijn
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2020

3:30 PM SB06.11.01
Modeling of Intrinsically Discorded Protein Mimicking Hybrids for Membraneless Organelles Formation Kalindu S. Fernando and Ying Chau; Hong Kong University of Technology, Hong Kong

Dynamic assembly and formation of membraneless organelles (MLOs) via liquid-liquid phase separation (LLPS) is a versatile mechanism for the spatiotemporal regulation of living cells. These MLOs actively regulate biochemical reactions and are enriched in various biomolecules to improve cell functions. Due to these functionalized abilities of MLOs, there has recently been an increasing trend to develop synthetic biomaterials that mimic natural MLOs. We have developed a multi-scale computational framework to predict the LLPS behavior of both Intrinsically Discorded Proteins (IDPs) and IDP mimicking hybrids developed in our lab extracting interactive motifs from FUS, a widely studied model for MLOs.
Our computational model draws essential inspiration from the sticker-spacer representation described in associative polymer theory. The potential stickers are identified using the LARKS (low complexity aromatic rich kinked segments) identifier followed by molecular dynamics (MD) and Monte Carlo (MC) simulations to capture the interaction energies and represent the stochastic nature of MLOs, respectively.
First, we identified 18 LARKS available in FUS protein using LARKSdb as potential stickers, and in-between peptide segments are considered spacers for modeling purposes. Molecular docking, followed by MD simulations for stickers, demonstrated that 13 stickers could form transient beta-sheet-like structures, and others can only form random coils. Further, their suitability for stickers was confirmed by the radius of gyration (6.18 ± 0.6 Å) and solvent-accessible surface area (7.3 to 12.0 nm2). Using the molecular mechanics Poisson−Boltzmann surface area (MMPBSA) method, the estimated pairwise interaction energies between stickers ranged from ~100 kJ/mol. All spacers were enriched in over 70% of disorder-promoting residues and had less than 30% of charged residues at physiological pH conditions by employing the CIDER webserver.
Next, we generated lattice Monte Carlo simulations to describe the stochastic movements of IDPs under physiological conditions incorporating interaction energies found above. IDP chains were configurated as strings of coarse-grained beads and randomly placed in a three-dimensional simple cubic lattice as a canonical ensemble. We performed 106 orders of hypothetical Monte Carlo movements as self-avoiding random walks on the lattice to obtain an equilibrated system using the Metropolis-Hastings algorithm as movement acceptance/rejection criteria. We could qualitatively demonstrate the dynamic assembling and disassembling behavior of the system. We also used the radial distribution function to identify the system's phase boundaries and estimate the degree of LLPS propensity.
FUS-full protein, FUS-prion-like domain, and FUS-RNA binding domain separately found that FUS-full protein has the highest propensity to undergo LLPS and FUS-RBD domain has the lowest propensity to undergo LLPS while FUS-PLD has an in-between propensity. These findings have a good agreement with available experimental observations. Hence the model was validated. Then we applied the computational framework to IDP mimicking hybrid having only two stickers from FUS protein incorporated with dextran as spacers. Our model could successfully track the synthetic hybrid system's dynamic assembly and disassembly behavior. These computational estimations were also verified by turbidity testing and confocal microscopic observations.
In summary, our approach will provide a comprehensive theoretical framework to predict the LLPS behavior of IDPs and IDP-mimicking hybrids. It also provides a fast and economical means to guide the design of such systems to regulate the LLPS process efficiently.

The authors would like to thank the funding support from the Hong Kong Research Grants Council (GRF 16102520). M.K.S.Fernando receives financial support from the Hong Kong Ph.D.Fellowship Scheme.

3:45 PM SB06.11.02
Sequence-Tunable Phase Behavior and Unexpected Fluorescence in Designed, Dynamically Interacting Peptide Networks Deborah Sementa[1], Rachel S. Fisher[2], Dhwanit Dave[1,3], Tong Wang[1], Ye He[1], Shana Elbaum-Garfinkle[1] and Rein Ulijn[1,3]; [1]CUNY Advanced Science Research Center, United States; [2]Columbia University, United States; [3]Hunter College, United States

The liquid-liquid demixing of proteinaceous material is sustained by a network of weakly binding interactions among amino acids’ side chains (e.g.,

electrostatic, cation- and -) and it has been demonstrated that the distribution of such side chains significantly affects their phase separation behavior.
Here, we report *de novo* engineering of peptide analogues for systematically depicting the impact on the phase behavior of the chemical structure of the amino acids' moieties and their nonrandom allocation. Uniformly mixed solution, aggregates, or simple coacervates can be obtained tuning the composition and the patterning of repeats of the motif R/HxxxY, in a pH responsive manner.
Moreover, self-coacervating peptides exhibit a sequence-specific intrinsic fluorescence that is readily observable by confocal microscopy, allowing their specific characterization without any additional dye. Displaying a high cell uptake efficiency, these artificial membraless compartments readily cross the cell membrane and can potentially serve as label-free delivery platform for macromolecular therapeutics.

4:00 PM SB06.11.03
Peptide-Based Coacervates as Catalytic Microreactors Sara V. Pereira[1], David Reis[1], Ana Priscila Ramos[1], Pedro M. Pereira[1], Leonor Morgado[2,3] and Ana S. Pina[1]; [1]Instituto de Tecnologia Química e Biológica António Xavier Universidade NOVA de Lisboa, Portugal; [2]UCIBIO – Applied Molecular Biosciences Unit, NOVA School of Science and Technology, NOVA University Lisbon, Portugal; [3]Associate Laboratory i4HB – Institute for Health and Bioeconomy, NOVA School of Science and Technology, NOVA University Lisbon, Portugal

Enzymes' machinery has been hypothesized to be evolved from much simpler functional precursors such as peptides (*1*). Peptides are well-implemented as chiral catalysts in organic reactions (*2*). However, their use in aqueous reactions is still limited and remains a challenge in molecular engineering. However, the modest efficiency of peptide catalysts in aqueous media could arise from their heterogeneity in conformation, which is challenging to control (*3*). Different strategies have been used to tackle peptides' conformational heterogeneity, yet their catalytic efficiency is still modest(*4*).
Cells organize their biochemical reactions in membraneless compartments, formed by liquid-liquid phase separation (LLPS) of intrinsically disordered proteins by specific peptide motifs or by their interaction with nucleic acids. Coacervates, also created by LLPS, are associated with the origin of life as primitive models of protocells (*5*) and provide mechanisms for shielding oligomers from bulk solutions and concentrating biomolecules, thus facilitating a variety of processes such as catalytic function(*5*). Therefore, the compartmentalization of catalytic peptides seems an exciting route to evolve catalytic role in often modest peptides and a strategy to constrain their conformational flexibility often observed in bulky solutions(*4*).
In this work, we show for the first time the creation of dynamic micro-sized liquid condensates formed by a catalytic peptide, whose primary sequence (KVYFSIPWRVPM) (*6*) is composed of phase-separating residues (Arg, Lys, Tyr, Phe, Try, and Pro). Simultaneously, the peptide can hydrolyze phosphate ester compounds and bind to phosphotyrosine assemblies with supramolecular selectivity(*6*).

Sequence-structure-function relationship is critical for the formation of these catalytic coacervates. Turbidity measurements and optical microscopy revealed that the peptide could phase separate and form coacervates. However, a delicate balance between peptide concentration and environmental conditions could also lead to peptide aggregates. Circular Dichroism and NMR revealed that the peptide presents a fully-folded β-hairpin structure only in the coacervate phase, and the LLPS driven by cation-π and aromatic interactions. Compared with peptide soluble and aggregated states, the peptide shows a partially folded hairpin-like structure or a lack of structure. The dynamics and sequestration ability of the coacervates towards a range of guest molecules ranging from small molecules to phosphorylated assemblies was exploited. The partitioning of the molecules showed to be controlled by charge interactions. However, the hydrophobicity character of the catalytic peptides seems to play a role in mediating this process, which further influences the microenvironment of the catalytic coacervates.

Ultimately, these catalytic coacervates-based reactors' efficiency was studied and compared to the peptide in bulky solution. This work provides a substantial opportunity to leverage the field of catalytic peptides to regulate catalytic efficiency through the compartmentalization of short peptide catalysts in aqueous media.

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4:15 PM SB06.11.04
A Novel Insect Cuticle Peptide-Based Nano-Capsule Platform Haopeng Li[1], Xuliang Qian[1], Harini Mohanram[1], Tian Liu[2], Huajian Gao[1,3] and Jing Yu[1,1]; [1]Nanyang Technological University, Singapore; [2]Dalian University of Technology, China; [3]A*STAR, Singapore

Nano-capsules can be used to transport a variety of substances into eukaryotic cells. Herein, we develop a novel insect cuticle peptide (ICP)-based nano-capsule platform with the potential for cytosolic drug delivery applications. Originated from insect cuticular proteins, the ICPs can form hollow nano-sized capsules in mixed solvents, via an unusual liquid-liquid phase separation (LLPS) mediated self-assembly process. However, the underlying mechanism of ICP self-assembly remains unclear. By combining molecular dynamics (MD) simulations and biochemical experiments, we present the first study to unravel the mechanics of ICP self-assembly, and to demonstrate the tunability of ICP nano-capsules simply by controlling the peptide sequences. The successful co-delivery of hydrophilic and hydrophobic drugs with synergistic effects is confirmed experimentally. With this work, we aim to exemplify the potential of our ICP-based nano-capsule platform for important biomedical applications, such as drug delivery, cancer therapy and precision medicines.

4:30 PM SB06.11.05
Cell-Like Containers with Inner Organelles Formed by Coacervation of Proteins and Biopolymers Faraz Burni and Srinivasa R. Raghavan; University of Maryland, United States

Eukaryotic cells contain multiple inner compartments (organelles) that enable cells to carry out a variety of biochemical processes. Some of these organelles (such as the nucleolus) lack any external membrane. Recent studies have shown that these membraneless organelles are formed by liquid-liquid phase separation, which is also called coacervation. This coacervation is a dynamic process, and it can be turned 'on' and 'off' as desired; in turn, the nucleolus forms when needed by the cell, and at other times it disappears.

In this study, we mimic cellular architecture by creating biopolymer capsules with a membraneless compartment inside. The inner compartment is created by complex coacervation, which is a liquid-liquid phase separation of a solution containing two oppositely charged polymers. Much like the nucleolus, this compartment can reversibly form and disintegrate by changes in environmental stimuli such as pH, ionic strength, and polymer composition. Different biomolecules and colloidal species can be sequestered by this compartment and in turn, can be released when the compartment disintegrates. Owing to the 'smart' inner compartment, the overall capsules exhibit interesting behaviors and can be used for a variety of applications like drug delivery, biosensing, and reaction engineering. The ability to reversibly assemble such membraneless organelles can also provide insight into important biochemical processes.

4:45 PM SB06.11.06

Biophotovoltaics—Converting Sunlight to Electricity with Photosynthetic Protein Complexes Nahid Torabi[1,2], Xinkai Qiu[3], Andreas Herrmann[2,4] and Ryan Chiechi[1,5]; [1]University of Groningen, Netherlands; [2]Zernike Institute for Advanced Materials, Netherlands; [3]University of Cambridge, United Kingdom; [4]RWTH Aachen University, Germany; [5]North Carolina State University, United States

The incorporation of light-harvesting photosynthetic proteins into device architectures has attracted tremendous attention in the past years. Biophotovoltaic devices utilize the components of natural photosynthetic proteins such as Photosystem I/II (PSI/II) to generate electrical energy under illumination by exploiting light-harvesting pigments as a photosensitizer for light-induced charge separation. Photosynthetic proteins have several desirable characteristics for inclusion into biophotovoltaic devices including rapid charge separation, carbon neutral production, non-toxic, high internal quantum efficiency approaching unity, and highly abundant starting materials. In different works, we have explored several unique strategies to improve interfacial electron transport between PSI proteins and electrodes. In our first work, we demonstrated that self assembled monolayers of simple fullerene derivatives are capable of orienting phtosystem I complexes such that they form a monolayer that injects electrons into the fullerene layer when irradiated. We formed these assemblies on nano structured electrodes embedded in microfluidic channels filled with a redox couple and a liquid metal electrode to complete a dye-sensitized biophotovoltaic device. These proteins guide the photosystem to the electrode such that they are in direct contact, allowing us to compare the efficiency of charge injection with and without the mitigation of the fullerenes. We find that the fullerenes reduce recombination in the complexes, presumably by acting as selective contacts. Moreover, the unique architecture of these devices enables self-regeneration; by circulating fresh photosystem complexes through the device, inactive complexes are replaced by active complexes via self-assembly. Also, self-regeneration is a key feature of these devices because it mimics the replenishment process in biological systems using unmodified, wild-type photosystem I and does not require any encapsulation or other interventions. The performance of devices fabricated using a fullerene, phenyl-C61-butyric acid (PCBA), was superior as determined via the short circuit current, open circuit photovoltage, and power output. The PCBA linkers self-assemble onto the bottom electrodes, simultaneously directing the orientation of PSI and facilitating the collection of photo-generated electrons. In another work, we reported a power conversion efficiency to date of 0.64% in a solid-state biophotovoltaic device by tailoring the transport layers to maximize the extraction of charges from a layer of photosystem I. Specifically, we inserted complexes of gold nanoparticles into reduced graphene oxide to adjust the level alignment without sacrificing carrier mobility. We paired that layer with a polytyrosine-polyaniline hole-extraction layer. The active layer is fabricated by self-assembly, requiring only contact with a solution containing photosystem I. We achieved an overall increase in efficiency by raising the short-circuit current without sacrificing fill-factor or open-circuit voltage. This work establishes a foundation for utilizing the unique properties of graphene-based materials decorated with metal nanoparticles in future biophotovoltaic devices. Furthermore, in other research, solid-state charge transport measurements via PCBA/PSI junctions were carried out at room temperature and down to 150 kelvin. The junctions comprising PCBA/PSI demonstrated excellent stability and reproducibility on different days during around 4 months of measurements over room temperature. The efficient electron transfer through PSI protein complexes opens up possibilities for using such protein complexes as current-carrying elements in solid-state bioelectronic devices.

SESSION SB06.12: Poster Session II: Biomedical Applications of Peptide and Protein-Based Materials
Session Chairs: Daniela Kalafatovic, Jose Carlos Rodriguez Cabello and Jacek Wychowaniec
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SB06.12.01

Light and Heat-Responsive Collagen-Based Hybrid Nanoparticles for Controlled Delivery of Functional Proteins Doyun Kim[1], Seungki Lee[1], Sunho Hong[1], Jungwoo Choe[1], Jeong-Min Seo[2] and Inhee Choi[1]; [1]University of Seoul, Korea (the Republic of); [2]NeoRegen Biotech Co., Ltd, Korea (the Republic of)

Stimuli-responsive nanoparticles have been widely studied to improve the stability of bioactive molecules such as proteins and their targeted delivery efficiency. To this end, hydrogel nanoparticles are promising since they can store cargo with high efficiency and minimize the loss of activity. Moreover, the introduction of stimuli-responsive moieties into the hydrogel nanoparticles allows for controllable drug release at the designated sites or times. Here, we present light and heat-responsive collagen nanoparticles (CNPs) for the controlled delivery of functional proteins. Via fast radical polymerization, biocompatible collagen and thermosensitive polymer are simultaneously incorporated into hydrogel nanoparticles and gold-embedded CNPs (Au-CNPs) are simply obtained by adding gold precursor ions to the reaction mixture. Using the Au-CNPs, the functional proteins with different molecular weights, EGF, FGF2, and SOD1, were successfully loaded with high loading efficiency of 68.9%, 65.3%, and 50.3%, respectively. Under light illumination, the photothermal conversion effect from the Au-CNPs leads to the enhanced release kinetics and diffusion of loaded proteins. SOD-encapsulated Au-CNPs are successfully internalized into cells and effectively reduce ROS levels through light-responsive release. Through the wound healing test, we also observe rapid recovery in the case of treatment with EGF-encapsulated Au-CNPs without losing the activities compared with the treatment of EGF only. Furthermore, using three-dimensional cellular spheroids, we demonstrate increased proliferation rates owing to the enhanced penetration of released FGF2. We envision that the proposed light and heat-responsive CNPs will be a promising carrier to improve the physicochemical stability in the protein delivery process and improve intracellular delivery efficiency.

5:00 PM SB06.12.02

Recombinant Keratins Coating for Enhanced Skin-Implant Interface Suyoung Lee[1], Bumjoon Kim[1], Tijana Z. Grove[2], Mark E. Dyke[1,1] and Minkyu Kim[1,1,1]; [1]The University of Arizona, United States; [2]Virginia Tech, United States

Percutaneous osseointegrated prosthetics (POP), composed of metallic implants that penetrate bone and skin, are an alternative to socket-limb connection. Although POP devices have advantages for clinical usage, device failures can occur for long-term usage due to the decrease of epithelial cell attachment, epidermal down growth, inflammation, and avulsion at the skin-implant interface. To enhance the soft tissue-hard implant interface, surface modifications of the device have been conducted using morphological, physicochemical, and biochemical methods. Inspired by the skin-fingernail interface, we have investigated improving the promotion and maintenance of epidermal cell-to-device adhesion by using keratin coatings on the device. Nails, consisting of keratin, form a stable interface with mechanically mismatched skin without mechanical tearing or infection. In addition, keratins extracted from hair, wool, and feather have already been used in various biomaterials, due to its biological and mechanical durability, low immune responses, and cell adhesion properties. In our previous study, we identified that the keratin coating on metallic biomaterials facilitated the attachment of epidermal cells through focal adhesions that promoted a mature phenotype. These in vitro findings translated to an animal model where the results demonstrated reduced epidermal downgrowth. However, the work showed that the keratin coating degraded sooner than desired for the application of interest. This could be caused by various keratin nanostructures from extracted keratins that include various keratin types and contaminants due to a limitation in current keratin extraction techniques. In this study, we biosynthesized recombinant keratin to elucidate their self-assembly behaviors, depending on keratin types and explored the relationship between the self-assembled keratin nanostructures on the surface of metallic biomaterials and epidermal cell adhesion. Throughout the investigation, we examined the possibility to use recombinant keratin materials for enhanced soft tissue-metallic implant interface.

5:00 PM SB06.12.03
Multivalent Vesicles of Stimuli-Responsive Elastin- and Resilin-Based Block Copolypeptides with an Anti-Angiogenic Peptide Shahzaib Shahid, Min Jeong Kang, JaeHee Lee, Jae Sang Lee and Dong Woo Lim; Hanyang University, Korea (the Republic of)

Self-assembled nanostructures of stimuli-responsive block copolypeptides fused with a variety of functional peptides have been of growing interest because they can present multivalent functionalities and show biocompatibility and biodegradability for advanced drug delivery systems, biosensing and bioimaging applications. In this study, we developed multivalent vesicles of stimuli-responsive elastin- and resilin-based diblock copolypeptides (EBP-RBP) with the anti-angiogenic peptide, a vascular endothelial growth factor receptor 1 (VEGFR1, fms-like tyrosine kinase-1, Flt1) antagonist known as anti-Flt1 peptide, to control over migration and tube formation of human umbilical vein endothelial cells (HUVECs) because it competitively binds to the VEGFR1 in the presence of VEGF for anti-angiogenesis. The anti-Flt1-EBP-RBPs were molecularly cloned, over-expressed in *E. coli* and non-chromatographically purified with high yield by inverse transition cycling. The anti-Flt1-EBP-RBPs were self-assembled into vesicles under physiological conditions by thermal trigger due to aggregated RBP block below the UCST (upper critical solution temperature) and soluble EBP block below the LCST (lower critical solution temperature). In contrast to EBP-RBPs, the anti-Flt1-EBP-RBPs showed decrease in LCST and an increase in UCST because of hydrophobicity of the anti-Flt1 peptide (GNQWFI). The vesicles of the anti-Flt1-EBP-RBPs showed concentration and incubation dependent intracellular localization in HUVECs through molecular interactions of multivalent anti-Flt1s against the VEGFR1. Especially, migration and tube formation of HUVECs was largely inhibited in a dose-dependent manner by the vesicles with multivalent anti-Flt1s on the condition of VEGF-triggered angiogenesis signaling. Therefore, the self-assembled block copolypeptide-based vesicles with multivalent VEGFR1 antagonists would be of great potential as targeted drug delivery systems for anti-angiogenesis such as treatment of retinal and choroidal neovascularization.

5:00 PM SB06.12.04
Macro-Scaled M13 Bacteriophage-Based Hierarchical Fiber for Piezoelectricity-Induced Cell Regeneration SangMin Lee, YuJin Lee, CheongWoo Park and Ju Hun Lee; Hanyang University, Korea (the Republic of)

Regenerative medicine is a major domain of medical technology that aims to restore and develop tissue or organs' own functions by replacing or regenerating damaged human cells, tissues, and organs. Of these targets, tissue engineering is a promising method used to identify damage from aging, injury, and degenerative diseases by reestablishing structural and functional properties of tissues, or organs. Previously, scaffolds produced with biocompatible materials have been developed that stimulate tissue regeneration at the cellular or molecular level. However, most of the research regarding scaffolds with biomaterials focused on mechanical support and biofunctionality, which is related to the enhancement of biological interactions with bodily components. These interactions provoke stimulatory actions, although, the effect is insufficient to regenerate the tissue of interest and to make a clinical trial. In this regard, we proposed a system that produces microcurrents, relatively weak currents that mimic the spontaneous generation of currents in the human body, for tissue-specific generation and promotion of cell development/regeneration. These microcurrents induce a therapeutic effect that treats damaged bodily tissues retaining piezoelectric coefficients. The system is composed of an M13 bacteriophage-based material that was hierarchically self-assembled to create a fibrous structure using a bottom-up strategy. A magnetic field was applied to M13 phage solution for unidirectional alignment of the material, followed by fixation. The optical anisotropic property of the aligned macrostructure was qualitatively analyzed using polarized optical microscopy, and quantitatively analyzed using birefringence measurements. When sample was placed between the polarizer and analyzer, there were difference of image appeared between the highly aligned structure and randomly aligned structure. The highly aligned structure presented a higher birefringence value (Δn=|n_e-n_o|) than randomly aligned structure that was not applied magnetic field. Furthermore, Unidirectional alignment of the structure was qualitatively, and quantitatively confirmed through Second Harmonic Generation (SHG) microscopy and its SHG intensity due to the non-linear polarization induced by interactions between photons of incident electromagnetic waves and electrons of molecules constituting non-centrosymmetrical material. The piezoelectric coefficient of the structure can be increased by unidirectionally aligning the bio-piezoelectric M13 phages, which can be adjusted depending on the concentration of the phage and intensity of the applied magnetic field to mimic the piezoelectric coefficient of the target tissue. Specifically, we investigated the piezoelectric response of osteoblasts to bone piezoelectricity-mimetic material. When mechanical force was applied, the phage-based macrostructural material generated a piezoelectric response specific to the bone and promoted proliferation and differentiation of the osteoblasts to osteocytes in vitro. To the best of our knowledge, this is the first case in which biomolecules of a single type are assembled to fabricate a piezoelectric macrostructure that produces a piezoelectric coefficient comparable to signals from bodily tissues. We plan to further develop the system to characterize effects of 3-dimensional scaffolds that made up of M13 phage-based hierarchical materials into various cells or tissues in vitro as well as in vivo.

5:00 PM SB06.12.05
***In Situ* Gelation of Stimuli-Responsive Elastin and Suckerin-Based Tri-Block Copolypeptides with Adhesive Properties** Dong Woo Lim, JaeHee Lee, Jae Sang Lee, Min Jeong Kang and Shahzaib Shahid; Hanyang University, Korea (the Republic of)

Recombinant protein-based bioadhesives have been of great importance for biomedical applications because their amino acid sequences, molecular weights, and physicochemical properties are precisely controlled at gene level while they have biocompatibility and biodegradability. There have been some studies on mussel foot protein-, suckerin- and elastin-based bioadhesives based on the l-3,4-dihydroxylphenylalanine (DOPA)-mediated cross-linking as well as the cross beta sheet. In this work, we rationally designed, bio-synthesized, and non-chromatographically purified a series of ABA type tri-block copolypeptides composed of sticky elastin-based polypeptides (EBPs) and beta sheet-forming suckerin-based polypeptides (SBPs) at different block length ratios for injectable hydrogels with controlled surface adhesion properties. Especially, in order to introduce the adhesive properties of stimuli-responsive EBPs, sticky EBPs with varied ratio of Lys and Tyr residues were prepared for pi-cation interactions and DOPA-mediated surface adhesion by enzymatic hydroxylation. We hypothesized that SBPs would form the stable cross beta sheets while sticky EBPs having DOPA-induced adhesive- and cohesive interactions. The modified ESE (mESE) triblock copolypeptides showed controlled lower critical solution temperature (LCST) behavior depending on the length of SBP under the identical EBP block. Moreover, the mESE triblock copolypeptides under dilute conditions exhibited self-assembled nanostructures mediated via molecular interactions between SBP blocks below LCST. The concentrated mESE triblock copolypeptides with sodium periodate rapidly formed hydrogels via formation of the cross beta sheets of the SBP block and periodate-mediated crosslinking of DOPAs. The physically and chemically cross-linked mESE triblock copolypeptide hydrogels with controlled mechanical properties showed finely tuned adhesive strength in the range of 0.5 – 5.5 MPa depending on the concentration of sodium periodate and SBP block length. In conclusion, the injectable triblock copolypeptide hydrogels with controlled adhesive strength under wet conditions make them ideal candidates for biomedical applications such as sealants after anastomosis and tissue adhesives.

5:00 PM SB06.12.06
Aptamer-Guided Site-Specific Bioconjugation Enables Ultra-Efficient Covalent Coupling of a Nucleic Acid with an Intact Protein Hyesung Jo and Seung Soo Oh; Pohang University of Science and Technology, Korea (the Republic of)

Specific bioconjugation of a nucleic acid to a protein is not only used to identify, manipulate and functionalize the native protein but also provides a programmable linker that can interconnect the active protein with other functional molecules. Currently, most bioconjugation methods apply random modification, thereby disrupting the integrity of the protein structures and functions; otherwise, genetically engineered proteins are required for site-specific modification, significantly increasing its complexity and costs. Site-specific bioconjugation of intact proteins with functional nucleic acids has been an unmet need while fully securing the activity of the conjugated proteins. In this work, we propose the engineered aptamer-guided covalent conjugation of a nucleic acid to an unmodified protein as the guanine analogue, formed by nitrosation of guanine, can mediate activation-free crosslinking with nearby natural proteins. By inventing a synthetic way to prepare the reactive base-containing aptamer, we demonstrate that the newly synthesized aptamers targeting many different proteins can form a covalent linkage to the aimed location of the target proteins with exceptionally high specificity and efficiency.

5:00 PM SB06.12.07
Semi-Permeable Protocells Enable Direct Target Detection in Non-Purified Blood Jinmin Kim and Seung Soo Oh; Pohang National University, Korea (the Republic of)

In controlling the transport of molecules, many different types of size-selective membranes have been used in various applications, including water purification, electrolyte separation of batteries, and biological compartmentalization. In particular, regulation of molecular transport can be beneficial for biosensors; effective exclusion of fouling molecules can be directly linked to sensitive and selective detection of targets, even in complex body fluids. In this work, we explored the potential of semi-permeable protocells for point-of-care testing with no sample purification. Due to the small size, the membrane of the protocells can exclusively allow the entry of analytes with no access to nucleases and charged proteins, which would be an optimal environment for encapsulated DNA sensing probes. To this end, we first introduced the water-in-oil emulsion to construct the semi-permeable microcapsules composed of self-assembled protein-polymer amphiphiles. In the microstructure of the cross-linked membrane, newly designed aptasensors were subsequently enclosed to report the presence of various biomarkers via fluorescent signaling. We demonstrate that the aptasensor-encapsulated protocells achieve multiplexing real-time detection of estradiol, dopamine, and cocaine, even in undiluted blood and serum.

5:00 PM SB06.12.08
TMD Nanosheets with Abiotic Recognition Phases for Pathogen Detection and Inactivation Sin Lee[1], Yoonhee So[1], Chanhee Choi[1], Lee Hyun ji[1], Hongwon Kim[1], Chul-Su Yang[1], Hwankyu Lee[2] and Jong-Ho Kim[1]; [1]Hanyang University, Korea (the Republic of); [2]Dankook University, Korea (the Republic of)

Antibodies are representative recognition molecules selectively binding to target antigens, leading to wide applications for sensing and therapy. However, antibodies have some limitations such as low stability, long production time, and high cost. Thereby, there is an increasing demand for the development of alternative recognition molecules in theragnosis. Several biomimetic strategies have been developed to circumvent these limitations, including molecular imprinting, peptoids, and engineering nanointerfaces. Despite these efforts, it is still of great interest to devise an effective strategy to mimic antibodies for simultaneous sensing and therapy. Herein, we report an effective approach for the design of biomimetic nanohybrids capable of the selective recognition and inactivation of pathogenic bacteria. Tripeptides with a nitriloacetate-Cu group were spontaneously assembled on transition metal dichalcogenide (TMD) nanosheets (TMD-TP) to form abiotic recognition phases for target bacteria, producing various types of TMD-TP antibody mimics. The resulting TMD-TP antibody mimics exhibited strong Raman scattering signals for bacterial sensing and photothermal effect under infrared irradiation for bacterial inactivation. The recognition mechanism of TMD-TP antibody mimics against the specific bacteria was thoroughly investigated by experiments and molecular dynamics simulations. Finally, the TMD-TP antibody mimics could sensitively recognize each target bacteria up to a single copy from human serum and urine in a rapid manner. In addition, the $MoSe_2$-CHC antibody mimic was successfully applied for the effective eradication of *S. typhimurium* infecting the wounds of mice under NIR irradiation. These biomimetic nanohybrids can be extended to theragnosis of a variety of biomolecules.

5:00 PM SB06.12.10
The Protein-Like Polymer (PLP)—A Tunable Proteomimetic Nanoplatform for the Development of Rationally Designed Cancer Vaccines with Therapeutic Efficacy in Multiple Tumor Models Max M. Wang[1], Mi Ran Choi[1], Brayley Gattis[1], Baofu Qiao[2], Monica Olvera de la Cruz[1], Bin Zhang[1] and Nathan C. Gianneschi[1]; [1]Northwestern, United States; [2]Baruch College, United States

Background
Utilizing tumor antigens for the development of patient-specific cancer vaccines has been a promising therapeutic strategy. However, significant challenges remain in delivering subunit vaccine components in a manner capable of eliciting antitumor immune responses. To overcome these, we developed rationally designed cancer vaccines using a novel nanoplatform called the Protein-Like Polymer, a reference to its globular structure reminiscent of native proteins, with unique characteristics allowing for sustained targeted delivery of tumor antigens in conjunction with immunomodulatory STING agonists.
Methods
PLPs containing peptide antigens were synthesized via ring-opening metathesis polymerization (ROMP) and characterized using NMR, HPLC, ESI, and SEC-MALS. A library of compounds with different sidechain linkage chemistries, degrees of polymerization (DP, number of side chains per polymer), and inclusion/exclusion of Oligo(ethylene glycol) (OEG) were made. Cell uptake and functional assays using payload-specific T Cells were conducted using polymers with or without fluorescent labels. Immunization in independent tumor models was done to show generalizability. Ability of PLPs to co-deliver adjuvants was tested by electrostatically coupling a small molecule STING agonist, 2’3’ cGAMP, forming stable nanostructures.
Results
Dense brush polymers wherein every side chain extending off a hydrophobic polymer backbone consists of peptide antigens were successfully generated with narrow polydispersity and predetermined DPs. Conjugating peptide antigens to the polymer backbone using a cleavable disulfide linkage, designed to reduce intracellularly in antigen presenting cells (APCs), resulted in increased endosomal localization, higher levels of induced T cell proliferation, cytokine production, and expression of activation markers in CTLs and APCs. Incorporating a diluent amount of OEG side chains reduced enzymatic degradation while increasing immunogenicity and uptake by APCs. Additionally, increasing the DP, and therefore the density of antigen side chains, further improved vaccine efficacy and resistance to proteolysis. Antigen-PLP conjugates enhanced dendritic cell activation and T-cell response only when paired with cells from their cognate system, with no response in immune cells not expressing receptors for the payload, further demonstrating antigen-specificity. Mice bearing established B16F10 melanomas treated with PLPs containing gp100 resulted in significant increases in survival time, reduced tumor burden, and corresponding changes in immune cell profiles. Impressively, mice treated with STING electrostatically complexed to antigen-PLPs showed significantly smaller tumors vs non-complexed combination treatment while allowing for subcutaneous administration of 2’3’ cGAMP, which alone requires intratumoral injection due to rapid diffusion. Studies on MC38, TC-1, and LLC1-OVA tumors, paired with adpgk, HPV-E7, and OVA-bearing PLPs respectively, as well as pools of neoantigens multiplexed onto a single PLP are ongoing.
Conclusion
This work validates the ability of PLPs to overcome major limitations in cancer vaccine development, enabling sustained delivery of antigens and adjuvants. The modularity of the platform allows for complex nano-architectures including systems capable of delivering challenging compounds, ie small

molecule STING agonists, subcutaneously through stable electrostatic coupling. The ability to multiplex multiple different antigenic sequences as mosaic structures further highlights the PLP platform's potential to revolutionize cancer vaccinology.

SYMPOSIUM

April 11 - April 25, 2023

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SESSION SB07.01: Dynamic Polymer Network I—Self-Healing
Session Chairs: Pengfei Cao, Ximin He and Qiming Wang
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2018

10:45 AM SB07.01.02
Theoretical Understanding of Self-Healing Polymer Networks with Dynamic Bonds—from Hydrogels and Elastomers to Thermosets Qiming Wang; University Southern California, United States

Polymer networks crosslinked by dynamic bonds have received intensive attention because of their special crack-healing capability. Diverse DPNs have been synthesized using a number of dynamic bonds, including dynamic covalent bonds, hydrogen bonds, ionic bonds, metal-ligand coordination, hydrophobic interaction, and others. Despite the promising success of polymer synthesis, the theoretical understanding of their self-healing mechanics is still at the very beginning. Here, we present a series of polymer-network-based theoretical models to understand the constitutive and interfacial healing behaviors of these dynamic polymer networks. Our theoretical system can explain various polymer networks in form of hydrogels, elastomers and thermosets, and various dynamic bonds. We expect our model to be a powerful tool for the self-healing community to invent, design, understand, and optimize self-healing polymer networks with various dynamic bonds.

11:00 AM SB07.01.03
Self-healing Cellulose Ionogels—Circularity for Stretchable Electronics Yu Jun Tan; National University of Singapore, Singapore

Cellulose is a bio-based and biodegradable material that can be made self-healing to enhance its durability and lengthen its lifetime. Here we choose carboxymethyl cellulose as the base material for its high chain mobility from the partial substitution of the cellulosic chains. We report a cellulosic ionogel with autonomous self-healing ability and ionic conductivity by adding a non-toxic ionic liquid to carboxymethyl cellulose [1]. The ionogel shows repeatable electro-mechanical self-healing due to the dynamic bonds between the cellulosic hydroxyl groups with the ionic liquid. We also develop an ionically conductive hydrogel by crosslinking the carboxymethyl cellulose network with citric acid and trivalent cation [2]. The hydrogel autonomously self-healing damages thanks to the hydrogen and metal coordination bonds. Due to the presence of free-moving ions in these ionogels, they exhibit high ionic conductivity in the order of 10^{-3} to 10^{-2} S/cm. Along with their high optical transparency, these ionogels show the potential to be employed in a wide range of practical applications, from strain sensing applications to optoelectronics.
References:
[1] Self-healing cellulose ionogel for stretchable electronics (manuscript in preparation)
[2] 3D printing of a self-healing cellulose hydrogel for wearables (manuscript in preparation)

11:15 AM *SB07.01.04
Self-Healable Covalently Adaptable Networks (SH-CAN) Marek W. Urban; Clemson University, United States

The effectiveness of van der Waals (vdW) interactions formulated the new path (Science 2018) for the development of acrylic-based copolymers that exhibit self-healing. Taking advantage of the large polarizability of copolymer side groups, non-directional vdW interactions between neighboring macromolecular segments are enhanced, which upon mechanical damage return to their initial conformations. This process can be accelerated by the presence of confined water molecules. Since dipole-dipole, dipole-induced dipole, and induced-dipole induced dipole interactions significantly impact viscoelastic response controlling macroscopic autonomous multicycle self-healing, the presence of ionic liquid units copolymerized into one macromolecular chain also alters vdW forces, thus providing an opportunity for applying electric fields to accelerate self-healing. The last part will focus on the most recent developments of self-healable and reprocessable covalent adaptive networks (CANs).

SESSION SB07.02: Dynamic Polymer Network II—Self-Healing

Session Chairs: Ximin He, Lihua Jin and Qiming Wang
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2018

1:30 PM SB07.02.01
Tunable and Patterned Biomimetic Networks via Secondary Metal-Ligand Complex Formation Declan Shannon, Josh Moon, Christopher Barney and Craig Hawker; UCSB, United States

Natural systems leverage multiple bonding motifs for reinforcing polymer networks, and as a result biological materials provide an excellent guide for the design of next generation high performance networks. Mixed crosslinking motifs based on covalent and metal-ligand complexes in networks are ubiquitous in nature and have inspired the design of synthetic covalent networks reinforced via metal-ligand bonds. These materials have shown remarkable success in reinforcing mechanical properties of the softer polymeric networks. We report a versatile synthetic procedure for the preparation of modular networks that allows independent tunability of both the covalent and metal-ligand crosslink density. Control over the covalent network is achieved through photopolymerization, followed by post polymerization incorporation of ligand units, allowing different networks to be prepared with a variety ligands. By tuning the ratio of each building block, covalent networks reinforced by metal-ligand bonds exhibit a wide range of properties (elastic moduli up to ~245 MPa), well beyond what can be achieved through purely covalent crosslinking. This facile approach also permits local patterning of metal complexed regions through soft lithography techniques forming distinct hard and soft regions. To showcase the spatiotemporal control of this techniques, biomimetic constructs were fabricated with this modular platform that cannot be achieved through traditional methods, showing promise for applications ranging from composites, to soft robotics, and metamaterials.

1:45 PM SB07.02.02
Valency-Dependent In 3D-Architected Metallo-Polyelectrolyte Complexes Exhibiting Tunable Mechanical Behavior Seola Lee, Seneca Velling, Pierre J. Walker, Cyrus J. Fiori, Zane W. Taylor, Zhen-Gang Wang and Julia R. Greer; California Institute of Technology, United States

Metallo-polyelectrolyte complexes (MPEC) represent a unique class of materials where metal ions embedded into soft organic frameworks undergo reversible electrostatic interactions through the formation and dissociation of dynamic bonds. These molecular-level processes give rise to a wide range of material dynamic responses, for example, stimuli-responsiveness, self-healing, dissolution in solvent, and improved toughness through enhanced energy dissipation. We synthesized a 3D-architected MPEC, with dimensions of a millimeter to a centimeter, fabricated via in-situ polymerization of acrylic acid with divalent and trivalent metal ions such as Ni(II) and Al(III) via stereolithography. Water-solvated metal ions dynamically cross-link with the pendant carboxyl group of polyacrylic acid to form a dense network capable of significant mechanical deformation. From the uniaxial tensile test, the resulting materials with trivalent metal-ions are stiff and tough, with a modulus of ~3MPa and elongation strains upward to ~700% in contrast to the divalent metal-containing gels, whose modulus is about 500kPa to 1MPa with elongation upwards of ~1400%. A large hysteresis in stress-strain response and fracture toughness for trivalent metal-containing gels indicates the significant contribution of dynamic bonds in energy dissipation. The valency of the solvated metal cation critically governs the mechanical and rheological properties of the polymer network. Experiments conducted with a Dynamic Mechanical Analyzer (DMA) demonstrate that the association/dissociation of the metal cation cross-linker induces distinct dynamic properties of the gels: the storage modulus, from ~500kPa to ~5MPa, and a loss factor, tan delta, from less than 0.5 (viscous-solid like) to close to 1 (viscous-liquid like) in the ambient temperature, each varying with the valency and concentration of metal ions. Stress relaxation experiments reveal the gels with trivalent metal ions are ~60 times slower, yet the long-term relaxation process was more apparent than the ones with divalent metal ions. The local lability of the metal ions with the polymer chains serves as the origin of global material properties. To probe the mechanisms of local interaction and their manifestation in global parameters, Molecular Dynamics (MD) simulations have been employed. Using MD simulation, we examine the effects of ion valency on ionic binding within polymer chains of an equilibrated gel, both at equilibrium and under stress. Further, fundamental thermal characterization via Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA) – including kinetic analysis and thermodynamics of bonding – has demonstrated the role of solvating water in mediating this valency control and has corroborated the greater enthalpic cost of thermally-activated processes in trivalent compared to divalent metal systems. We utilize valency-dependent material properties to control the nonlinear mechanical instability in 3D-printed multi-material architectures. Uniaxial compression and tension experiments conducted at strain rates of 10^{-4} to 1 s^{-1} demonstrate the strong dependence of instability deformation mode on material compositions and mechanical inputs (applied strain rate or relaxation time). These results demonstrate the synergetic effect of MPEC’s valency-dependent, tunable viscoelastic properties with nonlinear mechanical response of compliant architectures, permitting control of deformation modes in soft mechanical meta-materials.

2:00 PM SB07.02.03
Novel Click Chemistries for Intrinscically Chiral, Highly Functional and Dynamic Covalent Polymers—Bulk and Single-Polymer Studies Han Zuilhof; Wageningen University, Netherlands

Click chemistry has revolutionized many facets of the molecular sciences, with the realization of reactions that are ‘‘modular, wide in scope, give very high yields, generate only inoffensive byproducts that can be removed by nonchromatographic methods and are stereospecific”.

[i] Yet surprisingly little attention has been given to the development of intrinsically chiral click reactions (potentially enantiospecific rather than ‘only’ enantioselective due to chiral auxiliary groups), while the modularity of many click reactions is best compared to one-dimensional LEGO. Of course, much could be done within the constraints – hence forementioned revolution – but it drove attention towards an extension of available click chemistries.
The talk will focus on the resulting investigations in the field of S(VI) exchange chemistry, with specific emphasis on two fields: a) the development of the first intrinsically enantiospecific click reaction and its use to make synthetic polymers with 100% backbone chirality,[ii] and b) the development of multimodular click chemistry and single-polymer studies by a combination of AFM, TEM, scanning Auger microscopy.[iii]
[i] Kolb, H. C.; Finn, M.; Sharpless, K. B., Click chemistry: diverse chemical function from a few good reactions. *Angew. Chem. Int. Ed.* **2001**, *40*, 2004-2021.
[ii] A) Silicon-free SuFEx reactions of sulfonimidoyl fluorides: scope, enantioselectivity, and mechanism. Liang, D.; Streefkerk, D.E.; Jordaan, D.; Wagemakers, J.; Baggerman, J.; Zuilhof, H. *Angew. Chem. Int. Ed.* **2020**, *59*, 7494-7500. B) Liang, D.D.; Pujari, S.P.; Subramaniam, M.; Besten, M.; Zuilhof, H. Configurationally chiral SuFex-based polymers. *Angew. Chem., Int. Ed.* **2022**, *61*, e202116158

[iii] Li, S.; Li, G.; Gao, B.; Pujari, S.P.; Chen, X.; Kim, H.; Zhou, F.; Klivansky, L.M.; Liu, Y.; Driss, H.; Liang, D.D.; Lu, J.; Wu, P.; Zuilhof, H.; Moses, J.; Sharpless, B. SuFExable polymers with helixal structure derived from thionyl tetrafluoride. *Nat. Chem.* **2021**, *13*, 858-867.

2:15 PM SB07.02.04
Autonomic Damage Visualization in Covalent Adaptable Networks Tae Ann Kim and Subin Yoon; Korea Institute of Science and Technology, Korea (the Republic of)

Autonomous polymers that report damages prior to loss of function and simultaneously self-heal are highly relevant for not only preventing catastrophic failures but also extending the lifetime use of the materials, thus ultimately keeping us on the path to sustainability. Particularly, visualizing damages have been achieved by incorporating mechanochromic molecules that change optical properties in response to mechanical stresses into polymeric materials. Spiropyran (SP) is a well-studied mechanochromic molecule that undergoes a force-induced reversible 6p electrocyclic ring opening reaction to a merocyanine (MC) form. Various SP-linked mechanochromic polymers have been developed using polyacrylates, polyurethanes, silicone rubbers, polystyrenes, polyesters, and polycarbonates. But there is no attempt to integrate SP molecules into CANs, especially derived from DA chemistry. Since some DA isomers undergo force-induced retro-DA (rDA) reactions, SP incorporated DA networks would be an interesting subject to study how two different force-sensitive molecules can be mechanically activated in a single polymeric system.
Here we demonstrate self-healing and re-processable thermosets that visualize damages in optical changes by using mechanochromic SPs and thermo-reversible DA chemistry. When the thermoset is mechanically deformed or damaged, affected areas change color and emit fluorescence by SP to MC transition. Upon thermal treatment, colored MC reverts to colorless SP and reversible DA and rDA reactions reorganize polymer networks, resulting in self-healing and reprocessing. Mechanical activation of SPs in DA polymeric networks is investigated both by Ab initio steered molecular dynamics simulation and mechanical testing. We also evaluate self-healing abilities and thermomechanical properties of mechanochromic thermosets after multiple recycling processes.

2:30 PM SB07.02.05
Mechanics Underpinning Phase Separation of Hydrogels Yu Zhou and Lihua Jin; University of California, Los Angeles, United States

This work reveals the underpinning role of mechanical constraints and dynamic loading on triggering volume phase transitions and phase separation of hydrogels. Using the Flory-Rehner free energy that does not predict phase separation of hydrogels under equilibrium free swelling, we show that mechanical constraints can lead to coexistence of multiple phases. We systematically obtain the states of equilibrium for hydrogels under various mechanical constraints, and unravel how mechanical constraints change the convexity of the free energy and monotonicity of the stress-stretch curves, leading to phase coexistence. Using a phase-field model, we predict the pattern evolution of phase coexistence, and show many features cannot be captured by the homogeneous states of equilibrium due to large mismatch stretch between the coexisting phases. We further reveal that the system size, quenching rate, and loading rate can significantly influence the phase behavior, which provides insights for experimental studies related to morphological patterns of hydrogels.

2:45 PM BREAK

3:15 PM SB07.02.06
Hydrogels Crosslinked with Dynamic Thia-Conjugate Bond and Incorporated with Poly(ethylenedioxythiophene) Nanoparticles as Photothermally Responsive Controlled Release System Kushal Thapa[1], Joanna Zepeda[1], McKenzie Siller[1], Edgar Torres[1], Mackenzie Otakpor[1], Thomas FitzSimons[2], Anne Crowell[2], Adrianne M. Rosales[2] and Tania Betancourt[1,1]; [1]Texas State University, United States; [2]The University of Texas at Austin, United States

Introduction: Hydrogels are a class of soft materials formed by crosslinking of hydrophilic polymers. The nature of crosslinks at the molecular level determines the properties of the hydrogels at the macroscopic level. In our research, we utilized a thia-conjugate bond as means of crosslinks in our poly(ethylene glycol) or PEG based hydrogel. This dynamic covalent bond provides a self-healing ability to the hydrogel.[1] Additionally, the equilibrium of the crosslinking reaction can be shifted with thermal, mechanical, or pH stimulus.[2] For the bulk hydrogel, this translates to a controllable transition between gel and sol state by modulating these stimuli. We investigated the thermal response of the hydrogel to develop an on-demand, pulsatile drug delivery system. Further, we incorporated poly(ethylene dioxythiophene) or PEDOT nanoparticles within the hydrogel to facilitate photothermal modulation of the drug release by administering clinically relevant near-infrared (NIR) light.

Materials and Methods: We used Michael addition of thiol-ene pairs from four-arm PEG thiol (PEG-SH) and four-arm PEG benzylcyanoacetamide (PEG-BCA) to form dynamically crosslinked hydrogels. PEDOT nanoparticles were synthesized using an emulsion polymerization process and were entrapped within the hydrogel. The nanoparticles' size, polydispersity index, zeta potential, absorbance spectra, and photothermal profile upon 808 nm laser irradiation were characterized. As for the hydrogel-PEDOT complex, its micromorphology was visualized using scanning electron microscopy (SEM) and its gel-to-sol transition temperature was characterized using rheology. BSA-FITC, a fluorescently labeled protein, was loaded into the hydrogel-PEDOT complex and its release behavior into a buffer upon direct thermal stimulation and photothermal stimulation with an 808 nm laser was investigated. The injectability of the hydrogels was studied using hypodermic needles. The biocompatibility of the hydrogel-PEDOT complex was characterized on the MDA-MB-231 cell line using the MTT assay.

Results and Discussion: PEDOT nanoparticles had an average size of 56.3 nm, a polydispersity index of 0.252, and zeta potential of -77.7 mV. Visible-near infrared (Vis-NIR) spectroscopy showed that the nanoparticles had an absorbance peak at 780 nm. The photothermal stimulation of these nanoparticles with an 808 nm laser (3 W/cm^2) showed a fast increase in temperature plateauing within the first five minutes. The nanoparticles also showed photothermal stability on repeated pulsatile laser stimulation. As for the hydrogel, SEM showed a 3D net-like porous microstructure while rheology showed a gel-sol transition temperature ranging from 33-55 °C depending on the hydrogel weight percent. This transition temperature range being tunable and physiologically relevant lends itself to applications in biomedical engineering. Drug release studies on BSA-FITC loaded hydrogel-PEDOT complex showed zero-order release profiles on continuous thermal and photothermal stimulation. Pulsatile release upon thermal and photothermal stimuli was observed, but the latter method suffered from low reproducibility potentially due to inhomogeneous nanoparticle distribution or uneven hydrogel heating. MTT studies showed that the hydrogel-PEDOT complex is not cytotoxic.

Conclusions: Our dynamically crosslinked hydrogel loaded with PEDOT nanoparticles showed photothermally stimulated drug release in a clinically relevant environment. Future works will investigate the in-vitro performance of this hydrogel-PEDOT system.

References:[1]FitzSimons, Macromolecules, 2020, 53, 3738-3746; [2]FitzSimons, ACS Polym Au, 2022, 2, 129-136.

3:30 PM SB07.02.07

Periodic Dynamic Polymers: Engineering Self-assembled Microstructures to Design Artificial Muscles and Underwater Adhesives Christopher B. Cooper and Zhenan Bao; Stanford University, United States

Polymer networks formed through dynamic noncovalent or covalent bonds exhibit robust and tunable mechanical properties (e.g., tough, elastic, self-healable, stimuli-responsive, and reconfigurable). In nature, these networks are often hierarchically-ordered to perform precise functions and assemble via cooperative interactions of many weak bonds as opposed to the independent association of a few strong bonds. Here, we use these principles to design linear polymers with periodically-placed dynamic bonds that collectively assemble into supramolecular nanofibers at equilibrium and under strain. We show that when the overall molecular weight (M_n) is below the polymer's critical entanglement molecular weight (M_c), self-assembly of supramolecular nanofibers occurs, increasing the bulk film modulus by over an order of magnitude and delaying the onset of terminal flow by more than 100°C. We then design a periodic dynamic polymer with record-high shape memory recovery stress (12.8 MPa) and energy density (18.9 MPa) based on the formation of strain-induced supramolecular nanostructures. While initially, polymer chains adopt an amorphous structure ($M_n > M_c$), during strain the polymers form nanostructures that trap the elongated backbones, enabling use as an artificial muscle. Finally, we design periodic dynamic polymers with a controlled nanophase morphology to enable high-strength underwater adhesives that can be reversibly adhered to a variety of substrates and fully recycled after use. These examples show how periodic dynamic polymers are a promising class of materials whose material properties arise from well-defined backbone periodicity.

Publication Reference:
Using Periodic Dynamic Polymers to Form Supramolecular Nanostructures
DOI: 10.1021/accountsmr.2c00101

High Energy Density Shape Memory Polymers Using Strain-Induced Supramolecular Nanostructures
DOI: 10.1021/acscentsci.1c00829

Multivalent Assembly of Flexible Polymer Chains into Supramolecular Nanofibers
DOI: 10.1021/jacs.0c07651

3:45 PM SB07.02.08
Role of Stereochemistry in Reconfigurability of Diels-Alder Polymer Networks and Nanocomposites Svetlana A. Sukhishvili[1], Junho Moon[1], Zhen Sang[1] and Frank Gardea[2]; [1]Texas A&M University, United States; [2]Weapons and Materials Research Directorate, DEVCOM Army Research Laboratory South, United States

Diels-Alder polymers (DAP) networks formed by the furan-maleimide "click" reaction demonstrate the unique ability to reconfigure their permanent shapes through the mechanism of network plasticity. We report the important roles of stereochemistry of DA junctions and crosslinking density in the rates of bond reshuffling and reconfigurability of DA networks. Specifically, using a combination of DSC and variable-temperature FTIR techniques, we demonstrate that the rate of bond reshuffling is dependent on the stereochemistry of DA junctions and that this rate is faster for *endo* DA isomers as compared to their *exo* counterparts. We quantify the rates of temperature-dependent conversion of *endo* to *exo* isomers and relate them with changes in Young's moduli, the degree of strain recovery, and stress relaxation in DAP materials. We demonstrate that due to the higher thermal stability of *exo* adducts, the elastic modulus of the DAP networks and strain recovery both improve during temperature annealing. Taking advantage of the facile control of content of *endo* isomers in DAP networks via crosslinking density and flexibility of crosslinks, we introduce a concept of constructing multi-materials with programmable, spatially controlled shape morphing properties. Finally, we show that DAP networks present a powerful platform for constructing conductive nanocomposites with extremely low percolation threshold and re-programmable shape morphing controlled by stereochemistry of DA junctions and driven by electric field.

SESSION SB07.03: Poster Session: Unconventional Polymer Networks
Session Chairs: Julia Koerner and Yuran Shi
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SB07.03.02
Adaptable Sliding Hydrogels Accelerate Cartilage Regeneration via Enhancing Mechanosensing Julia M. Johannsen, Sarah J. Jones, Xinming Tong, Manish Ayushman and Fan Yang; Stanford University, United States

Introduction: Acute injury to articular cartilage is a leading cause of osteoarthritis, yet effective regenerative therapies remain lacking. Hydrogels have been utilized for cartilage repair due to their injectability and minimally invasive delivery of cells and bioactive molecules. Our lab has previously reported sliding hydrogels (SG) with covalent crosslinks and ligands attached to ring structures, which can slide along linear PEG backbones. This unique design facilitates cellular reorganization of the local niche and accelerates MSC chondrogenesis and cartilage formation compared to non-mobile chemical hydrogels (CG) [1]. Physically-crosslinked alginate hydrogels were recently used to show that viscoelasticity also enhances cartilage deposition by chondrocytes in 3D and correlates with increased cell volume [2]. We hypothesize that introducing viscoelasticity into SG would further enhance chondrocyte-based cartilage formation in 3D. To test this hypothesis, the goals of this study are to develop adaptable sliding hydrogels (ASG) with tunable stress relaxation for enhancing cell-based cartilage formation and to elucidate underlying biophysical mechanisms by characterizing cellular mechanosensing.

Material and Methods: To introduce dynamic crosslink in SG, hydrazine-functionalized polyrotaxane (PR-Hyd) and 8-arm-alkyl- and benz-aldehydes (AA and BA) were used. Three ASG groups were tested, with stress relaxation tuned by varying the ratio AA to BA. To characterize the mechanical properties of hydrogels, unconfined compression and shear-based rheological testing were used. Juvenile bovine chondrocytes were encapsulated at 10M/mL and cultured in chondrogenic medium for 21 days. Cartilage formation was evaluated by biochemical assays for sGAG and collagen, histology, immunostaining, and mechanical testing. Cell proliferation and cell volume change were also quantified. To evaluate the effect of tuning stress relaxation in ASG on cell mechanosensing, IF staining and western were performed to assess expression levels of markers for focal adhesion, cytoskeletal tension and nuclear mechanosensing.

Results and Discussion: By tuning the ratio of AA:BA, ASG with tunable stress relaxation were obtained (slow, intermediate, and fast). Compared to elastic SG, introducing viscoelasticity significantly accelerated sGAG and total collagen production in a dose-dependent manner. The same trend was observed for cell proliferation, interconnectivity of newly deposited cartilage, and type II collagen—a marker for articular cartilage phenotype. Impressively, cell-deposited cartilage matrix led to over 100 fold increase in compressive moduli after 21 days of culture to a range closer to that of native cartilage. Unlike previous alginate hydrogels, ASG-enhanced cartilage formation did not induce changes in cell volume, indicating the involvement of different molecular mechanisms. Increasing stress relaxation also led to enhanced cytoskeletal formation, suggesting ASG-enhanced cartilage formation is mediated through enhanced mechanosensing. Notably, our ASG achieved robust cartilage formation with only 10% of the cell density used in a previous alginate-based study, which is promising in overcoming donor scarcity. Together, these results support our hypothesis and demonstrate that ASG is promising for enhancing cell-based cartilage regeneration with restored mechanical functions.

Acknowledgements: NIH R01DE024772 (F.Y.), R01AR074502 (F.Y.), NSF Graduate Fellowship DGE-1656518 (S.J.), Stanford Interdisciplinary Graduate Fellowship (M.A.), and Stanford Bioengineering REU (J.J.).

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[2] Lee, H., Gu, L., Mooney, D. et al. Mechanical confinement regulates cartilage matrix formation by chondrocytes. Nature Mater 16, 1243–1251 (2017). https://doi.org/10.1038/nmat4993

5:00 PM SB07.03.03
Effects of Silica Nanospheres on the Sol-Gel Transition of Thermo-Responsive Polymers Based on poly(N-vinylcaprolactam) Lucas Ribeiro[1], Renata L. Sala[1,2] and Emerson R. Camargo[1]; [1]Federal University of São Carlos, Brazil; [2]University of Cambridge, United Kingdom

The insertion of nanoparticles in smart polymers allows the addition of new functionalities to the material, as well as the improvement of some of its properties. However, the design of these materials needs to be done with care so that the stimulus-response property is not lost. An example of a responsive polymer is poly(N-vinylcaprolactam) (PNVCL), which suffers a transition when heated above the lower critical solution temperature (LCST). This transition occurs due to a decrease in the mixing entropy that leads to the breaking of hydrogen bonds between the polymer and the water molecules. As a consequence, the polymer self-aggregates through predominant hydrophobic interactions. This polymer is used in biomedical applications, mainly in tissue engineering and drug delivery systems, making its mechanical properties essential to support the daily movements of the human body. One way to enhance this property is through the insertion of nanoparticles of silica that can improve the rheological properties of polymers. Thus, nanocomposites of PNVCL and silica nanospheres were synthesized in situ by radical polymerization. Nanoparticles, of two different sizes (80 and 330 nm) were added at the proportion of 5% and the reaction was carried out for 4h at 70 °C in an inert atmosphere. The LCST and the energies involved during the transition were calculated from the analysis of a polymer aqueous suspension (1% m/v) by UV-vis spectrophotometry. The material changes from a transparent to opaque system when heated, allowing to be studied by its transmittance at different temperatures. All three synthesized polymers showed a LCST close to 34 °C, which results in gel formation in the body temperature. In addition, the pure polymer presented constant transmittance before the transition. On the other hand, the nanocomposites presented a diffuse decay of transmittance with increasing temperature not previously observed for pure polymer, indicating a diffuse transition. This behavior is related to changes in the solvation of PNVCL chains. The presence of nanoparticles disrupts the interactions between water molecules and polymer chains, facilitating phase separation [1]. This phenomenon was confirmed by the dynamic light scattering technique, in which the hydrodynamic diameter of the pure polymer remained constant at 4 nm during heating, while the mean globule size of the nanocomposites increased. The insertion of nanoparticles in the PNVCL can affect not only the transition profile but also its thermodynamics. The calculated enthalpy change during the sol-gel transition for the pure polymer was 9752 kJ/mol. However, the nanocomposites presented lower values, close to 6400 kJ/mol. This decrease was previously reported for crosslinked systems of thermosensitive polymers, indicating that in addition to interfering with the solvation of polymer chains, these nanoparticles also act as crosslinking agents [2]. Furthermore, the size of the nanoparticles did not interfere in the variation of the transition enthalpy. Considering the application of these biocompatible sensitive polymers as injectable systems, the effect of the nanospheres on the rheological properties of PNVCL was analyzed. When the solutions were heated to 37 °C, they still presented the loss modulus higher than the storage modulus, confirming the transition of the materials to the agglomerated state, however with no hydrogel formation. In addition, the nanocomposites presented higher values of G′ and G″ when compared to the pure polymer, confirming that the addition of the nanoparticles can improve the rheological properties after the transition. Thereby, the insertion of silica nanoparticles, despite altering the transition profile of PNVCL, manages to improve rheological properties without affecting their temperature sensitivity.

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5:00 PM SB07.03.04
Two-Way Shape Memory Polymer from a Crosslinked Periodic Dynamic Network Yuran Shi, Christopher B. Cooper, Jiancheng Lai and Zhenan Bao; Stanford University, United States

We recently reported a high-performance one-way shape memory polymer that includes periodic dynamic bonds and exhibits supramolecular nanostructures under stain. The strategy of incorporating periodic dynamic bonds into the polymer greatly enhances shape memory material properties such as energy density and stretchability. The strain-induced supramolecular nanostructures are stable at room temperature and trap the chains in an elongated state. Upon heating, the supramolecular nanostructures become unstable, causing stretched chains to quickly contract. While this material outperforms other one-way shape memory polymers, its practical applications are hindered by the need for the mechanical re-programming after each triggering. Two-way shape memory polymer material is very desirable in many applications especially in the field of biomedical, soft robotics, and actuators. Thus, we incorporate thermal and light initiated crosslinkers into the materials to try and achieve reversible actuation upon change in temperature. Polymer chains will be aligned under strain; at the same time, dynamic bonds will hold the aligned chains in place and crosslinkers will permanently record chain conformation at the stretched state. There were already various realizations of two-way shape memory materials by employing semi-crystalline polymers and liquid crystal networks. We aim to make two-way shape memory polymer from a new approach by using this periodic dynamic network.

5:00 PM SB07.03.05
Shape Fixation of Magnetically Deformed Micropillar Arrays via Dynamic Covalent Bonds Hojun Moon[1], Jae Gyeong Lee[1], Woongbi Cho[1], Jisoo Jeon[2], Jeong Eun Park[3] and Jeong Jae Wie[1]; [1]Hanyang University, Korea (the Republic of); [2]Georgia Institute of Technology, United States; [3]Inha University, Korea (the Republic of)

Polymeric micropillar arrays containing magnetic particles can perform magnetic shape reconfiguration when an external magnetic field is applied. The magnetically actuated shape of micropillar arrays, however, is temporary and recover its original geometry upon removal of magnetic field. Toward the shape-fixation of actuated geometry, in this study, we employed dynamic covalent bonds for the matrix polymer of magnetic composites to provide exchange reactions in chemical networks in response to external stimuli. Magnetic deformation is achieved by the inclusion of hard magnetic particles in the polymer composites at various concentrations. We will discuss the concentration dependent structure-property relationships and optimum concentration of the magnetic particle to maximize the magnetic deformation of micropillars. Finally, we will demonstrate the thermomechanical shape fixation of magnetically actuated micropillars by constructing new chemical networks with adjacent micropillars via dynamic covalent bonds.

5:00 PM SB07.03.06
Understanding Polymer Shear Rates and Their Relation to Molecular Architectures in Micro-Compounders Narcedalia Anaya Barbosa[1,2], Joshua Goetze[2], Christopher J. Ellison[2] and Frank Bates[2]; [1]University of Texas Rio Grande Valley, United States; [2]University of Minnesota, United States

This research provides a better understanding of the rheological behavior of polyethylene at different processing conditions using the DSM Xplore 5 and 15 cc micro-compounders. Polymers used were high density polyethylene (HDPE) with a linear architecture, low density polyethylene (LDPE) showcasing a long chain branched structure, and linear low density polyethylene (LLDPE) exhibiting a short chain branched architecture. Measurements obtained in the micro-compounders were compared to those obtained with an ARES-G2 rheometer for a range of shear rates (50, 100, 150, 200 and 250 RPM), temperatures (150°C, 200°C), fill volumes (80%, 90%, 100%) and polymers. The measurements were used to evaluate the accuracy of the micro-compounders and scalability between the systems. Comparing the rheometer data and micro-compounder predictions can aid in identifying differences related to the polymer architecture and help to understand the impact of simple and extensional shear on the polymer when it is processed.

5:00 PM SB07.03.07
Liquid Crystalline Thermoplastic Polyurethane with Self-Healing Properties SeYeon Baek and Ho Sun Lim; Sookmyung Women's University, Korea (the Republic of)

Self-healing means autonomously recovering original functions from any physical damage. Self-healing polyurethane(PU) has the common advantages of polyurethane as well as the ability to heal itself without external help. Liquid crystalline polyurethane(LCPU) with such self-healing properties can be widely used in the field of electronic materials, films, and displays. Unlike general liquid-crystalline polyurethane, it can heal itself, so it can be used for a long time by preventing it from being weakened and destroyed over time. In this study, we synthesized the self-healing LCPU through the condensation of a mesogenic diol with a diisocyanate having quadruple hydrogen bonding moieties. To confirm the self-healing properties, a heating test was conducted on damaged PU specimens and they were restored to their original shape after heating. In addition, a polarization microscope and thermal analysis were performed to observe the liquid crystal phase of synthesized LCPU.

5:00 PM SB07.03.09
Biodegradable Nancomposites of Poly(Butylene Succinate) and Cellulose Nanocrystals—Rheological Design of Mechanical and Hydrolytic Properties Hyeonjeong Kim, Youngho Eom and Hyo Jeong Kim; Pukyong National University, Korea (the Republic of)

Petroleum-based plastics are essential commodity in our everyday life because they are light, inexpensive, versatile and easy to process. However, the recent environmental pollution caused by discarded plastic wastes becomes severe owing to the non-degradability of industrial plastics. In order to solve such environmental problem, biodegradable polymers were considered as a practical solution. Both industrially and academically popular biodegradable polymers include poly(lactic acid), poly(butylene succinate) (PBS), and poly(butylene adipate-co-terephthalate). Unfortunately, the poor mechanical performance and relevant low longevity of the biodegradable polymers compared to the petroleum-based plastics have limited their commercialization. The preparation of nanocomposites using reinforcing fillers provides a solution capable of enhancing the performance of the biodegradable matrix. Then, inorganic fillers are unfavorable option because the non-degradability of metals and ceramics makes the sustainability of biodegradable polymers useless. In this regard, biomass-derived natural nanomaterials are indispensable choice for preparing the biodegradable nanocomposites. Using bio-renewable nanofibers such as cellulose nanocrystals(CNCs), cellulose nanofibers, chitin or chitosan, and nanowiskers has emerged as a promising alternative to inorganic fillers. In particular, CNCs have a high aspect ratio, high crystallinity (54-88%) and numerous polar functional groups, making it easy for secondary interaction with the organic polymer matrix.
In this study, PBS/CNC nanocomposites were prepared through solution mixing and precipitation procedures. Owing to the thermally infusible feature of CNCs, the solution blending method using dimethyl sulfoxide (DMSO) as a co-solvent was adopted to fabricate the PBS/CNC nanocomposites. The PBS/CNC mixed solutions in DMSO were precipitated with deionized water as a coagulant. The washed PBS/CNC powder was dried in a vacuum oven at 60 °C for 24 h to obtain the desired nanocomposites. The CNC loading relative to the total polymer content varied from 0 to 3.0 wt%. The PBS/CNC nanocomposites will henceforth be referred to as "CNC*n*" with *n* denoting the CNC loading (wt%).
The ultimate tensile strength (UTS) varies non-steadily with CNC loading, indicating a 1.17-fold increase until 0.8 wt% (33.3 MPa for neat PBS to 39.2 MPa for CNC0.8), followed by a progressive decrease upon further incorporation up to 3 wt% (34.9 MPa for CNC3.0). The increasing extent of Young's modulus (E), UTS, and toughness per unit of CNC loading (1 wt%) [(fold-1) wt%-1] was calculated and shown as a function of the CNC loading in order to assess the effectiveness of CNCs as reinforcing elements in PBS. We identified that at a crucial CNC loading, the reinforcing efficiency shows a noticeable trend change. In relation to E, up to 1.5 wt% CNC loading, reinforcing efficiency increases; after that, it starts to decline. PBS-CNC nanocomposites were hydrolyzed in a chemical condition that contained 0.1 N NaOH. For PBS-CNC nanocomposite films even after the hydrolysis for 6 days (below 0.8 wt%), the films above the critical CNC content (CNC1.0, 2.0, and 3.0) exhibits specific morphology due to an extensive chemical etching by hydroxyl anions in contrast to the less-degraded neat PBS.
By investigating the phase properties and homogeneity, the rheological percolation threshold may be explained. It is rational to assume that the CNCs' percolation behavior in the polymer matrix may be connected with the considerable change in the CNCs' reinforcing efficiency at a certain loading. This study suggests a rheological basis to understand and efficiently control the characteristics of biodegradable nanocomposites of PBS and CNC by adjusting the percolation behavior of the nano-fillers.

5:00 PM SB07.03.08
Tailored Smart Hydrogels as a Potential Sensing Material for Exhaled Breath Analysis Sitao Wang[1], Gerald Gerlach[1] and Julia Koerner[2]; [1]Technische Universität Dresden, Germany; [2]Leibniz University Hannover, Germany

Smart hydrogels are a very promising sensing material, especially for biomedical applications, due to their stimulus responsiveness, easily achievable biocompatibility and wide range of material compositions. Many different physical or chemical stimuli (e.g. temperature, pH, ionic strength, biomolecules) can cause the volume-phase transition of the polymer which is usually based on the uptake or release of liquid. Hence, in most cases smart hydrogels are employed in aqueous environments [1].
The development of a smart hydrogel material able to maintain the swelling response in gaseous environments would allow to extend the potential for very high selectivity and sensitivity towards analytes in gases such as volatile organic compounds (VOCs).

We have investigated different synthetic smart hydrogel materials with regard to their ability of exhibiting a measurable swelling response in varying relative humidity for the target VOC analytes acetone and isopropanol. The materials include the homopolymers polyacrylamide (PAM), polyacrylic acid

(PAA) and poly(*N*-isopropylacrylamide) (PNIPAAm), and their co-polymer combinations. The swelling response for varying relative humidity from 2% to 100% and different VOC concentrations (up to 100 ppm) was studied by weighing and through piezoresistive pressure sensing. In the latter case, the hydrogels were directly polymerized on a silicon membrane by mask-based UV-polymerization.
We found that PNIPAAm exhibits the most significant swelling response for both target analytes. It furthermore allows to distinguish between the analytes as the weight change for isopropanol is much higher than for acetone.

In a second study we focused on enhancing the stimulus-responsiveness of the material further by increasing porosity through adding of polyethylene-glycol (PEG) into the PNIPAAm pregel solution. After polymerization, PEG is washed out by keeping the sample in deionized water for thirty days, resulting in a porous structure.
However, the pores are not stable and irreversibly collapse when the hydrogel is air-dried for use in a gaseous environment. In order to stabilize the porous matrix and maintain the enhanced swelling response, we determined that the following treatment is necessary after polymerization and washing: (i) freeze-drying of the sample (liquid nitrogen or freezer), and (ii) conditioning in high relative humidity (90 – 100 %). The first step is crucial to preserve the porous network after fabrication. In that state, the polymer chains are stretched and not in equilibrium due to the swelling during washing. In order to allow for relaxation and reordering of the polymer chains, the subsequent conditioning is required where the material shrinks.
Scanning electron microscopy studies confirmed that these steps are essential in preserving the fabricated porous structure. It is furthermore indicated that the addition of PEG is crucial in stabilizing the pores as well. Without PEG, freeze-dried and conditioned samples exhibit the same structural collapse as PEG-modified air-dried and pure air-dried samples [2].

Based on these investigations, we can draw the following conclusions: (i) smart hydrogels can maintain their swelling-response in gaseous environments for a wide range of relative humidity, (ii) PNIPAAm is a promising candidate for acetone and isopropanol detection in gases and (iii) the swelling response can be strongly enhanced by adding of PEG and subsequent freeze-drying and conditioning to stabilize the porous structure.
This study provides a basis for extending the application range of smart hydrogel materials to VOC sensing. Due to the potential for further tunability of the hydrogel material and its favorable mechanical properties, miniaturizable wearable sensor concepts can be envisioned for the future.

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5:00 PM SB07.03.10
Synthesis and Characterization of MXene-Modified PNIPAAm Hydrogel for VOC Gas Sensing Sitao Wang[1], Gerald Gerlach[1] and Julia Koerner[2]; [1]Technische Universität Dresden, Germany; [2]Leibniz University Hannover, Germany

MXene, as a novel two-dimensional (2D) material, has gained tremendous attention due to its unique chemical and physical properties. Especially in gas sensing, the large specific surface area and potential for tailoring by means of surface functionalization are very favorable. To date, most of the sensing devices are based on interdigitated electrodes (IDEs) where the metallic conductivity and p-type sensing behavior of the MXene are harnessed [1]. However, the conventional drop-casting method for material fabrication on IDEs generally creates a compact and dense layer of MXene flakes stacked together which reduces the number of active sites and decelerates gas adsorption and desorption.

In our work, we aim at combining the favorable properties of MXene with smart hydrogels to create fully three-dimensional, highly sensitive and selective composite materials specifically tailored for detection of volatile organic compounds (VOCs). The role of the MXene is twofold: (i) Enhancement of gas sorption and swelling response of the hydrogel and (ii) providing a means for direct transduction of the hydrogel's analyte-dependent swelling-state, constituting a sensing material with integrated transduction.

As a first step, we focused on synthesizing a truly 3D $Ti_3C_2T_x$ bulk MXene by ice-templating and subsequent cation-induced stabilization based on [2]. The gas sorption ability was studied by gravimetric experiments in varying relative humidity from 2% to 100% and different acetone and isopropanol concentrations as test VOCs. In the weighing studies, 3D MXene demonstrated a stable sorption for both analytes without being severely affected by changing humidity. In order to compare the response of our 3D MXene to conventionally drop-cast-fabricated ones, we furthermore synthesized both types on IDEs and tested them in the same gas environments. This revealed a faster response of 3D MXene for both test analytes. Images acquired by scanning electron microscopy (SEM) verified the successful fabrication of a 3D porous MXene. However, the 3D structure oxidized rapidly, leading to material degradation and a significant increase in resistance after few tests.

In a second step, we incorporated the MXene into a smart poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel. We have recently demonstrated that this type of smart polymer is well suited for VOC detection and which fabrication steps are necessary to achieve a stable 3D porous structure for a fast response [3].
Composite fabrication was achieved by mixing $Ti_3C_2T_x$ MXene suspension with NIPAAm pregel solution containing poly(ethylene glycol) (PEG) as porogen. Leaching of PEG and subsequent freeze-drying of the swollen gel create a porous structure [3]. In order to explore the gas sorption ability of the composite material, gravimetric measurements were carried out in the same manner as described above.
SEM analysis and energy-dispersive X-ray spectroscopy confirmed the formation of a highly porous composite matrix with homogeneous MXene distribution. However, the weighing results did not indicate an improvement of the gas sorption ability (amount of swelling, time constants) of the MXene-enhanced PNIPAAm composite compared to the unmodified PNIPAAm. On the contrary, the achievable delta-weight change was reduced which we ascribe to the fast degradation of the MXene and its, yet unknown, effects on the hydrogel matrix. This will be studied further in fundamental investigations of the interactions between polymer matrix and MXene in order to combine the favorable properties of both for future applications.

References
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5:00 PM SB07.03.11
Sodium Alginate/Nanochitosan Nanocomposite Films with Enhanced Mechanical Performance for Food Packaging Applications Hyo Jeong Kim, Hyeonjeong Kim and Youngho Eom; Pukyong National University, Korea (the Republic of)

The petroleum-based plastics were regarded as an imperative commodity of our daily life and as a result, the amount of plastic products consumed is increasing exponentially. In addition, the conventional plastic-based disposable materials including plastic cups and straws are not able to be reused and recycled. Consequently, the environmental pollutions caused by the single-use plastics have become severe. To alleviate these issues, biodegradable and sustainable food packaging materials that can replace the traditional polymeric materials and films have attracted significant interests in both academic and industrial fields. Food packaging films are essential component to guarantee the food safety from the external contaminant, damage, and spoilage. Accordingly, as an alternative to the non-degradable plastic-based packaging films, the eco-friendly packaging films should satisfy several properties such as high mechanical strength, water-resistance, and gas barrier.

Natural polysaccharides polymers such as sodium alginate, starch, cellulose, and chitosan have been regarded a promising alternative to the petroleum-driven polymer packaging films. Among them, sodium alginate (SA) extracted from the brown algae is a co-polymer composed of two linked anionic monomers, β-d-mannuronic acid, and α-l-guluronic acid. Especially, owing to the negative charge of SA, this polysaccharide favors ionic interaction with cationic polymers when blended. Considering this feature of SA, we prepared the SA nanocomposite films by incorporating chitosan nanowhiskers (CSWs) with positively charged surface. CSW originates from the chitin biomass, and then was synthesized through two-step process as follows. Chitin was disintegrated using 3 N hydrochloric acid aqueous solution by refluxing for 3 h. The suspensions were centrifuged and washed with deionized (DI) water for several times. The suspensions were neutralized to pH 7 and then dialyzed with DI water for 7 d. The obtained chitin nanowhisker (CNW) suspensions were deacetylated by adding the excess NaOH and then CSW suspensions were eventually obtained. The CSW molecules have positive charge on the surface, in contrast to cellulose nanocrystal (CNC) with negative charge structure, which is another popular bio-derived nano-filler. Thus, it is expected that the interaction between SA and CSW produces the synergistic effect.

The SA/CSW and SA/CNC nanocomposite films were prepared by the solvent casting method. First, CNC powders were dispersed in DI water, whereas CSW aqueous solution with a specific concentration was prepared by diluting CSW suspension with extra DI water. The concentrations of two aqueous solutions were set to 0, 0.5, 1.0, 1.5 w/w% with respect to the SA amount. SA powders were then dissolved in each CNC and CSW aqueous solution at 60 °C for 2 h and then 12.5 g of the respective solutions were poured on petri dish, followed by drying at 40 °C for 20 h. Finally, the structural, mechanical, morphological, water-resistant, and gas-barrier properties of the obtained SA and nanocomposite films were assessed.

In order to identify the network of functional groups and the intermolecular interactions between SA and the natural nano-fillers, the FT-IR characterization was performed. For the neat SA film, the -OH stretching band was observed around 3700-2700 cm^{-1}. On the other hand, the -OH and -NH stretching bands of CSW were observed in SA/CSW nanocomposite films in the identical region. Furthermore, the sharp carbonyl peak of CSW nanocomposites film was shifted to higher wavenumber. This result suggests the intermolecular interactions between anionic SA and cationic CSW. The tensile strength and elongation at break of CSW nanocomposite films were higher than SA films, exhibiting a 1.85, 1.55-fold increase (121 MPa, 9.5% for SA to 223 MPa, 14.7% for CSW 1.5 w/w%) than SA films with increasing CSW contents whereas CNC nanocomposite films were similar to SA films (103 MPa, 5.5% for CNC 1.5 w/w%).

5:00 PM SB07.03.12

Improvement of Thin-Film Stretchability Through Synthetic Tailoring Diketopyrrolopyrrole Based Polymer for Organic Field-Effect Transistors. Bao-Nguyen T. Nguyen, Xiaozhou Ji, Hao-Wen Cheng, Yilei Wu, Song Zhang and Zhenan Bao; Stanford University, Chemical Engineering Department, United States

Materials with good mechanical and electrical properties are key components for high performance stretchable electronic devices. Well-known for their high charge mobility, diketopyrrolopyrrole- (DPP-) based conjugated polymers are popularly used in many organic devices, such as organic field-effect transistors, solar cells, and sensors. Owing to their high crystallinity, DPP-based polymers often lose their electrical performance under strain. To improve the stretchability and fatigue resistance, both crystalline and amorphous domains of the DPP-based polymers are tuned to accommodate mechanical stretch, such as by introducing long and branched alkyl chains bound to the DPP nitrogen atoms or incorporating flexible units into the aromatic backbones. Here, we report semiconducting polymers synthesised from methyl substituted thiophene DPP (MeTDPP) as an acceptor unit and thienylenevinylene (TVT) as a donor unit. Compared to the analogous TDPP-TVT polymer with no methyl substituted groups, MeTDPP-TVT polymer exhibited higher stretchability with comparable charge mobility. The crystallinity of the polymers was confirmed by GIWAX. The planarity of the polymers was investigated by DFT calculations showing gas-phase torsional angles at the optimised structures. The calculations suggested that the methyl substituted groups disrupted the planarity of the TDPP units, causing the thiophene rings to twist more prominently and thus reducing the crystallinity of the polymer chains. MeTDPP-TVT also showed a shallower HOMO energy level measured by UPS, aligning with its stronger aggregation in thin film state observed in UV-Vis-NIR absorption spectrum.

SESSION SB07.04: Tough Polymer Networks
Session Chairs: Ximin He and Qiming Wang
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2018

8:30 AM *SB07.04.01

Soft Materials by Design: Unconventional Polymer Networks Give Extreme Properties Xuanhe Zhao; Massachusetts Institute of Technology, United States

Soft materials are ubiquitous in nature and everyday life. The first part of the talk is focused on a general strategy to design soft materials possessing extreme properties. The second part of the talk is specifically focused on the toughening of soft materials. The ratio between fracture toughness and intrinsic fracture energy of a soft material defines its toughness enhancement. Soft materials' toughness enhancement has been long attributed to their bulk stress-stretch hysteresis induced by dissipation mechanisms such as Mullins effect and viscoelasticity. With a combination of experiments and theory, here we show that the bulk dissipation mechanisms significantly underestimate the toughness enhancement of soft tough materials. We propose a new mechanism and scaling law to account for extreme toughening of diverse soft materials. We show that the toughness enhancement of soft materials relies on both bulk hysteric dissipation, and near-crack dissipation due to mechanisms such as polymer-chain entanglement. Unlike the bulk hysteric dissipation, the near-crack dissipation does not necessarily induce large stress-stretch hysteresis of the bulk material. The extreme toughening mechanism can be universally applied to various soft tough materials, ranging from double-network hydrogels, interpenetrating-network hydrogels, entangled-network hydrogels and slide-ring hydrogels, to unfilled and filled rubbers.

9:00 AM SB07.04.02

Designing Gels to Absorb Impact—How a Thin Gel Can Protect an Egg from Breaking Mahima Srivastava[1], Sairam Ganesh[1] and Nikhil Subraveti[2,1]; [1]University of Maryland, United States; [2]Princeton Center for Complex Materials, United States

In recent years, several routes have been devised to make hydrogels that are strong, flexible and bendable, with prominent examples being the double-network hydrogels. This work investigates whether such strong and flexible gels can absorb impact. That is, can such a gel be wrapped around a brittle or fragile object (such as an egg) and protect the object if it is dropped onto a hard surface. We have studied a range of gels, including gels made by either physical cross-linking (e.g., gelatin) or chemical cross-linking (e.g., acrylamide, AAm) or both (double network gels of AAm and alginate). None of these bare gels are able to absorb impact. We also studied the same gels with various particulate additives, including iron-oxide, carbon-black, and graphene: again, none of these particles improve the protective abilities of the bare gels.

The central result from our work is that the addition of starch granules greatly enhances the protective abilities of any gel. This is observed both with gelatin and AAm gels. When a load strikes a gel containing 20% starch, the peak impact force is reduced by 25% when compared to a bare gel without the starch. Correspondingly, the coefficient of restitution (COR) is also lowered by the presence of starch (i.e., a ball bounces much less on a starch-bearing gel). An egg covered with a starch-bearing gel survives impact on a hard surface from a height of 25 inches. Similarly, a blueberry covered with the gel resists being crushed when a weight is dropped on it.

We correlate the impact-absorbing effects of starch granules to their ability to shear-thicken water. When starch granules are gelatinized by heat, they no longer give rise to shear-thickening, and in turn, their protective ability in a gel is also eliminated. Our research can guide the rational design of protective coatings or armor for fragile objects, which could be applied in the sports, defense, and consumer sectors.

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9:15 AM SB07.04.03
A Multiscale Model for Reversible, Thermally Activated Chain Scission and Healing in Polymer Networks and Interfaces Rui Huang; The University of Texas at Austin, United States

Rate-dependent fracture and healing have been observed for many polymer networks and interfaces. Here, we propose a multiscale approach to modeling reversible chain scission as a mechanism for rate-dependent fracture and healing, considering the energetics of bond stretching, the entropic effect of long molecular chains, the kinetics of thermally activated chain scission, and the statistical distributions of chain lengths. These multiscale features are seamlessly assembled to formulate a rate-dependent model, linking the macroscopically measurable properties (e.g., toughness and strength) to the underlying molecular structures of the polymer network, while the rate dependence results naturally from the kinetics of damage evolution as a thermally activated process. Through this model we seek to answer the following questions: (1) What is the enery barrier for the thermally activated chain scission, and how does it change with continuous loading or deformation? (2) Under what conditions can the broken chains heal? (3) Can such a model simulate a dynamic polymer network under cyclic loading?

9:30 AM BREAK

10:00 AM SB07.04.04
Molecular Stiffness Cues of Interpenetrating Hydrogel Networks for Cell Adhesion Bin Li, Arzu Colak, Johanna Blass, Mitchell Han, Aránzazu del Campo and Roland Bennewitz; Leibniz Inst for New Materials, Germany

The response of cultured cells to the mechanical properties of hydrogel substrates depends ultimately on the response of single crosslinks to external forces exerted at cell attachment points. We performed single-molecule force spectroscopy experiments using AFM to probe the mechanics of single cross-links which mediate the cell attachment and spreading. We compared hydrogels of varying elastic modulus which exhibited significant differences in fibroblast spreading and derived an effective spring constant for the displacement of single cross-links at the hydrogels' surface. A factor of ten in the elastic modulus E of the hydrogel corresponded to a factor of five in the effective spring constant k of single crosslinks, indicating a transition in scaling with the mesh size ξ from the macroscopic $E \propto \xi^{-3}$ to the molecular $k \propto \xi^{-2}$ [1].
We also prepared an interpenetrating network (IPN) design based on a stiff PEGDA host network interlaced within a soft 4-arm PEG-Maleimide/thiol (guest) network. The IPN presents different mechanical cues at the molecular scale, depending on which network is linked to the probe, but the same mechanical properties at the macroscopic length scale as the individual host network. Cells attached to the interpenetrating (guest) network of the IPN or to the single network (SN) PEGDA hydrogel modified with RGD adhesive ligands showed comparable attachment and spreading areas, but cells attached to the guest network of the IPN, with lower molecular stiffness, showed a larger number and size of focal adhesion complexes. The observations indicate that cell adhesion to the IPN hydrogel through the network with lower molecular stiffness proceeds effectively as if a higher ligand density is offered [2].
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10:15 AM SB07.04.05
Effect of Crosslink Homogeneity on the High Strain Behavior of Elastic Polymer Networks Victoria Kong and Jennifer Laaser; The University of Pittsburgh, United States

The topology of polymer networks affects critical material properties such as elastic modulus and toughness. While the effects of crosslink homogeneity and topological defects are well understood in low strain regimes, quantifying their effects in the high strain regime has proven difficult because of premature network fracture. Here, we address this problem using a double network approach, in which the network of interest is swollen in a mixture of monomer and crosslinkers that is then polymerized to generate a secondary network that helps dissipate stress. We examine the effect of crosslink homogeneity by comparing the low and high strain behaviors of randomly and regularly crosslinked butyl acrylate networks. Regularly crosslinked networks are synthesized via coupling of n-butyl acrylate star polymers, while randomly crosslinked networks with comparable moduli are synthesized by free-radical polymerization. We find that the randomly crosslinked networks exhibit a much earlier onset of non-Gaussian strain stiffening behavior than the comparable regularly crosslinked networks, indicating the importance of strand length distribution, and particularly the shortest strands, in determining the high strain behaviors of elastic polymer networks.

10:30 AM SB07.04.07
WITDRAWN (NO SHOW) 5/5/23 SB07.04 Design Rationale for Polymer Networks—From Stimuli Responsive Hydrogels to Dual-Cure 3D Printable High Performance Polymers Xiao 'Matthew' Hu; Nanyang Technological University, Singapore

This presentation aims to discuss the design rationale of a class of thermally responsive semi-IPN hydrogels and a series of photo and thermal dual curable liquid monomers that are fit for high resolution precision 3D printing via projection micro-stereolithography (PμSL), leading to 3D printed polymers that are of high strength, stiffness and glass transition temperatures. In the former case, systematic investigation was carried out and discussed on how swelling and deswelling ratios and their kinetics are uniquely tunes and controlled in these stimuli responsive semi-IPN hydrogels. Furthermore, the semi-IPN structure turns out to be ideal for surface deposition of highly robust and conformal polyamide layers onto these hydrogels via interfacial polymerization. In the latter case, the discussion focuses on design dual cure high Tg and high strength polymer networks. Their photo curability and low monomer viscosity allow high resolution stereolithography 3D printing to be readily carried out via a free radical polymerization. Their subsequent thermal curability allows the formation of an extra network via a ring opening reaction. Although unlike the reported double-network systems, these dual network structure endows these polymers with not only extra-robustness such as thermal resistance, high strength and stiffness, but also intrinsic flame resistance among other attributes. Both polymer systems have potentials for various functional and engineering applications.

SESSION SB07.05: Stimuli-Responsive Polymer Networks
Session Chairs: Pengfei Cao and Qiming Wang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2018

1:30 PM SB07.05.01
Shape-Morphing Liquid Crystal Elastomer-Based Tissue Adhesives Mahjabeen Javed, Yoo Jin Lee and Taylor H. Ware; Texas A&M University, United States

Current tissue adhesives for wound management face ongoing challenges and limitations such as insufficient adhesion strength to soft and wet tissue and poor mechanical properties. Chemical-based adhesives, such as cyanoacrylates, provide high bond strength but can elicit an inflammatory response due to toxic monomers. Alternatively, mechanical systems are commercially available for clinical applications, such as sutures and staples, but these approaches can cause excessive penetration trauma. Recently, microneedle (MN) array adhesives have been developed. These mechanical adhesives offer enhanced tissue adhesion while reducing trauma and clinician time. We are developing shape-morphing liquid crystal elastomer (LCE) based microscale tissue adhesives, capable of providing strong fixation to soft and wet tissue through mechanical interlocking. The key advantage of this approach is that we can create sub-millimeter scale polymeric structures with controlled forms that can be used as MN adhesives. We employ thiol-ene click chemistry to synthesize liquid crystal elastomers capable of crystallizing after polymerization. The combination of liquid crystallinity and semicrystallinity enables these microneedles to not only exhibit large and programmable deformation strain but also high elastic modulus and toughness. Directed self-assembly is used to spatially pattern the molecular orientation of the material prior to crosslinking. This orientation dictates the shape of the polymer at body temperature. In this manner, flat sheets are able to morph into their programmed out-of-plane bent state when released from the underlying glass carrier without requiring an external stimulus. These curved needles are then inserted into the model tissue of interest. The relationship between microneedle curvature and adhesion will be discussed. The semicrystalline LCE-based MN arrays have sufficient strength to first be able to puncture and then mechanically adhere to both agarose tissue model as well as chicken tissue. The maximum pull-out force of an LCE-based microneedle is 9.6 ± 0.9 mN force per needle in an agarose tissue model. We expect that by leveraging this class of stimuli-responsive polymers, we can enable microneedle arrays to provide a safe and effective strategy for high-strength tissue adhesion.

1:45 PM SB07.05.02
Color and Shape-Switchable Biocatalytic Liquid Crystal Elastomers Responsive to Multiple Classes of Biomolecules Albert Velasco Abadia, Grant E. Bauman, Timothy White, Daniel K. Schwartz and Joel L. Kaar; University of Colorado Boulder, United States

The incorporation of enzymes into stimuli-responsive materials has the potential to sensitize their response to specific biomolecules, providing unique materials for applications such as coatings, smart textiles, drug delivery, or sensing. Among stimuli-responsive polymers, liquid crystal elastomers (LCEs) have emerged as a leading actuator platform due to their inherent programmability, realizing shape transformations and large strains upon exposure to stimuli. The immobilization of enzymes in LCEs presents an unprecedented opportunity to create polymers that undergo shape reconfigurations in response to specific biosignals. In this presentation, we will discuss the immobilization of the enzymes *Candida rugosa* lipase, glucose oxidase, and trypsin into acid-responsive LCEs. This imparted the LCEs with sensitivity to chemical signals that belong to different major classes of biomolecules, such as carbohydrates, lipids, or peptides. Enzyme-containing LCEs doped with methyl red readily switched color from yellow to red upon exposure to their enzymatic substrate. Multiple processing methods, such as twisted nematic patterning or 4D printing, were used to showcase the versatility of biocatalytic LCEs, which transformed from flat films or disks into curls or cones, respectively. Multiplexed responsiveness was demonstrated using a connected array of disks, each containing a different enzyme, highlighting the excellent chemical selectivity of enzymes. This work presents a novel platform of versatile bioresponsive color-switchable actuators that may have application in a wide range of biological fields.

2:00 PM SB07.05.03
Mussel-Inspired Strain-Responsive Adhesive Microcapsules for Self-Regulatable Antibacterial Therapy Yun Kee Jo; Kyungpook National University, Korea (the Republic of)

Bacterial infection of a wound is a major complication that can significantly delay proper healing and even necessitate surgical debridement and other complications. Conventional non-woven fabric dressings, including gauzes, bandages and cotton wools, often fail in treating wound infections in a timely manner due to their passive release mechanism of antibiotics. Here, we propose adhesive mechanically-activated microcapsules (MAMCs) capable of strongly adhering to a fibrous matrix to achieve a self-regulated release of antibiotics upon uniaxial stretching of a non-woven fabric dressings. To achieve this, a uniform population of polydopamine (PDA)-coated MAMCs (PDA-MAMCs) are prepared using a microfluidics technique and subsequent oxidative dopamine polymerization. The PDA-MAMC allows for robust mechano-activation within the fibrous network through high retention and effective transmission of mechanical force under stretching. By validating the potential of a PDA-MAMC-laden gauze to release antibiotics in a tensile strain-dependent manner, we demonstrate that PDA-MAMCs can be successfully incorporated into a woven material and create a smart wound dressing for control of bacterial infections. This new mechano-activatable delivery approaches will open up a new avenue for a stretch-triggered, on-demand release of therapeutic cargos in skin-mountable or wearable biomedical devices.

2:15 PM SB07.05.04
Fabrication of Bendable Microstructures Using Chiral Liquid Crystal Elastomers Yoo Jin Lee, Mustafa Abdelrahman and Taylor H. Ware; Texas A&M University, United States

Dynamic microstructures that respond to changes in environmental conditions such as temperature, light, and chemical stimuli are ubiquitous in nature. For example, wheat awn undergoes reversible bending in response to humidity to propel seeds into the ground. To synthesize synthetic materials with such controlled shape change at the microscale, processing strategies that control the microstructure of shape changing polymers are required. In this work, we will discuss controlling the reversible bending of arrays of microactuators made from liquid crystal elastomers (LCEs). Directed self-assembly of liquid crystal monomers with controlled chirality within a 3D micro-sized mold results in a gradient in the molecular orientation. We varied the concentration of chiral dopants to adjust the pitch and induce an asymmetric molecular orientation inside the microactuators. When doped with a certain value of chiral dopants, one side of the actuator expands, and the other side contracts, resulting in bending. When heated up to 150 °C, the microactuators produced an average bending angle of 28.8 ± 9.6 °. We were able to confirm the asymmetric molecular alignment inside the 3D structure by sectioning the actuators using a microtome and observing those sections with a polarized optical microscope. Our new platform to synthesize microstructures utilizing chirality allows the fabrication of bendable actuators on a microscale and can further be applied in soft robotics and healthcare devices.

2:30 PM SB07.05.05
Photo-Switchable Hydrogel Friction Allison Chau, Sophia J. Bailey, Kseniia Karnaukh, Javier Read de Alaniz and Angela A. Pitenis; University of California, Santa Barbara, United States

Stimuli-responsive hydrogels have a wide range of applications spanning drug delivery to soft robotics. Hydrogel mechanics and swelling are often tuned via external stimuli such as temperature and pH, but there is an increased need for bio-orthogonality in order to improve the biocompatibility of these hydrogels. Recently, light has been used as a stimulus through the incorporation of photo-responsive molecules that isomerize in response to light irradiation. One common photochromic molecule is water-soluble spiropyran, which is copolymerized into hydrogel networks to control the swelling and deswelling kinetics, resulting in light-induced actuation and bending. However, the tribological properties (e.g., friction and lubrication) of these photo-switchable hydrogels remain largely unknown. In this work, spiropyran-methacrylate was conjugated with acrylamide to form a copolymerized hydrogel network (p(SP-*co*-AAm)). In visible light, the photoswitch is hydrophobic in its spiro form (ring-closed). Once irradiated with UV light, the photoswitch isomerizes to its hydrophilic merocyanine form (ring-open), inducing macroscopic hydrogel swelling. Using a custom-built microtribometer, we characterized the friction coefficient before and after irradiation and demonstrated spatiotemporal control over the tribological properties of these hydrogels. In comparison, light-responsive spiropyran-based surfactants (SP-DA-PEG) were introduced in solution to the interface of self-mated poly(2-hydroxyethyl methacrylate) (pHEMA) hydrogels, which typically possess high friction. Under UV light irradiation, we demonstrated a decrease in friction coefficient. Based on these findings, we hypothesize that the increase in hydrophilicity with light irradiation is responsible for changes in the tribological properties of photo-switchable hydrogels and surfactants, leading to decreases in friction coefficient. Additionally, incorporation of these photo-switchable molecules at the sliding interface may be all that is necessary for friction reduction rather than incorporation into the bulk material.

2:45 PM BREAK

3:15 PM SB07.05.06
Effect of Porosity on Silk's Water-Responsive Actuation Yeojin Jung[1,2], Maheen Khan[1,2], Darjan Podbevsek[2], Raymond S. Tu[1,2] and Xi Chen[1,2,3]; [1]City College of New York, United States; [2]Advanced Science Research Center, United States; [3]The Graduate Center of the City University of New York, United States

Water-responsive (WR) materials that mechanically swell and shrink in response to changes in relative humidity or water gradient have shown capability to exert higher energy than conventional actuators and artificial muscles, and thus hold potential to be used as high-energy actuating components for various engineering applications, including robotics, shape morphing, and smart structures. Despite the growing interest in this emerging category of WR materials, the underlying mechanisms of their significant performance are still not fully understood, hampering any rational design. One common feature of high-performance WR materials, such as bacteria peptidoglycan, is that they consist of hierarchical and stiff structures with nanoscale pores. Here, we systematically varied the porosity of *Bombyx (B.)* mori silk and tested the effect of porosity on silk's water adsorption and WR performance. To fabricate porous silk, blends of regenerated silk fibroin and Poly(ethylene glycol) solutions were cast on thin polyimide substrates, and subsequently treated with methanol and immersed in water to extract PEO. The porosity was varied by controlling the volume concentration of PEO from 0 to 60%. We found that *B. mori* silk's WR actuation energy densities increased first with increasing PEO concentration, and then decreased when the PEO concentration is higher than 20%. Notably, when silk is processed with 20%PEO, the silk showed extremely high WR energy densities of ~3 MJ m^{-3}, which is about four hundred-fold higher than that of mammalian muscles (~8 kJ m^{-3}). Further studies on silk's secondary structures, water adsorption, and water structures using scanning electron microscopy (SEM), dynamic water vapor sorption (DVS), and Fourier transform infrared spectroscopy (FTIR) showed that increasing silk's porosity can lead to dramatic changes in water-silk interactions and the structure of water confined within silk's nanopores. Our finding suggests that the pore structure-dependent water properties could play a crucial role in silk's WR performance.

3:30 PM SB07.05.07
Dynamic Device Based on Stimuli-Responsive Materials for Urethral Support: Potential Treatment for Stress Urinary Incontinence Seelay Tasmim[1], Zuha Yousuf[2], Farial Rahman[2], Mario Romero-Ortega[2], Philippe Zimmern[3] and Taylor H. Ware[1,1]; [1]Texas A&M University, United States; [2]University of Houston, United States; [3]University of Texas Southwestern, United States

Stress Urinary Incontinence (SUI) is the involuntary leakage of urine in response to increased intra-abdominal pressure such as during coughing or sneezing. This condition affects nearly 50% of adult women. Bothersome SUI can be treated with the insertion of a synthetic or autologous sling underneath the urethra to provide needed support. A limitation of current mid-urethral slings is their fixed level of support, which cannot be modulated to adjust for voiding. Here, we report the design and fabrication of a dynamic sling based on stimuli-responsive materials such as liquid crystal elastomers or magnetic elastomers. These devices are capable of achieving shape change to adjust urethral support in response to safe stimuli such as transcutaneously delivered infrared light or magnetic field in physiologically relevant environments. A scar-tissue phantom model was developed to characterize the shape change of these devices. An *in vitro* urinary tract model was designed to study the efficacy of these stimuli-responsive devices on continence and flow. Both devices achieved significant shape change in response to IR light or magnetic field when embedded in an agar gel with 100kPa stiffness, mimicking scar tissue. Furthermore, both devices increased urethral resistance to flow, and allowed unimpeded voiding upon activation, thus affecting the sphincteric mechanism. When illuminated with IR light, the LCE-based device significantly decreased ($p<0.0001$) time to void 20mL of water from 5.2min ± 1min to 2min ± 0.5min. Likewise, the magnetic elastomer-based device reduced abdominal pressure by 0.51cmH_2O ± 0.14cmH_2O in the presence of a magnetic field, thereby reducing time to void in this in vitro model. Future work will focus on further analysis of the mechanical properties of these materials and testing for biostability. The devices will be implanted in rabbits, a viable animal model for SUI, to test the devices *in vivo*.

3:45 PM SB07.05.08
Improving the Redissolution Kinetics of Thermoresponsive Hydrogels for Biomedical Applications in Higher Temperatures Mahsa Rezaiyan, Frances Yau, Darius A. Shariaty and Mark E. Thompson; University of Southern California, United States

Stimuli-responsive materials that respond to specific triggers, such as thermoresponsive hydrogels, are in high demand for biomedical applications. Due to their biocompatibility and water content similar to tissue, they have been used as contact lenses, wound healing bioadhesives, and drug delivery platforms. Biocompatible thermoresponsive sealant (TRS) is of great interest in the wound management of those injuries that risk substantial impairment with delayed treatment, such as open globe ocular injuries. TRS exhibits non-adhesive behavior at cold temperatures and is easily deployed; however, it becomes viscous and adhesive at body temperature and is capable of sealing penetrating injuries. Fast and reversible phase transitions of TRS upon cooling are required for their application after storage in variable temperatures. The kinetics of redissolution of a thermally treated TRS is slower for high molecular weight materials.

Herein we present a unique strategy for significantly increasing the redissolution kinetics of thermoresponsive hydrogels via the utilization of a high surface area host material. As an example of any other injectable in-situ forming hydrogels, which have suitable mechanical strength but slow transition times, the increase in the redissolution kinetics of hydrophobically-modified poly(N–isopropyl acrylamide) (pNIPAM) in the presence of a high surface area, open cell foam host is demonstrated. The recovery measurements show enhanced recovery (74-99%) across a range of foam types and pore sizes when compared to samples stored without a host (9% recovery). Maximizing a host surface area with an open cell foam demonstrated the greatest increase (~ten-fold) in TRS recovery after storing the TRS solution at 50 °C and cooling for ten minutes. The rheological analysis revealed that the viscosity, storage, loss modulus, and mechanical strength are not significantly affected by storage over a foam host.

This work is supported by the US Army Medical Research and Materiel Command under Contract No.W81XWH-16-C-0086, and partially was supported under Research Project Award MTEC-20-14-Ocular-006 as executed by Delivery Order No. W81XWH-21-9-0003.

4:00 PM SB07.05.10
Probing Temperature-Responsivity of Microgels by Superresolution Microscopy Xhorxhina Shaulli[1], Rodrigo R. Barbosa[2], Maxime J. Bergman[1], Chi Zhang[1], Nicoletta Gnan[2], Frank Scheffold[1] and Emanuela Zaccarelli[2]; [1]University of Fribourg, Switzerland; [2]Sapienza University of Rome, Italy

The ability to observe microgel morphologies at nanometer scale and its response to temperature changes opens exciting opportunities to design and precisely control the behavior of microgels for various applications [1]. In this context, super resolution microscopy is a well-established tool used to investigate colloidal systems e.g. poly(N-isopropylacrylamide) (pNIPAM) microgels [2]. An important role when performing advanced microscopy experiments on such particles plays the interface where the microgels are established, as they have to be fixed during the experiment. We use super resolution microscopy and molecular dynamic (MD) simulations to investigate how individual microgels anchored on hydrophilic and hydrophobic surfaces change morphology with temperature. Super resolved images of individual microgel particles at different collapsing stages are analyzed and their density profiles are obtained. The results suggest that the anchoring parts of the microgel stick to the surface as the temperature is increased. For these surfaces the experimental data and the MD simulations are in very good agreement. Such study is relevant to establish a technique for the investigation of more complex systems along lower critical solution temperature (LCST), where molecules of interest can be incapsulated in the microgel network and controllably released with temperature.

References
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4:15 PM SB07.05.11
Multi-State Hydrogel Device Programmed by DNA Sequence Instructions Ruohong Shi, Kuan-Lin Chen, Joshua Fern, Siming Deng, Yixin Liu, Noah Cowan, David H. Gracias and Rebecca Schulman; Johns Hopkins Univerisity, United States

Living systems can convey information and drive complex chemomechanical processes such as metamorphosis using biomolecules as signals. Yet, synthesizing macroscale soft structures that can likewise interpret and respond to such signals by undergoing chemomechanical changes has been challenging. Here, we create a new family of programmable polymeric materials, DNA polymerization gels, whose shape change can be programmed by DNA sequence instructions. The growth and shrinking of these DNA polymerization gels are driven by the polymerization and depolymerization of DNA via hybridization chain reactions. The actuation mechanism was studied in-depth for optimized sequence design to perform high-degree growth and reliable reversibility. We developed a multi-step photolithography process that enables the fabrication of centimeter-scale gel devices consisting of multiple micro-segments. Several orthogonal DNA systems that can selectively execute “grow” or “shrink” instructions were designed to direct material transition repeatedly between different configurations. Finally, we introduced a machine learning-assisted design method for creating “seed” structures, which in response to different DNA instructions, could transform into one of a large set of functional target configurations: four different letters and either every even or every odd Arabic numeral. Our work offers a general architecture for manipulating polymeric materials by dissipative chemical cycles, programming functions into the structures by molecular designs, and encoding complex, continuous transformations of curved mechanical structures into precise molecular instructions and protocols.

SESSION SB07.06: Sustainable Polymer Networks
Session Chairs: Kay Saalwaechter and Qiming Wang
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2018

8:00 AM SB07.06.01
High-Performance, Low-Cost, and Recyclable Photopolymers via Dual-Cure 3D-Printable Polyesters Grant Musgrave and Chen Wang; The University of Utah, United States

Among the 3D printing technologies available for polymers, vat photopolymerization or stereolithography (SLA) is promising for future manufacturing because it uses photopolymers to print parts with incredible speed and complexity. The material properties of traditional, filament-fabricated 3D-printed parts are often inferior due to their inherent brittleness and poor interlayer bonding. Similarly, 3D-printed photopolymers are also often weaker than traditional polymers due to their structural heterogeneity. To dramatically reduce the heterogeneity, latent chemistries will be introduced into the resin that will re-organize the molecular structures to homogenize the photopolymer. This will result in photopolymers with robust properties that will enable the implementation of vat photopolymerization in mainstream manufacturing. These “dual-cure” polyesters reduce the structural heterogeneity of 3D printed photopolymers, and thus, improve material properties, decrease costs, and enable recyclability of the photopolymer. Herein, “dual-cure” refers to an initial "photo-cure" mediated by UV-light, followed by a secondary "heat-cure" where a thermal-meditated reaction takes place. This unconventional network enables a new direction of high-performing polymers for 3D printing and chemical recyclability via ester-based chemistry.

8:15 AM SB07.06.02
Upcycle Commodity Plastic Waste to Fully-Recyclable and Self-Healable Polymers Qiming Wang; University Southern California, United States

Over 300 million metric tons of plastics are created globally every year but more than 79% of the plastic waste goes to landfills, but only a small fraction (~9%) is recycled and most of the recycled plastic is down-cycled to low-value products such as garden furniture or pots. The accumulation of unrecycled plastics has become a huge global challenge. Here we present a general strategy to upcycle commodity plastic waste to a class of fully-recyclable and self-healable polymers. The idea is that we functionalize the commodity plastic powder with photosensitive dynamic chemical groups can enable light-activated self-assembly of plastic powder into a polymer composite. Thanks to the light-controlled reversible association and cleavage reactions, the mechanical properties of the polymers can be on-demand tuned by the external light. Besides, the interfacial crack can be healed by light-activated re-association reaction. Furthermore, the synthesized polymer can be ground into powder and then reprocessed back to a solid polymer with rebuilt mechanical properties. We show our strategy is universal to various commodity plastic wastes, such as PS, PP, PET, and PE.

8:30 AM SB07.06.03
Simple Upcycling of Virgin and Waste Polyethylene into Covalent Adaptable Networks—Catalyst-Free, Radical-Based Reactive Processing with Dialkylamino Disulfide Bonds John M. Torkelson, Logan M. Fenimore and Boran Chen; Northwestern University, United States

Polyethylene (PE) is a ubiquitous commodity polymer that faces significant barriers to efficient recycling despite its thermoplastic nature. PE can be permanently cross-linked to enhance its properties and expand its applicability, but conventionally cross-linked PE (PEX) is not reprocessable in the melt-state and thus cannot be recycled for high-value use. Here, we have transformed thermoplastic PE into PE covalent adaptable networks (CANs) via reactive radical-based, melt-state processing with 1 wt% dicumyl peroxide and 5 wt% bis(2,2,6,6-tetramethyl-4-piperidyl methacrylate) disulfide (BiTEMPS methacrylate), a dynamic covalent cross-linker. The simple, catalyst-free, one-pot reactive process employing dialkylamino disulfide dynamic chemistry was used to upcycle both commodity and waste thermoplastic PE into thermally stable and reprocessable PE CANs, and the thermomechanical properties of resulting CANs are tunable without sacrificing their recyclability. Low-density PE CANs and high-density PE CANs fully recover cross-link densities and associated properties after multiple reprocessing steps, resist creep deformation at elevated temperature relative to their thermoplastic precursors, and, like PEX but unlike some PE vitrimers, exhibit no phase separation. This novel procedure opens the door to the development of CANs based on reactive processing of ethylene-based copolymers as well as cross-linked PE nanocomposites and foams.

8:45 AM SB07.06.04
Modeling Erosion of Polymer Networks with Stimuli-Responsive Degradable Bonds Olga Kuksenok and Vaibhav Palkar; Clemson University, United States

Understanding and controlling degradation of polymer networks on the mesoscale is critical for a range of applications ranging from regulating growth of complex tissues and neural networks to controlled drug delivery. Degradation that can be controlled by external stimuli, for example photo-controlled degradation, permits spatially-resolved dynamic control of materials properties. We develop a dissipative particle dynamics (DPD) approach that captures degradation and erosion of hydrogels at the mesoscale. To overcome unphysical topological crossings of bonded polymer chains, we utilize a modified Segmental Repulsive Potential (mSRP) formulation. We focus on hydrogels formed by the end-linking of multi-arm polyethylene glycol macromolecular precursors. We track the degradation via measuring the fraction of the degradable bonds intact and spatial distributions of network fragments or clusters. We demonstrate that the dispersity and the fraction of broken-off fragments scales with the relative extent of reaction. Reduced weight average and reduced z-average degrees of polymerization allow us to identify the reverse gel point. We characterize the erosion process in solvents of various qualities via tracking the mass loss that accounts for the broken-off fragments remaining in contact with the percolated network. We quantify the dependence of the mass loss on the extent of reaction and on the hydrogel properties. These results elucidate the main features of degradation and erosion on the mesoscale and could provide guidelines for future design of degrading materials with dynamically controlled properties.

9:00 AM SB07.06.05
Circularity in Plastics via Understanding and Controlling Polymer Reactivity Across Scales Brett A. Helms; Lawrence Berkeley National Lab, United States

Polydiketoenamine (PDK) is an emerging class of plastics that can be efficiently deconstructed to the original triketone and amine monomers using low intensity chemical processes. Controlling the rate at which bonds in the polymer are hydrolyzed in strong acid is an emerging area of interest, enabling chem. recycling of complex products made from several classes of PDK resins. Likewise notable is the impact of formulation on recycling rates, hlghlighting the importance of examg. the foundations of polymer reactivity beyond the bond. I discuss this multi-lengthscale perspective, where a convergence of experiment, theory, and advanced characterization bring into focus design rules. I will discuss how to minimize parasitic losses in chem. recycling, toward infinite recyclability. I will also discuss how such considerations can be applied to the chem. recycling of polymers with a broad range of useful and advantaged properties. As most PDK resins can be produced from biorenewable raw materials, the platform appears well poised to address the sustainability of plastics as we transition to plastics as a service in a circular economy.

9:15 AM SB07.06.06
Bio-Renewable Feedstock for Circular Polydiketoenamine Networks Jeremy Demarteau[1], Benjamin Cousineau[1], Zilong Wang[2], Baishakhi Bose[1], Corinne Scown[1,2], Jay D. Keasling[2,1] and Brett A. Helms[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]Joint BioEnergy Institute, United States

Bio-synthesized plastics and durable goods thermosets are usually difficult to pair with circularity because of their various application fields, opposite lifetime and different chemistry. Here, we show that circular polydiketoenamines (PDK) vitrimers are produced with aromatic biorenewable monomer. Odd-even effects over different PDK spacer length are translated in a change of density and tensile modulus values. Chemical recycling is realized in a low intensive acid process with large monomer recovery variations through PDK series due to an increased degradation occurring in formulations featuring shorter spacers. While reaching high monomer recovery in powdered PDKs, PDK plastics with longer spacers enable higher monomer recoveries. Bioproduction of aromatic monomer is achieved from both glucose and glycerol in engineered *E. coli* using non-native thiolase BktB under fed-batch fermentation. System analysis scaling-up of the monomer production provides the estimated cost and greenhouse gas emission with different scenarios. Our results demonstrate the versatility of the circular PDK platform incorporating aromatic biorenewable synthons and potentially opening the way to chiral circular polymers.

9:30 AM SB07.06.07

Superabsorbent 'Gel Sheets' with Fabric-Like Flexibility—A 'Better Picker-Upper' for Water and Blood Hema Choudhary, Christine Zhou and Srinivasa R. Raghavan; University of Maryland, United States

Materials that can absorb aqueous liquids have evolved along two parallel tracks for the past millennia. On the one hand, there are flexible, foldable materials like cloth or paper towels that are convenient to use but not very absorbent. On the other hand, we have superabsorbent polymer hydrogels (SAPs) with the ability to absorb more than 100x their weight in water, but in dry form these become fragile solids. Here, for the first time, we report the synthesis of **'gel sheets'** that combine the above properties in the same material. The sheets are prepared at macroscopic sizes (e.g., 10 x10 cm) by foam-templating (polymerizing monomers around the bubbles of a foam), followed by addition of a plasticizer (glycerol) and ambient drying. The dried sheets are macroporous (pore sizes ~ 240 µm, porosity > 80%), flexible, soft, and robust; they can be folded, rolled up, and cut with scissors to desired sizes, much like fabrics. At the same time, they can rapidly absorb substantial amounts of water, like hydrogels. Remarkably, these sheets ***expand as they absorb water***, which is unlike any sponges or absorbents made from fabric or paper. The sheets are also able to absorb viscous liquids like blood as well as viscoelastic, non-Newtonian liquids like polymer or surfactant solutions. Absorbed liquids are retained within the gel sheet when it is lifted up whereas with typical commercial controls, excess liquid drips down. Due to their unique properties, these gel sheets could be useful in cleaning up spilled liquids in a variety of locations, including homes, labs, and hospitals. They could also be useful tools for absorbing biological fluids during surgeries or other medical procedures.

9:45 AM BREAK

SESSION SB07.07: Multifunctional Polymer Networks
Session Chairs: Kay Saalwaechter and Qiming Wang
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2018

10:15 AM SB07.07.01
Mechanical and Electrical Properties of Polyelectrolyte Elastomers in Bulk and at Interface Baohong Chen and Shu Yang; University of Pennsylvania, United States

Unlike conventional polyelectrolyte solutions and gels and conventional elastomers, polyelectrolyte elastomers are both solvent-free and ion-conductive. We developed polyelectrolyte elastomers and investigated their unique mechanical and interfacial properties. With collaborators, the tunability of ion transimission in the polyelectrolyte elastomer and the rectification of ionic current across their interfaces are reported. Recently, we observed a novel electrical manifestation of polyelectrolyte elastomers. In a preciously engineered reversible mechanical process, the polyelectrolyte elastomer transforms the mechanical loss into an electrical gain. This phenomenon depends on the appropriate design of the electro-mechanical-chemical responsive network of the polyelectrolyte elastomer. We experimentally and theoretically bridged the molecular picture of a polyelectrolyte elastomer to quantifiable characteristics. In addition to inheriting the benefits of the parent ionic liquids and elastomers in various applications, polyelectrolyte elastomers lead to advanced applications in areas including energy harvesting, sensors, and soft robots.
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10:30 AM SB07.07.02
Rubbery Organic Frameworks-Tuning the Gaz-Diffusion through Dynameric Membranes Mihail Barboiu; Institut Europeen des Membranes, France

High permeability whilst keeping a reasonable selectivity is the most important challenge in developing membranes for gas separation. Valuable performances are usually obtained with membranes for which the gas transport is controlled by the gas-diffusivity in glassy polymers and by gas-solubility in rubbery polymers. During the last decade, important advances in this field are related to the molecular control of the gas separation properties. The combination/replacement of classical glassy polymers with metal-organic frameworks (MOFs, ZIFs, zeolites…) embeded in polymeric matrixes provided reasonable permeability through porous free volume network and high selectivity due to so-called "selectivity centers", specifically interacting with the gas molecules. Despite the impressive progress, important difficulties are observed to get dense mechanically stable thin layer MOFs on various supports. Taking advantage of high permeabilities observed with the dynamic covalent rubbery polymers and to their flexible casting properties, there should be very interesting to build rubbery organic frameworks-ROFs, as alternative for molecularly controlled membranes for gas separation. Here we use low macromolecular amino-functional connectors and aldehyde core centers in order to constitutionally generate such adaptrive dynameric ROFs. Differently to classical rubbery polymeric membranes the ROFs performances depend univocally of diffusionl behaviors of gas molecules through the network. For all gases, a precise molecular composition of linear and star-type macromonomers generates an optimal free volume for a maximal diffusion through the matrix. These results should initiate new interdisciplinary discussions about highly competitive systems for gas separation, constitutionally controlled at the molecular scale.

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10:45 AM SB07.07.03
Photodegradable Hydrogel Materials for Encapsulation, Isolation and Recovery of Functionally Rare Bacteria from Complex Microbial Communities Ryan Hansen, Niloufar Fattahi, Niloy Barua, Mohammadali Masigol, Esther L. Radaha, Andre J. van der Vlies, Prathap Parameswaran and Tom G. Platt; Kansas State University, United States

Photodegradable hydrogel materials can be used for cellular encapsulation and for spatiotemporally-controlled cell release, and therefore have been explored as materials for use in cell isolation applications. While most studies have focused on mammalian cells, here we extend the use of photodegradable polyethylene glycol (PEG) hydrogels towards isolation of bacteria with rare or unique function from complex microbial communities, which often contain thousands of unique species. Hydrogels are formed using the photocleavable macromer, PEG *o*-nitrobenzyl diacrylate, which is crosslinked into a hydrogel through thiol-acrylate Michael-type addition reactions with PEG-tetrathiol macromers. PEG molecular weights are selected to form hydrogels with a 10 nm mesh size, enabling physical encapsulation and immobilization of bacteria cells while also allowing for the transport of nutrients, chemical cues, and waste products throughout the material for culture. A patterned illumination tool is used to expose the hydrogel to user-defined 365 nm light patterns at 5-mm spatial resolution to selectively release desired cells from the hydrogel interface after phenotypic observations for recovery, genomic characterization, and application.

With this foundational approach, three applications will be highlighted. The first involves screening bacteria mutant libraries for phenotypically rare cells. Cells from mutant libraries are directly encapsulated into the hydrogels for high-throughput, microscopic observation. After identification of the desired cellular phenotype, rare cells are released with patterned light and recovered for whole genome sequencing, enabling one to link phenotype to genotype. Second, these materials are integrated into microdevices containing microwell arrays for bacteria co-cultures. These devices are designed to screen thousands of different co-cultures to uncover microbe-microbe interactions that impact beneficial or pathogenic bacteria. Finally, photodegradable hydrogels have been functionalized with lectin proteins, enabling high-affinity capture and removal of bacteria from young biofilms on host surfaces. After capture, bacteria can be sectioned from the hydrogel using patterned light for sequencing and characterization. We have applied this approach to study membrane biofouling in wastewater treatment systems, and specifically to identify early-colonizing bacteria from wastewater that accelerate the membrane biofouling process. Current and future work involves investigating the use of upconversion nanoparticles in these hydrogel systems for release of cells using near infrared light.

11:00 AM SB07.07.04
Flexible Porous Gels Synthesized by Templating Organofoams—Ability to Selectively Absorb Oil from Water Hema Choudhary, Christine L. Zhou and Srinivasa R. Raghavan; University of Maryland, College Park, United States

Porous absorbents are being explored rigorously for recovering volatile organic solvents and oils from water bodies. However, most existing synthesis techniques are limited to the fabrication of small-size absorbents. These techniques are based on modifying polymer sponges towards a greater affinity to organic solvents. For large-scale manufacturing, these methods turn out to be arduous, energy-intensive, and expensive. Here, we devised a simple strategy to create porous absorbents, using an inherently hydrophobic polymer, that can be easily scaled up. Our approach involves the generation of foams in an organic monomer solution by mixing it with an aqueous acidic solution and sodium bicarbonate. The acid-base reaction produces CO_2 gas bubbles, and simultaneously, oil-in-water type emulsions are formed, with the monomers being the oil phase. Both the emulsion and bubbles are stabilized by a silicone surfactant present in the monomer solution. This foamed-emulsion solution is quickly polymerized to give a porous solid named ‘oleosponge’ or ‘oleosheet’. It retains the interconnected pores from the foam, which have an average size of 277 µm. The material is flexible and mechanically robust, withstanding several cycles of deformation. It can sustain more than 90% compression and 35% tensile strain and has a tensile modulus of 40 kPa. The material also shows a contact angle of ~130° with water and 0° with oils. When immersed in a toluene-water mixture, it selectively absorbs the toluene and expands by ~75% linearly. In solvent absorption, the oleosponge outperforms commercially available polyurethane sponges, which have been used for designing hydrophobic absorbents in many previous studies. Our material shows very high absorption for a wide range of organic solvents (> 50 g/g), and it can be reused for more than 100 cycles without showing a significant reduction in its selective absorption capacity. For large-scale clean up, we have created oleosheets with dimensions of 10 x 7 cm and a thickness of 4 mm. The sheet instantly absorbs solvent and expands when spread over a large spill. The expanded sheet is robust enough to be picked up by hand and holds solvent within when held vertically. Compared to commercial oil-absorbing sheets, our oleosheets absorb and retain a much higher volume of organic solvent. Another exciting aspect of our synthesis technique is that we can attain additional interesting properties in the oleosponge simply by adding nanoparticles of interest to the monomer solution. We have created a magnetic responsive oleosponge that can be remotely lifted up by a magnet after solvent absorption. Lastly, we designed a hybrid sheet of two distinct layers with opposite wettability for water: one side can absorb solvents and oils while the other absorbs only aqueous fluids. This type of hybrid sheet could have applications in cosmetics and household use in addition to oil spills.

11:15 AM SB07.07.05
Regenerative Repair of a Critical-Size Rat Femoral Segmental Defect Guided by a Chemically Crosslinked Degradable Shape Memory Polymer-Hydroxyapatite Composite Scaffold Jordan D. Skelly, Xiaowen Xu and Jie Song; UMass Chan Medical School, United States

Facile surgical delivery and stable fixation of synthetic bone graft substitutes play roles just as critical as osteoconductivity and osteoinductivity in ensuring successful scaffold-guided bone regeneration. Shape memory polymers (SMPs), when engineered with a multitude of appropriate characteristics, may serve as smart synthetic bone graft substitutes to meet these challenges. We previously showed that rigid polyhedral oligomeric silsesquioxanes (POSS) nanoparticles could be covalently integrated with urethane-crosslinked polylactide (PLA) to prepare high-strength, degradable POSS-SMP nanocomposites that exhibit stable temporary shape fixation at room and body temperatures, and efficient shape recovery with a safe thermal trigger. By crosslinking star-branched POSS-PLA building blocks with hydrophilic polyethylene glycol diisocyanates (PEG-DI), we recently prepared amphiphilic POSS-SMPs in the presence of 20 wt% osteoconductive mineral hydroxyapatite (HA). The resulting amphiphilic mineral composite exhibited desirable surgical handling characteristics (compliance, toughness) and excellent shape recovery (>95%) at a safe triggering temperature. The incorporation of HA mitigated the negative impact of the composite’s acidic hydrolytic degradation products on the proliferation and osteogenesis of bone marrow derived stromal cells. Here we further examine the *in vivo* efficacy and safety of macroporous 20 wt% HA/POSS-SMP composite scaffolds, tailored for a 5-mm rat femoral segmental defect and fabricated using 3D printed sacrificial molds, in guiding long bone regeneration with or without 400-ng recombinant human osteogenic bone morphogenetic protein-2 (rhBMP-2). These compliant macroporous scaffolds may be conveniently press-fit within the defect and allowed to recover to their pre-programmed shape at body temperature and/or upon hydration *in vivo,* resulting in stable graft fixation within the femoral segmental defects in skeletally mature SASCO SD rats. Using a combination of longitudinal microCT analyses over 16 weeks and terminal femoral histology analyses, we demonstrated robust new bone formation throughout the defect, guided by the macroporous degrading amphiphilic scaffolds in the absence of exogenous rhBMP-2. With the addition of 400-ng rhBMP-2, new bone formation, new bone remodeling, and scaffold resorption were significantly accelerated, resulting in complete bridging of the defects as early as 5 weeks after implantation. Histological analyses confirmed scaffold-guided osteointegration and coordinated osteoblastic/osteoclastic remodeling by 8 weeks in both treatment groups. Systemic organ pathology did not reveal any detrimental effects of the degrading nanocomposites. To further accelerate the full resorption of the scaffold and functional restoration of the mechanical integrity of regenerated long bone, an amphiphilic scaffold with larger macroporosity and/or more expedited degradation rates may be considered. These findings combined support this amphiphilic osteoconductive degradable SMP composite as a promising class of next-generation synthetic tissue grafts.

11:30 AM SB07.07.06
Additive Manufacturing of Polymer Networks Based on Dissociative and Associative Dynamic Covalent Bonds Francesca Furia, Aleix Costa Cornellà, Guy Van Assche and Joost Brancart; Vrije Universiteit Brussels, Belgium

Additive manufacturing (AM) techniques allow rapid prototyping of complex 3D shapes and custom-made products, in fact they attracted soon the interest of many researches and the range of materials that can be used is rapidly expanding. Curing and melting are the two main characteristics taken into account when deciding which techniques used, but recently polymers networks based on dynamic covalent bonds have been introduced into this world. Two main mechanism can be differentiated: associative and dissociative covalent chemistries. In the former, the crosslink density of the network stays constant with temperature, but the speed at which these dynamic covalent bonds exchange increases. In the latter, the crosslink density changes as a function of temperature. The main drawback for additive manufacturing of dissociative networks is the sharp and drastic change from a rubbery network to a low viscosity liquid at temperatures above their gel transition. In recent work, this limitation has been overcome by the addition of fillers that allowed the printing of overhangs and eventually the addition of other properties to the network. The fillers improved the printability of these materials, but at the same time they had a stiffening effect of the mechanical properties and obtaining a homogeneous dispersion is challenging.

In this study, dissociative and associative dynamic bonds were combined in the same network, providing the dissociative network the thermal and mechanical support needed during the AM processing at high temperatures.

Thermoplastics polymers such as PLA and ABS are usually printed taking advantage of the melting temperature or the devitrification of the polymer to have a high viscous flow in material extrusion AM. When using a polymer network based on dissociative thermoreversible Diels-Alder (DA) bonds, the gel transition temperature (T_{gel}) is used. When heated above T_{gel}, the dynamic equilibrium shifts towards the dissociation of the DA adducts to the extent that the polymer can flow through the nozzle as a viscous melt. Once in contact with the printing bed at a temperature below T_{gel}, the dynamic equilibrium shifts back to the formation of the adducts, reforming the polymer network structure. Differently from PLA or ABS, this is a reactive type of printing based on the reaction kinetics of the DA bonds, which are not fast enough to hold the shape of the object and cure before starting to flow on the print bed.

Associative covalent networks present different types of exchange reactions. Recent studies showed that in presence of the transesterification reaction it proved possible to extrude at high temperatures and pressures, though with a rough surface finish. There is no net change in the crosslink density, but the exchange speed is fast enough for the material to flow and they also present thermal stability.

When combining DA bonds and esters in the same network, it is possible to print objects with sharps edges and smooth finish using material extrusion AM. When heated at a temperature higher than the T_{gel}, the materials behave like a high viscous melt because the DA part of the network is completely dissociated and, once it reaches the bed, the network is hold together by the associative bonds present due to the vitrimers. Differential scanning calorimetry was used to verify the absence of degradation and side reactions when printing at temperatures much higher than the Tgel. Rheology measurements, such as small amplitude oscillatory shears, have been conducted on the materials and on commercial PLA used as a reference. The shear thinning behavior at high shears ensure extrudability and printability. Different percentages of the two dynamic bonds have been tested to evaluate the effect on the printability and to find the optimum composition. The healing property is also preserved after printing, the healing temperature is far from the printing temperature.

SESSION SB07.08: Virtual Session
Session Chairs: Pengfei Cao, Ximin He and Qiming Wang
Tuesday Morning, April 25, 2023
SB07-virtual

8:00 AM *SB07.08.01
Mechanically Robust Mechanically Interlocked Polymers Xuzhou Yan; Shanghai Jiao Tong University, China

Due to the unique topological structures and controllable mechanical motions under external stimuli, mechanically interlocked polymers have gained widely attention from the scientific community. Nevertheless, it is still a significant challenge to elucidate the influence of microscopic mechanical motion of mechanical bonds on the macroscopic mechanical properties of their aggregates. In this talk, we will firstly present a class of mechanically interlocked networks carrying densely rotaxanated backbones as a model system to understand macroscopic mechanical properties stemmed from the integration and amplification of intramolecular motion of the embedded [2]rotaxane motifs. Subsequently, we will introduce the coupling of dynamic covalent bond and mechanical bond to understand the dynamicity and reprocessability of mechanically interlocked vitrimers. Finally, we will showcase how we use densely mechanical bonds to realize the applications of mechanically interlocked networks in the fields of stretchable materials, aerogels, soft actuators. Our work promotes the development of mechanically interlcoked materials, especially on the understanding of the underlying mechanism of the relationship between microscopic mechanical motion and macroscopic mechanical performance.

8:30 AM SB07.08.02
Hygroscopic Tunable Multi-shape Memory Polymers Siya Huang; Shenzhen University, China

Tunable multi-shape memory polymers offer intriguing opportunities for memorizing multiple temporary shapes with tunable transition temperatures from one material composition. However, such multi-shape memory effects have been exclusively correlated with the thermoresponsive behaviors of materials, significantly limiting applications in heat-sensitive scenarios. Here we report on a nonthermal tunable multi-shape memory effect in hygroscopic cellulosic polymers, which exhibit a broad, reversible hygromechanical response at ambient temperatures. The polymers present a unique moisture memory effect, enabling diverse multi-shape memory behaviors (dual-, triple- and quadruple-shape memory effects) with excellent performance under highly tunable and independent control of humidity alone. Owing to the tissue-like mechanics and bio-benign triggering conditions, bio-adaptive medical devices such as self-deployable stents and self-tightening sutures were successfully demonstrated under physiological circumstances, exhibiting autonomous shape recovery in a fast and programmable fashion while supplying a biocompatible recovery stress that can be further tailored to tissue-specific requirements over a broad range (0.1 to 4 MPa). Such hygroscopic tunable shape memory effects with great design flexibility readily extend the implications of shape memory polymers beyond the conventional thermomechanical regimes.

8:45 AM *SB07.08.03
Polymer Networks with Embedded Reactivity Stephen Craig; Duke Univ, United States

The physical limits of polymer networks are determined by the physical limits of its constituent molecular strands: the energy a strand absorbs before breaking, the force at which it breaks, and the extension it achieves at that force. In many case, polymer strands are typically viewed as structureless entropic springs. In this talk, we discuss the consequences of treating strands as being both structurally active and chemically reactive, and of viewing macroscopic mechanical events such as crack propagation as a moving chemical reaction vessel, in which molecular strands undergo conformational and covalent chemical reactions that are tied to their specific molecular structure.

9:15 AM SB07.08.04
Mechanochromic Liquid Crystals and their Polymer Blends Kris Senecal[1], Paola A. D'Angelo[1], Todd E. Alexander[1], Walter Zukas[1], Christina Tang[2], Hong Zhao[2] and Timothy Lawton[1]; [1]U.S. Army DEVCOM SC, United States; [2]Virginia Commonwealth University, United States

The long term goal of this research is to understand the influence of structure and properties of polymer blends with cholesteric liquid crystals (LC) to facilitate the design of adaptive/responsive optical color change to mechanical strain. Cholesterol ester liquid crystals form into periodic helical structures and give these liquid crystals their unique responsive optical properties. The color of the light reflected depends on the pitch length of the liquid crystal and can be influenced by external stimuli like mechanical deformation or temperature. Temperature-dependent properties depend upon a transition between the smectic and twisted nematic mesophases. If the smectic phase exists, temperature dependent reflecting properties are observed. Temperature-insensitive formulations can be achieved by ensuring the absence of the smectic mesophase transition. Such mixtures reflect a single color below its clearing point. Practically, this has been achieved using mixtures of components that have a smectic A mesophase (e.g. cholesteryl perlagonate and/or cholesteryl oleyl carbonate) with a component that does not form a smectic A mesophase (e.g. cholesteryl chloride). Such formulations are expected to change color in response to mechanical shear while remaining relatively unaffected by temperature changes. To achieve these mechanochromic LC formulations, we are investigating ternary mixtures of cholesteryl benzoate (CC), cholesteryl pelargonate (CP), and cholesteryl oleyl carbonate (COC). Through investigations of the formulation space using a ternary diagram, the broadest range of colors (reflected wavelengths) can be achieved by varying the COC concentration at a 1:1 ratio of CP:CC. Formulations that appear blue, green, and red were selected and mechanochromic behavior was demonstrated when applying a shear stress using a doctor blade with an estimated strain rate of 180 s^{-1}. However, the fast relaxation times associated with the liquid nature of the LC formulations meant a rapid return to the original color. To both lengthen the relaxation times and incorporate the formulations into practical structural materials, various methods were employed to combine LC formulations with an aromatic polyether-based thermoplastic polyurethane (TPU). Long term stability of separate layers of LC and TPU proved physically questionable. Initial efforts to combine LC formulations with TPU in tetrahydrofuran showed good compatibility in cast films and wet-spinning of fibers. A series of TPUs with varying physical properties is currently being investigated. Characterization of the mechanochromic response of these blends and the relationship of the TPU properties to the LC structure will be presented.

9:30 AM SB07.01.01
Controlling the Thermomechanical and Viscoelastic Properties of Polymer Networks by Combining Associative and Dissociative Dynamic Covalent Bonds Aleix Costa Cornellà, Joost Brancart, Guy Van Assche and Francesca Furia; Vrije Universiteit Brussel, Belgium

Introducing dynamic bonds into polymer networks can produce materials that can be more easily processed, applied, and recycled than their permanent counterparts. Moreover, they show improved toughness, stretchability, and the ability to heal physical damage. This dynamicity can be introduced into polymers by means of supramolecular interactions, dissociative dynamic covalent bonding, or associative dynamic covalent bonding (vitrimers).
The behavior of these polymer networks heavily depends on the kinetics and thermodynamics of the dynamic bonds, which are entirely different for each mechanism. On the one hand, the viscosity of vitrimers show a linear behavior (Arrhenius behavior) as a function of inverse temperature. On the other hand, dissociative networks can exhibit abrupt changes in viscosity above a critical temperature. Both systems have their strengths and weaknesses, but both suffer from the same compromise. Having to choose whether to be able to self-heal/reprocess at mild conditions or to not creep at operation temperatures.
Here, we tackled this intrinsic problem by developing a strategy to engineer the relaxation time regime in dynamic polymer materials. We achieve this control by combining, in a single network, Diels-Alder and β-hydroxy ester bonds. Diels-Alder bonds based on furan and maleimide are dissociative dynamic covalent bonds and show an abrupt change in viscosity above a critical temperature. β-hydroxy ester bonds are associative dynamic covalent bonds and show an Arrhenius behavior. By tuning the ratio between Diels-Alder bonds and β-hydroxy ester bonds it is possible to access the complete range of relaxation times between the two mechanisms. The polymer network that is crosslinked exclusively by Diels-Alder bonds becomes liquid above its gel transition temperature of around 100 °C, with viscosity as low as 0.45 Pa.s at 125 °C. As the proportion of associative bonds increases, the gel transition temperature of the system increases until a point where it no longer degel, which means that the β-hydroxy ester bonds have a concentration high enough to create a network. For the network crosslinked only by β-hydroxy ester bonds, it remains solid and doesn't relax a measurable amount of stress at a time scale of >750 minutes at 130 °C. Even after the point where the material doesn't degel, healing of completely cut tensile specimens remains possible at a reasonable temperature of 90 °C for 30 minutes, without any external pressure. These conditions are notably milder conditions than the ones normally needed to self-heal materials based on transesterification.
The materials are also designed following the 12 principles of green chemistry. They are synthesized using 100% bio-based raw materials, based on fatty acids, without using any solvent, and are potentially (bio)degradable. As all the components have a similar backbone, the mechanical properties of the materials don't vary much between materials with different ratios of associative and dissociative bonds. The Young's modulus of the whole range of materials sits around 1.5 ± 0.5 MPa at room temperature.
With this strategy, the design of the mechanical properties is decoupled from the relaxation dynamics. Combining two types of dynamic bonds with very dissimilar relaxation dynamics empowers a range of applications where the materials can be tailored according to their application, processing, as well as the timescale of their use. Additionally, this approach is not exclusive to our system but can be generalized to any compatible pair of dissociative and associative dynamic covalent bonds.

SYMPOSIUM

April 11 - April 12, 2023

Symposium Organizers
Matteo Bianchi, University of Pisa
Charles Dhong, University of Delaware
Marcia O'Malley, William Marsh Rice University
Tristan Trutna, Facebook Reality Labs

* Invited Paper
\+ Distinguished Invited

SESSION SB08.01: Perception and Sensing I
Session Chairs: Matteo Bianchi, Charles Dhong, Marcia O'Malley and Tristan Trutna
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2012

10:30 AM SB08.01.01
Opportunities for Materials Chemistry in Haptic Interfaces Charles Dhong; University of Delaware, United States

Haptic devices have wide ranging applications, from entertainment in virtual reality, to accessibility aids, and even to advance basic knowledge in sensory biology. Here, show approaches from materials chemistry could be used to improve the quality, range, or portability of haptic devices. We highlight some of our work which show that humans are sensitive by touch to molecular scale changes in surfaces and also examine opportunities for materials innovation from the stimuli responsive and wearables community. We also introduce goals and research overlaps for the symposium to connect members of the materials research community to the haptics community.

10:45 AM *SB08.01.02
Effective Levels of Haptic Signal Complexity for Texture Rendering Across Diverse Displays Rebecca Friesen; Texas A&M University, United States

Our ability to assess and discriminate a vast variety of surface textures relies on densely packed mechanoreceptors embedded in our fingertips, which are exquisitely attuned to both temporal and spatial changes in skin deformation. Texture perception is critical for our ability to identify and evaluate the quality and material of every surface we touch, and dynamic changes in texture can also serve as an intuitive way to haptically communicate information such as finger location or changing dial settings. This range of utility suggests diverse and realistic texture rendering is an important modality to consider for any haptic display. Yet what exactly constitutes "diverse and realistic enough," balancing ability to render a wide breadth of realistic textures using a given haptic display while maintaining efficient signal representation and accommodating actuator limitations?
My recent research focuses on texture rendering for a diverse set of displays, from friction-modulated touchscreens to wearable vibrotactile rings and watches. These devices differ broadly in site of actuation, actuator bandwidth, and concurrent visual displays, but all rely on a vibration applied to the hand during movement as the primary method of texture rendering. We explored various methods of designing new vibration patterns, such as increasing the amount of spectral content or scaling different aspects of the vibration as a function of finger speed.
The impact of these texture design choices were evaluated via psychophysical ratings of both perceived haptic texture differences and similarity to real textures. Results indicate that for higher frequency vibrations, people can differentiate only a very limited amount of spectral complexity, and are also increasingly less sensitive to speed-dependent shifts in frequency. This suggests the set of fine texture sensations achievable via applied vibration alone can be composed using a manageably small set of design parameters and rendered with a few narrow bandwidth actuators.

11:15 AM *SB08.01.03
Multiphysics in the Human-Machine Interface—Impact on Friction and Haptic Perception M Cynthia Hipwell, Xinyi Li, Changhyun Choi, Sitangshu Chatterjee and Aditya Kuchibhotla; Texas A&M University, United States

Haptics is the field that deals with technology that stimulates the sense of touch and motion. Haptic researchers are working to create the same level of fidelity in touch-based recording and display that we currently have in audio and video. Why is this so complicated? One of the many reasons is the complexity of the finger-device interaction and the role that this plays in the generation of touch perception in humans. The finger-device interface is complex and variations with environment and person-to-person can cause finger material property changes that impact device performance and human perception of it. Multiphysics modeling of interfacial phenomena such as capillary forces and surface tension, electrowetting, electrophoresis, multiphase flow, and soft tissue contact mechanics can help predict friction under various conditions and enable purposeful design for consistent or enhanced performance. Examples of design for consistent performance with humidity, design for consumer preference, and consideration and use of temperature will be explored. Additionally, we will consider how human finger property changes can be used as bioinspiration for material design for active friction modulation in clutches and robotic grasping.

11:45 AM SB08.01.04
Skin Biomechanics and the Role of Neural Stimulation in Tactile Perception Sebastian Hendrickx-Rodriguez, Omar Elsafty and Reinhold Dauskardt; Stanford University, United States

Human skin regulates tactile perception of the world around us through interplay of the tissue's material properties and a system of cutaneous mechanoreceptors. However, the relationship between these properties, influenced by skin's hierarchical structure, and how we perceive sensations remains unclear. In this work, we establish a fundamental link between mechanical stresses in the top layer of skin, the stratum corneum (SC), and feelings of skin tightness [1]. We further show that these sensations can be dampened or enhanced via application of various cosmetic formulations [2].

Biomechanical changes in the stratum corneum (~20 m) stimulate cutaneous mechanoreceptors and sensory neurons in softer, underlying layers. Activated afferent neurons send signals to the central nervous system that are interpreted as perceptions. Dehydration of the SC is particularly relevant since water loss results in stiffening (from ~2 MPa to ~100-200 MPa) and contraction (by ~1.5%) of the SC, propagating strain fields into lower layers where they trigger sensations of tightness. Topical skin treatments can either augment tightness by driving more water loss (such as with cleansers), or reduce tightness by helping retain water in the SC (such as with moisturizers). Thin film characterization can measure SC mechanical stresses *in vitro*. Finite element simulations can model the resulting strain fields in full-thickness skin, and predict neuronal firing rates *in silico*. Results can then be compared to consumer perception scores gathered *in vivo*. We show a linear correlation between scores reported by volunteers up to 12 hours post application of cleansing and moisturizing formulations, and SC stresses measured in the lab. Predicted firing rates also correlate remarkably well with consumer scores. This framework can now aid in the development of novel formulations that carefully tune SC stresses for a desired sensation.

In this study, we establish a fundamental link between the SC's biomechanical state and tactile perception, and use this to quantitatively understand the mechanism underlying sensorial perception of our skin in response to topical treatments. This psychophysical framework can be extended to a full range of stimulations provided by haptic devices including wearable actuators and sensors. It also provides a novel way to study the body's sensing system which could serve as inspiration for the design of soft robotics and stimuli responsive materials.

[1]. Sebastian Hendrickx Rodriguez, Sophie Connetable, Barbara Lynch, Joseph Pace, Ross Bennett Kennett, Gustavo S Luengo, Reinhold Dauskardt, Anne Potter, "From decoding the perception of tightness to a clinical proof of soothing effects derived from natural ingredients in a moisturizer", International Journal of Cosmetic Science, 2022.

[2] Ross Bennett Kennett, Joseph Pace, Barbara Lynch, Yegor Domanov, Gustavo S. Luengo, Anne Potter, Reinhold Dauskardt, “Sensory Neuron Activation from Topical Treatments Modulates the Sensorial Perception of our Skin”, In preparation.

SESSION SB08.02: Actuation
Session Chairs: Matteo Bianchi, Charles Dhong, Marcia O'Malley and Tristan Trutna
Tuesday Afternoon, April 11, 2023
Moscone West, Level 2, Room 2012

1:30 PM *SB08.02.01
Thermo-Responsive Conducting Polymers Based on PEDOT:PSS Laure V. Kayser; University of Delaware, United States

Designing conductive materials for human-machine interfaces, robotics, and/or haptics requires materials with good electronic properties and mechanical properties close to that of biological tissues. Electronically-conductive hydrogels, composites of crosslinked and water-swollen polymers with a conducting material (polymer or inorganic nanoparticles), can address these requirements. But, two common issues arise from the traditional synthesis of conductive hydrogels. First, the elastic modulus of the hydrogels is increased at the high loadings necessary to achieve electronic conduction. Second, the crosslinking process is irreversible, making it difficult to process the materials in different form factors, inject them for implantable electronics, or remove the hydrogels after use. To address these issues, we have developed conducting polymers that undergo a sol-gel transition close to physiological temperatures: thermo-responsive conducting polymers. We focused on the polyelectrolyte complex of poly(3,4-ethylene dioxythiophene) and poly(styrene sulfonate) (PEDOT:PSS) as our conducting polymer for its high conductivity, low impedance, low toxicity, and dispersibility in water. To achieve thermally-gellable PEDOT:PSS, we used controlled radical polymerizations to create block copolymers of PSS with a thermo-responsive polymer, poly(N-isopropylacrylamide) (PNIPAm), and complex it with PEDOT. At the adequate ratio of each component, the PEDOT:PSS-*b*-PNIPAm block polyelectrolyte complex thereby synthesized gels in water at 37 °C. The gel displays both ionic and electronic conductivity of 0.13 mS cm^{-1} and 0.05 mS cm^{-1}, respectively. The thermal gelation process is completely reversible, providing exciting new opportunities in actuation for robotics or haptics, or injectable conductive hydrogels.

2:00 PM SB08.02.02
Electrically Driven Liquid Crystal Elastomer Actuator Matrix for Haptic Surfaces Giulia Spallanzani[1,2], Pengrong Lyu[2], Danqing Liu[2], Dirk Broer[2], Roel Kusters[1], Darragh Walsh[1], Charlotte Kjellander[1] and Peter Zalar[1]; [1]Holst Centre - TNO, Netherlands; [2]Technische Universiteit Eindhoven, Netherlands

Haptic surfaces are a flourishing research topic at the intersection of electronics, robotics, and biomedical sciences, aimed at the development of thin and flexible devices that mimic human-environment interactions. Liquid crystal elastomers (LCEs) have great potential to drive this innovation, thanks to their unique ability to reversibly actuate to high strains with light or heat exposure. Here, an electrically driven LCE actuator matrix with the potential to be scaled up to large area production is developed. The device functions by LCE thermal actuation driven by the Joule heating of a resistive element. The multilayer actuator array consists of series of active LCE elements coupled with an electronic layer used to interconnect the elements and operate the device. These two layers are then embedded within a flexible substrate which shields them from the external environment and simultaneously amplifies out-of-plane actuation. Such a device can produce local on-demand deformation with no foreseen limitation on the overall size of the matrix. The presented concept shows great potential for applications in texture-changing surfaces or surface-driven object motion, examples of which include self-cleaning surfaces or soft touch massage mats.

2:15 PM *SB08.02.03
Topography via Topology—Localized Stimuli-Response of Liquid Crystalline Elastomers Timothy White; University of Colorado, United States

Liquid crystalline elastomers (LCEs) are functional materials capable of undergoing large, complex deformations in response to stimulus. These deformations are attributed to order disruption between liquid crystalline mesogens incorporated within the polymer network. By controlling the orientation of mesogens during material fabrication, 3D shapes can be programmed into these actuating materials. This talk will detail our strategies for locally programming mesogen orientation to realize complex 3D shapes and topographical surfaces in LCEs.

In order to program mesogen orientation, the liquid crystalline moieties can be oriented before crosslinking the polymer network. One approach that we have taken in this respect is the use of photopatterned substrates as command surfaces for the liquid crystalline monomers. This method enables high resolution programming of local mesogen orientation, enabling a broad range of targeted 3D actuations to be patterned.

In addition to investigating routes to programming orientation during network synthesis, we have also recently explored opportunities for *re*programming the crosslinked materials using dynamic covalent chemistry. Using these LCEs with dynamic bonds, we demonstrate multi-stage programming that combines surface patterning with dynamic bond reconfiguration to realize additional levels of complexity in 3D actuated shapes.

2:45 PM SB08.02.04
Controlling Fine Touch Sensations with Polymer Tacticity and Crystallinity Abigail Nolin and Chun-Yuan Lo; University of Delaware, United States

Fine touch sensation is a critical source of information, especially for those with low vision or blindness. Tactile aids (e.g. braille reader) and surface-haptic interfaces typically produce fine touch sensation by using physical features, such as surface patterned bumps and pins, to alter frictional forces on the user’s finger. However, when interacting with everyday objects, frictional and adhesion forces arise not only from surface topography but also from the chemical properties of a material itself. This work aimed to generate tactile sensations by altering the materials chemistry and microstructure of thin film polymer surfaces with minimized variations in physical roughness. We demonstrated that humans are sensitive to the microstructure of chemically-similar, semi-crystalline polystyrene films due to the influence on mesoscale friction. Through dynamic friction testing with a custom mock finger mechanical test set-up, custom signals analysis, and human psychophysical testing, we demonstrated how materials phenomenon alone may be used to influence fine touch. These material phenomena may extend to broader classes of materials for design of higher graphic haptic technologies and tactile aids.

3:00 PM *SB08.02.05
Progress in the Design of Distributed Electroadhesive Haptic Displays James E. Colgate; Northwestern University, United States

Imagine an interface device that can be programmed to feel like burlap or velvet in much the same way that pixels on a screen can be arranged to look like one of those fabrics. Extending this analogy, we might reasonably ask what information a tactile pixel would need to encode, what pixel density is needed, how an "image" of a texture might be recorded, and of course how the tactile pixels ("taxels") could be designed and made to work. In this talk, I'll review the progress that our group has made in answering these questions.

Our work has been done in the context of "surface haptics." Here, a fingertip – either bare or outfitted with a wearable device – is swept across a physical surface. Virtual textures are created by using electroadhesion (i.e., electrostatic attraction) to modulate the friction at the sliding interface. I will present a simple model of electroadhesion and explain how it can be used to modulate friction at a very high rate, in excess of 50kHz.

Until recently, most of our haptic devices might be considered "single taxel": electroadhesion, although high-bandwidth, occurred in synchrony over the entire finger-surface contact patch. There is a logic to the single-taxel approach: almost a century ago, David Katz proposed the "duplex theory" of tactile perception, suggesting that texture depends upon a "spatial sense" for coarse textures and a "vibration sense" for fine textures, and modern neuroscience has supported the idea that fine textures are encoded temporally, not spatially. In other words, it is reasonable to expect that high-bandwidth control of a single tactile taxel would suffice to recreate realistic fine textures. Unfortunately, this turns out to be wrong. A recent study performed in our lab demonstrated that recording of the skin vibrations caused by sliding over a fine texture followed by precise electroadhesive playback, did not result in realism. Texture playback was perceived to be much weaker and qualitatively different.

In that study, vibrations on the side of the finger were carefully matched, but the mechanics of contact patch interaction may have been quite different between the physical and virtual cases. In particular, some degree of spatial inhomogeneity almost surely occurred during contact with physical textures, even though they were fine. If this is the source of the perceptual discrepancy, then it sheds some doubt on the duplex theory (to be fair, the theory is qualitative in nature and does not establish strict conditions for either fine or coarse texture). A follow-up study performed with a high-bandwidth pin array showed that inhomogeneity does, in fact, play a significant role in subjective experience: greater inhomogeneity leads to greater subjective intensity. Simulations further suggest that two different mechanoreceptor populations are involved: Meissner corpuscles respond strongly to spatiotemporal variation within the contact patch, while Pacinian corpuscles respond to surface waves that propagate up the side of the finger. Single taxel electroadhesion would address only the Pacinian population while physical textures would excite both.

The path to texture realism therefore, appears to require more taxels, even in the case of fine texture. While development of a rigorous specification is ongoing, we are currently targeting 2.5mm taxel spacing and a bandwidth of 300Hz. To realize this in a compact device, we are developing a wearable array of electroadhesive taxels (also known as "pucks"). A 4x4 array has been built on a latex backing with printed silver ink electrodes addressing each taxel. The taxels themselves are made from a commercially available conductive finger cot material, which is a nitrile doped with carbon nanotubes. Puck and fingertip behavior can be imaged through a transparent countersurface (glass with and ITO electrode, coated with SiO2). I will report on preliminary physical and psychophysical results.

3:30 PM BREAK

4:00 PM SB08.02.06
Octopus-Inspired Adhesive Skins for Intelligent and Rapidly Switchable Adhesion Michael D. Bartlett[1], A B M Tahidul Haque[1], Ravi Tutika[1], Chanhong Lee[1] and Eric Markvicka[2]; [1]Virginia Tech, United States; [2]University of Nebraska-Lincoln, United States

Emerging applications in soft robotics and haptic devices demand strong adhesives which can be easily removed on-demand and subsequently reused. This requires new paradigms in adhesive science and engineering to create new classes of multifunctional switchable adhesives. Nature can provide inspiration for these challenging adhesion scenarios. For example, the octopus couples controllable adhesives with intricately embedded sensing, processing, and control to manipulate underwater objects. Current synthetic adhesive–based manipulators are typically manually operated without sensing or control and can be slow to activate and release adhesion, which limits system-level manipulation. Here, we couple switchable, octopus-inspired adhesives with embedded sensing, processing, and control for robust underwater manipulation. Adhesion strength is switched over 450× from the ON to OFF state in <50 ms over many cycles with an actively controlled membrane. Systematic design of adhesive geometry enables adherence to nonideal surfaces with low preload and independent control of adhesive strength and adhesive toughness for strong and reliable attachment and easy release. Our bio-inspired nervous system detects objects and autonomously triggers the switchable adhesives. This is implemented into a wearable glove where an array of adhesives and sensors creates a biomimetic adhesive skin to manipulate diverse underwater objects.

4:15 PM SB08.02.07
Multimodal Sensing and Haptic Feedback to Improve Minimally Invasive Surgery Arincheyan Gerald, Rukaiya Batliwala, Patra Hsu, Jonathan Ye and Sheila Russo; Boston University, United States

Minimally invasive surgical (MIS) procedures suffer from limited haptic feedback to the surgeon and manufacturing limitations for embedded sensing capabilities on surgical instruments. The lack of sensing and haptic feedback results in the application of excessive forces on the tissue. This is exacerbated in instruments such as endoscopes where the tool's flexibility affects transmissions of friction forces, resulting in severe adverse advents (SAEs), such as bleeding, perforation, or splenic injury. Multimodal sensing, such as force monitoring or bleeding detection, combined with direct haptic feedback could be useful in reducing SAEs in colonoscopy. Similarly, haptic feedback combined with multimodal soft sensing could be beneficial in other MIS scenarios such as remote palpation or robot-assisted laparoscopies.

Previously, we created a force sensing soft robotic sleeve to mitigate excessive forces exerted on the colon wall. The sleeve contains optical waveguides and can be mounted directly onto the colonoscope. We further extended our work to develop biosensors that can detect bleeding in the colon. This is particularly important because the surgeon is often unable to detect bleeding as their field of view is limited to the endoscope's distal end camera. It is crucial that these sensors are integrated in a seamless manner that does not impede the functioning of the colonoscope or alter the clinical workflow. Thus, these sensors are designed to be soft and flexible with a low vertical profile (~1 mm). The sensor can easily be mounted onto the colonoscope at multiple points to provide bleeding detection. The sensor is manufactured by molding PDMS onto photolithographically patterned silicon wafers. The sensor contains micron scale soft optical waveguides that interface with a microfluidic channel allowing intake of blood. Presence of blood in the channel causes attenuation of the incident light thereby allowing detection.

To improve MIS, it is important to convey sensing modalities to the surgeon in an intuitive manner. It is essential to develop a comprehensive system that can accurately sense forces and other physical phenomena on the surgical tool, and then directly alert the surgeon through haptic feedback. Thus, we augmented the force sensing capabilities of the soft robotic sleeve by interfacing it with a pneumatic haptic feedback glove. The pneumatic actuators of the glove inflate proportionally to the incident forces on the soft robotic sleeve. Thus, the haptic feedback glove allows the endoscopist to feel the magnitude of forces exerted by the colonoscope onto the colon wall. Additionally, a comprehensive sensing and haptic feedback system can be beneficial in other MIS scenarios. Currently, we are developing a soft sensing and haptic feedback system for robotic palpation of tissue. Since the operator cannot physically feel the palpated tissue, it is difficult to detect the presence of tumors. The palpation sensor can be mounted onto a robot arm, which presses on tissue to detect tumors. The sensor consists of silicone layers of varying hardness embedded with waveguides. As the sensor presses onto tissue, the layers deform around harder areas that may be tumorous. The deformation of the layers causes a change in the waveguide signal. The sensor interfaces with a haptic glove consisting of silicone actuators mounted onto the fingertips. The sensation of tissue palpation can be translated to the user via actuator inflation.

The safety and efficacy of MIS must be improved by not only embedding sensors on the surgical tools but also developing solutions to convey the complex sensing data to the surgeon in an intuitive manner. This highlights the need for haptic feedback to enable the surgeon to process multimodal sensing cues in a manner that complements the clinical workflow. Future works that seek to embed sensing on robotic tools must evaluate optimal methods by which the sensing data is best relayed to the surgeon.

4:30 PM SB08.02.08
A Low-Voltage Electroadhesive Clutch for Untethered Wearable Devices Based on Ionoelastomer Heterojunctions Owen Lee[1], David Levine[2], Gregory Campbell[2], James H. Pikul[2], Kevin Turner[2] and Ryan C. Hayward[1,1]; [1]University of Colorado Boulder, United States; [2]University of Pennsylvania, United States

Electroadhesive clutches (EAclutches) in which frictional blocking forces can be modulated by an applied potential have recently enabled lightweight, compact wearable devices such as haptic clothing, soft exoskeletons, and controllable prosthetics. However, typical EAclutches based on electronic conductors with insulating dielectric layers suffer from low force capacities (1-25 N/cm^2) and operate using large working potentials (> 100 V), requiring tethers to specialized high-voltage circuitry. These performance limitations, along with safety concerns regarding the use of high voltages, have limited the practical implementation of EAclutches for untethered wearable devices. Previous work has sought to reduce EAclutch operating voltage by decreasing the thickness of the dielectric (< 10 µm), however, these devices are challenging to fabricate and are prone to short circuits due to defects or damage. Recently, our group developed a novel class of low-voltage electroadhesives based on oppositely charged polymerized ionic liquid elastomers (termed "ionoelastomers"). The large electric field developed across a nm-scale ionic double layer (IDL) allows for robust and reversible adhesion between two ionoelastomers at comparatively low working potentials (~ 1 V) even with overall layer thicknesses of ~ 100 µm. Despite this promise, high off-state adhesion and poor environmental stability have so far prevented the integration of ionoelastomers into practical EAclutch devices. In this work, a low-voltage, environmentally stable EAclutch based on ionoelastomer electroadhesives is demonstrated. Here, the integration of a perfluorinated comonomer enables enhanced delamination in the off-state by reducing the surface energy of the junction without significantly affecting the capacitive behavior of the IDL. Ionoelastomer EAclutches exhibiting high force capacities (60-80 N/cm^2) at low voltages (5-9 V) are fabricated. The ionoelastomer EAclutch is combined with a soft elastomer, allowing for electroprogrammable stiffness in an untethered kinesthetic haptic device. These findings provide a fundamental understanding of the mechanism of electroadhesion in ionoelastomer adhesives and broaden the scope of EAclutch integration into untethered wearable devices.

4:45 PM SB08.02.09
Poly(ionic liquid) Fillers for Dielectric Elastomer Actuators with Low Driving Electric Fields and High Actuation Performance Hui Wang, Matthew Tan, Wei Church Poh, Dace Gao and Pooi See Lee; Nanyang Technological University, Singapore

Dielectric elastomer actuators (DEA) have commonly been used as haptic devices because of their high actuation strain, quick response, large energy densities and low weight. However, the driving electric field is high, which leads to danger to users and incompatibility with portable power sources. In this work, a soft, stretchable, adhesive, transparent and all-solid-state poly(ionic liquid) (PIL) is introduced as filler into VHB to fabricate DEA. As a result, the dielectric constant increases from 4.8 to ~15 at 1 kHz and Young's modulus decreases to 0.11 MPa. Unlike liquid fillers, possibility of filler leakage reduces, minimizing short circuit which is dangerous to users. DEA with PIL filler delivers high area strain of 137% at 17 V/µm, exceeding that of most DEAs at similar electric field. The unimorph DEA with PIL filler shows a bending angle change of 38.6° under an electric field of 12.6 V/µm, which is over twice the value of the DEA without PIL. Finally, an unimorph DEA integrated with alternating-current electroluminescent layer is demonstrated. This work provides a promising strategy for building a high-performance and safer DEA for haptics.

SESSION SB08.03: Poster Session
Session Chairs: Matteo Bianchi, Charles Dhong, Marcia O'Malley and Tristan Trutna
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SB08.03.01
Tunable Soft Optical Sensors for Shape Sensing in Soft Continuum Robots and Multi-Modal Contact Sensing End Effectors Max D. McCandless, Frank Julia Wise and Sheila Russo; Boston University, United States

The design, control, and functionality of soft robotic manipulators and grippers are a growing area of research interest. Recent advancements are pushing toward closed-loop control via embedding proprioceptive and exteroceptive sensing into these soft platforms. Different soft sensing technologies have been explored, i.e., resistive, capacitive, and magnetic. Fully soft optical sensors are useful for both shape sensing and contact force recognition and have been utilized for a variety of soft gripper applications. However, these grippers are often attached to rigid robotic arms, which highlights the need for soft continuum robots with embedded sensing. Soft continuum robots can benefit from the integration of tunable soft optical sensors that provide the systems with real-time 3D shape sensing. The combination of shape sensing soft continuum robots and contact sensitive soft robotic grippers presents exciting application scenarios in minimally invasive surgery (MIS) and high-precision pick-and-place tasks.

Recently, we have developed a roughness tuning strategy for the fabrication of soft optical waveguide sensors (WG) to achieve shape sensing and contact recognition within a single multi-modal sensor. We integrated the sensors into a fully soft continuum robot consisting of a multi-directional bending module and a gripper. The robot module integrates two WGs for 3D shape sensing and three soft pneumatic actuators to steer the robot in all directions. The gripper embeds two soft pneumatic actuators to deploy itself, two soft pneumatic actuators to control grasping, and two WGs, one in each jaw of the gripper, with tuned roughness to monitor both gripper tip positions and subsequent occurrence of contact with an object. The deployment and grasping motions of the gripper cause measurable losses in optical power through the WGs. These losses are utilized to track the tip position of the gripper. Alternatively, when an object is contacted, we observe a distinct increase in the output power of the WG through the system, which allows us to distinguish the tip position tracking from contact recognition and thus create a multi-modal sensor. The proposed system simultaneously tracks the real-time shape of the robot body and the tip positions of the gripper via a graphical user interface (GUI). Furthermore, upon contact with an object, the GUI alerts the user of the successful grasping of an object. The robot module is calibrated so that the shape of the robot is mapped with an electromagnetic tracker throughout its entire workspace. This data is used to determine the true shape of the robot by using a constant curvature model, and then the WG signals are fit to a surface based on the data collected to predict the shape of the system in subsequent testing and controls. The surface fits implemented to use the WGs to predict the robot module shape had an average error of the tip position of less than 4 mm.

Our soft continuum robot can be utilized in a variety of pick-and-place applications where the integration of soft optical sensors can improve the accuracy of the control of soft robotic arms. Further, we have determined that proper tuning of the sensors can result in increased sensitivity across a large range of curvatures and enable a multi-modal sensor response, which allows for a reduced number of total sensors in the robot. These advancements in the tunability of soft optical sensors pave the way toward miniaturized devices and better closed-loop control of soft robots. Providing contact force recognition to continuum robots also pushes toward improving the capabilities of haptic feedback systems that can be integrated with soft sensors and soft continuum robots. Lastly, the low cost and scalable nature of the system presents opportunities for incorporation into a variety of MIS procedures where enhanced dexterity and sensor feedback is valuable for surgeons.

5:00 PM SB08.03.02
MXene-Silver Ink-Based 3D Printed Flexible Haptic Figure Tip Sensor—From Macro Sensing to Micro Sensing Jiaoli Li[1], Yun Li[2], Adam Sawyer[1], Mingyuan Sun[2], Bo Li[2] and Chenglin Wu[1]; [1]MST, United States; [2]Villanova University, United States

Soft sensors have been widely accepted and used in many fields. However, a technological breakthrough is still needed to gain a wider sensing range, faster response speed, and longer durability. In this work, we successfully fabricated an MXene-sliver ink-based interdigitated electrode via direct-ink-writing (DIW) 3D printing technology and assemble it into robotic gloves. Test results have shown the following advantages: (1) ultrafast response time (within several seconds) for surrounding detection at the macro level; (2) extremely accurate detection and object recognition; (3) ultrasensitive detection of omicron virus up to 110^{-22} molar at the micro level; (4) remarkable extension of the sensing range and targets. The 3D printed interdigitated MXene-sliver electrode could work as a figure tip sensor, as a result of being able to feedback continuously output impedance changes for any approaching objects. When functionalized with single-strand probe DNA, it can also work as a virus sensor and captures the target DNA in the environment by collecting signal changes through electrochemical response. This successful demonstration elucidates the broad prospects of MXene-based soft sensors for soft robotic devices.

5:00 PM SB08.03.03
A Self-Powered Triboelectric Tactile Sensing Device Shujia Xu[1,1], Shengjie Gao[1,1] and Wenzhuo Wu[1,1,2]; [1]Purdue University, United States; [2]Regenstrief Center for Healthcare Engineering, United States

Triboelectric sensors has been widely used for tactile sensing due to its self-powered attribute, low cost, and facile fabrication process. High-resolution tactile devices relying on densely arranged sensing units impose significant challenges to fabrication and signal readout for practical applications. Here we demonstrated a new touch-sensing mechanism for triboelectric tactile sensors. A trackpad with 9 sensing units was fabricated using an additive manufacturing method. The device can continuously track 25 touch locations on the panel based on a machine-learning algorithm. We also demonstrated the potential application of such device for user identification based on keystroke dynamics with random touch other than a predefined input sequence. The proposed new triboelectric sensor provide a new direction for TENG-based tactile sensing development leveraging artificial intelligence to boost the sensing performance.

5:00 PM SB08.03.04
Actively Increasing Force Transmission of a Millimeter-Scale Soft Robot for Tissue Interactions in Minimally Invasive Surgery Daniel Van Lewen, Taylor Janke, Harin Lee, Ryan Austin and Sheila Russo; Boston University, United States

Interest in soft robotics is rapidly growing in large part due to the ability to safely interact with humans. The use of soft materials allows for scalable fabrication processes that can combine various degrees of freedom into monolithic structures. Miniaturization enables soft robots to navigate in tortuous, narrow, and difficult-to-reach areas, allowing for broad applications ranging from exploration to minimally invasive surgery. However, force output scales with the robot's cross-sectional area, thus hampering significant robotic tasks and interactions with the surrounding environment at smaller scales.
Here, we present a 3.5 mm diameter soft robot that increases force transmission and, consequently, broadens the potential interactions that may be achieved within similarly scaled environments. These capabilities are accomplished by designing three fluidic-actuated, independent degrees of freedom. The proposed robot consists of a continuum body constructed out of two polymers with differing elasticity and an attached 3 mm linear bellows actuator. The continuum body contains actuation mechanisms for steering via a bending degree of freedom and for stabilization via a radially-expansive actuator. Fabrication of the continuum body is performed through a series of molding processes in which the stiffer of the two polymers, DragonSkin 10, forms the base of the body. Dowel pins run axially along the body for alignment and masking the cross-sectional off-center bending chamber. A 3D masking technique combined with the molded shape of the base are utilized for the creation of the radial stabilization actuator through the over-molding of the less stiff polymer, Ecoflex 00-30. The linear bellows actuator utilizes a layer-by-layer fabrication technology in which the application of heat and pressure bonds each bellow at predetermined locations. The bellows actuator is adhered to the tip of the continuum body to act as an end-effector deployment mechanism enabling the robot to utilize any increase in force transmission provided by the anchoring of the stabilization mechanism.
The increase in force transmission is measured through mechanical characterizations of the robot in states with stabilization activated and unactivated. An increase in the effective stiffness of the system of about five times is measured as a result of stabilization, demonstrating that, for displacements less than 2 mm, the robot can transmit up to 0.75 N of force to the deployment mechanism located at its tip. Characterization of the deployment mechanism further confirms the need for stabilization with blocked forces measuring up to 1.1 N. Results of both stabilization and deployment force measurements validate models that guided the robot design. To characterize dexterity of the robot, bending of the continuum body is measured displaying full retroflexion with a maximum bending angle of 196 degrees. Linear expansion of the deployment mechanism is also measured showing a range of 9.3 mm. The deployment mechanism is assembled with a needle to demonstrate the feasibility of the robot to be used as a platform for minimally invasive tissue biopsy in bronchoscopy procedures. Compared with typical surgical forces, characterizations of the robot verify its ability to puncture stiffer tumor tissues while maintaining safe levels of force on healthy tissue. An in-vitro setup places the robot within a lung model to demonstrate its ability to steer into a desired lung branch, stabilize within the chosen branch, and deploy a needle for tissue biopsy. The proposed soft robot demonstrates the potential benefits of more forceful interactions between miniaturized soft robots and their environments paving the way for the creation of soft robots as advanced surgical tools.

5:00 PM SB08.03.05
Tunable Actuation Response of Humidity-Driven Artificial Muscles by Means of Nanofillers Sevketcan Sarikaya[1], Frank Gardea[2], Hannah Strong[1], Jeffrey T. Auletta[3], David Mackie[3] and Mohammad Naraghi[1]; [1]Texas A&M University, United States; [2]DEVCOM Army Research Laboratory South, United States; [3]DEVCOM Army Research Laboratory, United States

Soft actuators can be driven via environmental humidity and provide biomimetic adaptation to environments. Humidity may serve as a passive stimulus, i.e., the desired actuation may be caused by uncontrolled changes in the humidity of the environment, or active stimuli, i.e., promoting an actuation response by controlling the humidity. Here, we report a humidity-responsive axial actuator and walking robot of sulfonated polyether ether ketone (SPEEK), which shows greatly tailorable actuation performance upon embedding graphene nanoplatelets (GNP). Three cases of SPEEK with no GNP, SPEEK with 0.5 wt.% GNP and 1 wt.% GNP was tested. Adding only 0.5wt% GNP increases the actuation by 50% and provides a maximum actuation stroke of 24% and work capacity of 230 J/kg. In addition, 0.5wt% GNP promotes faster actuation, with significantly enhanced rates of both contraction and expansion. However, the addition of 1wt% GNP slightly decreases the actuation magnitude and rates. The non-monotonic actuation tunability by GNP was correlated to changes in ion exchange capacity (IEC), water uptake, and GNP dispersion. By utilizing actuation magnitude dissimilarity, the axial actuators were converted into a walking robot stacked of two active layers consisting of fibers of the same material system. The bilayer robot demonstrated self-crawling and locomotion ability in response to humidity changes. This study shows a uniquely tailorable humidity actuator that demonstrates both linear and bending actuation.

5:00 PM SB08.03.06
Complete Foldable, Resilient, and Fatigue Resistant Electrode Insic Hong, Seunggon Lee, Yeonwook Roh, Daseul Lim, Dohyeon Gong, Je-Sung Koh, Daeshik Kang and Seungyong Han; Ajou University, Korea (the Republic of)

Development of mechanically and electrically robust electrode that can be completely folded and crumpled without fatigue degradation in substrate and electrode material has been demanded as a core component of next-generation foldable electronics and soft robot. Here, we report a nanocomposite electrode that can be completely folded in half, crumpled, and endure tensile load (3 N/mm) without changing electrical resistance using a simple composite structure consisting of Elastomer, Kevlar, PET film and silver nanowires (Ag NWs). We performed rigorous experimental and theoretical investigations based on the neutral axis and strain engineering, suppressed the plastic deformation causing crease pattern by an unprecedented method encapsulating a plastic substrate with elastomers, and increased tensile strength of the electrode dramatically via aligned Kevlar fiber reinforced elastomer. Furthermore, by successfully applying developed nanocomposite electrodes to a foldable wrinkle-free display and multifunctional sensor, it is expected that our electrode presents a methodology and tool with vast potential for soft robotics and next-generation foldable electronics.

5:00 PM SB08.03.07
Investigating Sensation Mechanics and Improving Actuation of the Soft Robotic Tongue and Ear from Simulation Selena Rodriguez, Deepak Ganta and Joaquin Contreras; Texas A&M International University, United States

Hepatic-based simulation plays a key role in designing and developing sensors and soft robotics for improving human-like robot interaction and sensing. For example, there is a huge demand for electronic tongues and ears in the food and defense industries for sound or air pressure detection and chemical and flavor analysis. The lack of availability of soft robots with human-like sensory features has motivated us to investigate, design, and simulate a human tongue's complex motions, including that of a human ear.

Human anatomy was studied in detail to modify the standard designs of the human tongue and the human ear. In the tongue model, adding embedded chambers at strategic locations was used to replicate various 3D motions (rolling, groove, twist, and elongation) of the human tongue necessary for improving the bio-chemical sensing capabilities. The FEM (Finite element method) simulations using ABAQUS software showed the relation between pressure and deformation range for various motions in a human tongue, including stress vs. strain relation for investigating the mechanical properties. Similarly, a study was conducted to test the mechanical properties of the human ear, and a load was applied on the ear's outer rim in a downward direction. The behavior of the ear was simulated under various loads, both compressive and tensile testing, to determine the stress vs. strain relation.

5:00 PM SB08.03.08
High Performance and Deformable Ionic Sensory Platform by Tailoring Gelator Design Jin Han Kwon, Yong Min Kim and Hong Chul Moon; University of Seoul, Korea (the Republic of)

Here, we propose versatile ionic conductors for high-performance, deformable and functional ionic sensory platforms by tailoring the mechanical properties of ionic conductors. For instance, porous ion gels simply fabricated by sugar cube can be effectively deformed by closing pores even with small pressure, a broad variation in the contact surface area of the porous ion gel and electrodes is induced, leading to a dramatic difference in electrical double layer (EDL) capacitance. More interestingly, the functionality of the porous ion gel is extended to include electrochemiluminescence (ECL), resulting in the production of emissive ECL ionoskins. Furthermore, the deformability of ionic conductors is tailored by using binary polymer blends as the co-gelators. To reduce the polymer chain entanglement of polymer gelators and induce effective dissipation of applied stresses, flexible and low glass-transition temperature(Tg) polymer is additionally doped into the relatively hard and high Tg polymer based-ionic conductors. The optimized ternary blend ionic conductors exhibit outstanding stretchability, mechanical elasticity and durability, indicating high feasibility for strain sensory systems.

5:00 PM SB08.03.09
Bioinspired Vibration-Resistant Sweat-Tolerant Haptic Adhesion Interfaces Jinhyung Kim[1], Da Wan Kim[1,2], Gui Won Hwang[1], Hyeongho Min[2], Jihyun Lee[1], Dohyun Lim[1], Tae-Heon Yang[3] and Changhyun Pang[1,2]; [1]Sungkyunkwan university, Korea (the Republic of); [2]Sungkyunkwan University, Korea (the Republic of); [3]Korea National University of Transportation, Korea (the Republic of)

Polymeric adhesives, which are thin, soft and flexible, with skin conformal interfaces are attractive for haptic interface technology capable of transmitting sophisticated mechanical stimulation. However, conventional polymeric skin adhesives cannot maintain adequate shear adhesion to the haptic interface, such as repetitive vibrations or sweaty skin. Here, we report skin adhesive patches inspired by the hybrid architectures of frog toe pads' water-drainable hexagonal arrays and snail pedal muscles' energy dissipation layer with interlocked structures. Hybrid frog-snail-inspired adhesive (FSIA) patch exhibits remarkable shear adhesion in both dry and sweaty conditions (max. ~36.0 kPa in dry conditions, and max. ~26.8 kPa in sweaty conditions). Adhesion force enhanced by the stress distribution was analyzed as a simple theory based on the capillary, elastic, and dissipation stresses, and the finite element method simulation according to the geometric and material parameters. Furthermore, we showed that the microchannels between the hexagonal arrays effectively drains the liquid in sweaty conditions. Our patch could tolerate high-frequency vibrations (~60 Hz) while maintaining vibrational transmissibility on even sweaty skin. For potential application, we demonstrated an integrated system combining skin-attachable patches with thin vibration actuators. Our haptic adhesion interface may establish new strategies for developing VR/AR technology.

5:00 PM SB08.03.10
A Multifunctional Pressure and Strain Sensor for Tactile Compliance Identification Arielle E. Berman[1], Chengyi Xu[1], Rahul Singh[2], Levent Beker[2] and Zhenan Bao[1]; [1]Stanford University, United States; [2]Koç University, Turkey

The development of human-like tactile sensation is vital to the advancement of robotic manipulation and the completion of highly nuanced tasks. A fundamental way humans understand and interact with their surroundings is the classification of touched object compliance, or the inverse of stiffness, via the activation of mechanoreceptors in the skin. Specifically, slow adapting (SA) I and II receptors, which sense pressure and skin stretch, respectively, are both needed to perceive compliance. We propose that such a functionality can be replicated with a multifunctional pressure and strain sensor fabricated from digitally printed conductive structures impregnated into an elastomer, such as styrene-ethylene-butylene-styrene thin films. Here, we design a novel device structure that combines pressure and strain sensing at the same pixel location, which has the potential to improve spatial accuracy and enable increased taxel density in an array. Although existing literature has reported object identification technologies, these devices require a known and controlled force or displacement. On the other hand, this work proves that both inputs can be sensed independently and are, thus, inherently deconvoluted. Additional advantages over the state-of-the-art include this device's stretchability and thin form factor. When integrated with robotic systems or eSkins on prosthetics, this novel biomimetic sensor can provide sophisticated sensory feedback for force modulation, safer human-robot interactions, and natural sensation on artificial limbs.

5:00 PM SB08.03.11
Arbitrarily Shape-Manipulation of High Stiffness Electronic Composite through Shifting Neutral Surface of the Material Dohyeon Gong, Yeonwook Roh, Changhwan Kim, Suhyeon Hwang, Dongwook Shin, Daseul Lim, Insic Hong, Doohoe Lee, Je-Sung Koh, Daeshik Kang and Seungyong Han; Ajou Univ, Korea (the Republic of)

Transformation a sensor of 2D type into 3D structure can realize a differentiated function. A sensor for 3D structure must be consisted of a thin or low-stiffness material to avoid a failure of sensor's electrode. However, when the sensor was transformed the 3D structure, it requires additional tools to maintain the 3D structure, because the structural stiffness is not sufficient. In this study, we produced an electronic composite that can be flexibly bent and transformed into an arbitrary 3D shape and maintain the transformed shape due to sufficient structural stiffness after deformation using the principle of moving the neutral surface of Shape Memory Polymer (SMP). This sensor is a multi-layer composite in which SMP embeds a high sensitivity crack-based sensor. The SMP has low stiffness (2.2 MPa) at high temperature (60 °C), so the electrode is not broken during transformation, and has high stiffness (1200 MPa) at low temperature (25 °C), so it may maintain a 3D shape even after transformation. For this reason, the composite initially made in 2D form can be transformed into three 3D structures. Each structure is activated to detect external stimuli that are not detected in the initial form; Large strain (2 to 35%), Small pressure (1 to 30 kPa), Small bending (1 to 15 °). In addition, even after transforming to all 3D shapes and returning to the initial shape, there was also a reversibility in which the resistance didn't change at all. Based on these results, we demonstrate that high stiffness electronic composites that can transform into arbitrary 3D shapes and maintain the transformed shape.

5:00 PM SB08.03.13
Realistic Haptic Rendering Based on Piezoelectric Multimorph Actuators for Human-Interactive Tactile Communication System Yulim Min[1,2], hanbit Jin[2], YunJeong Kim[2], Jeongnam Kim[1,2], Osman Gul[3,2] and Hye Jin Kim[2]; [1]UST, Korea (the Republic of); [2]Electronics and Telecommunications Research Institute, Korea (the Republic of); [3]Korea Advanced Institute of Science and Technology, Korea (the Republic of)

In an immersive virtual interaction, realistic sensory devices allow users to provide richer experiences such as vision, hearing, touch, smell, and even taste. Recently, several haptic devices including tactile gloves [1], full-body haptic suits [2], and joysticks [3] are interesting and significant attention for human perception. However, most commercial haptic solutions are insufficient to fully immerse users in virtual environments due to the haptic feedback which is not similar to the real-like feeling. To enable sophisticated tangible interactions, it is essential to reproduce the realistic haptic signals using rendering technology in haptic interfaces between the sensor and actuator. In this study, we proposed a human-interactive tactile communication system using a piezoelectric multimorph actuator capable of both sensing and actuating functions simultaneously. The piezoelectric actuator was designed with multimorph structure with improved displacement (> 800 um) than the traditional PZT ceramic. Our actuator also exhibited uniform vibrations with input signals of frequencies ranging from 1Hz to 1kHz. which is within the perceivable frequency ranges of the human Pacinian corpuscle. To demonstrate the proposed system, 3 different textures are prepared to represent the smooth and rough feeling of the surface. While dragging the textures with the device attached to the fingertips, the signals obtained from the self-sensing actuator are classified by principal component analysis (PCA) with high accuracy of 96 %. Subsequently, rendered signals are generated by extracting key features such as the envelope of the waveform, main frequency, and amplitude based on the PCA. Finally, the actuator reproduces the rendered haptic feedback in real-time. The tactile sensing/actuating communication system is utilized in fields of artificial skin for robotics, and remote tactile communication in virtual reality.

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Acknowledgement
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5:00 PM SB08.03.14
Color-Changing Miniature Heater Array for Emotional Expression DooSeung Um[1], Se-jin Kim[2,3], Qiang Liu[2], Mi-Jin Jin[3] and Chang-Il Kim[2]; [1]Sejong University, Korea (the Republic of); [2]Chung-Ang University, Korea (the Republic of); [3]Institute for Basic Science, Korea (the Republic of)

Recently, attempts to connect the virtual reality world with the real world have been actively conducted. Haptic devices that make you feel like you are interacting with real objects are at the center of the metaverse technology because they can make virtual reality more realistic when you interact with objects in virtual space. In order to further enhance the sense of reality, it is important to transmit various sensations to the human skin. In particular, Warmth, which expresses feelings of comfort and love, is important for expressing emotions. Therefore, we developed a functional miniature heater array that changes color depending on temperature change. A miniature heater array was integrated through the patterning process of silver nanowires. A thermochromic liquid crystal film was stacked on the heater array to visually represent the change in temperature. Moreover, this device was integrated into a flexible substrate (polyimide) to attach to the human skin or gloves.

5:00 PM SB08.03.15
4D Printing of Liquid Crystal Elastomer Fibers with Programmable Bending Sasha M. George, Taylor H. Ware and Manivannan Sivaperuman Kalairaj; Texas A&M University, United States

Liquid crystal elastomers are a class of shape-changing polymers capable of undergoing reversible shape changes in response to changes in temperature. Our goal is to create fibers of liquid crystal elastomers with a nematic to isotropic transition temperature that is sufficiently low to enable use in wearable, active textiles. A two-step reaction is used for the synthesis of the fibers. The first reaction is the Michael addition of a nematic diacrylate monomer with a dithiol. The resulting thiol-terminated liquid crystal oligomer can be extruded, creating long fibers on a rotating mandrel. The diameter of the fiber can be tuned from 210 um and 750 um based on the different speeds of mandrel rotation. During the printing phase, the fibers undergo a photocuring process to crosslink the aligned oligomers by a thiol-ene click reaction with a triallyl crosslinker. By varying the intensity of UV light, we can achieve different amounts of bending of the fibers. With the lower values of UV intensity, we observed that one side of the fiber contracts more than the other side resulting in bending. Fibers with 36% ± 6 reversible actuation strain between the temperatures of 25°C and 60°C have been synthesized with higher contractions ratios achieved by combining this strain with the bending of the fibers. As these fibers have significant actuation around body temperature, these fibers may be used for biomedical applications and active textiles.

5:00 PM SB08.03.16
Haptic Interface Systems Based on Low-Voltage Ionic Polymer Actuators Hyeonseong Ham and Moon Jeong Park; POSTECH, Korea (the Republic of)

Ionic electroactive polymer (EAP) actuators are promising candidates for wearable electronics, including artificial muscles and flexible haptic devices owing to their low-voltage operability and flexible form factor. Yet, major challenges remaining are the slow switching speed, low blocking force and lacks of motion control in real-time. Herein, we report haptic interface systems based on a sensing glove and sensor-integrated ionic EAP actuators, allowing the teleoperation of soft grippers. By using bifunctional polymer electrolytes and soft-conducting electrodes, fast switching speed and high mechanical strength were achieved simultaneously under 1.5V conditions. This enabled the development of efficient haptic feedbacks at the finger without the need for high external voltage. With an aim at controlling the actuation motion in real-time, a liquid metal strain sensor was integrated into both the ionic EAP actuators and sensing glove. The sensor signal was changed according to the degree of bending of fingers wearing the sensing glove, and an algorithm was generated to synchronize the resistance change with the mechanical deformation of sensor-integrated actuators. The physical contact between the object and soft gripper fabricated with sensor-integrated actuators was simultaneously estimated through the sensor signal generated from the actuators, which was delivered to the fingertip as haptic feedback. Given that the haptic feedback system can be operated with small portable batteries, this will be a platform in soft robotics, wearable haptic devices and biomimetic devices.

5:00 PM SB08.03.17
Electrostatic Actuation of a Liquid Crystal Elastomer with Three-Dimensional Electric Field Modulation Choi Moon Young[1], Keumbee Kim[2], Suk-Kyun Ahn[2] and Jun-Hee Na[1]; [1]Department of Convergence System Engineering, Chungnam National University, Korea (the Republic of); [2]School of Chemical Engineering, Pusan National University, Korea (the Republic of)

Liquid crystal elastomers (LCE) have gained enormous attention in the recent past because of their facile fabrication and reversible shape morphing when exposed to external stimuli such as heat, light humidity, and magnetic or electric force. Especially among these, the electrostatic force has several advantages including fast response, easy control, and low power consumption. Mostly, Maxwell's stresses have been employed to control the shape morphing of LCE, but electrode patterning is limited. Therefore, we propose a new type of stimuli to control the LCE based on electrostatic forces generated because of charge transfer between electrodes and LCE. As a result, we demonstrated various types of operations with a high degree of freedom by applying electrostatic forces. The above result could be achieved through three-dimensional control of the electric field according to the structure of the electrode and the application signal without a pre-program in the LCE samples. We believe this study will be very useful for developing LCE-based actuators for various operations using electrostatic control methods with a variety of electrode designs and field modulation.

SESSION SB08.04: Perception and Sensing II
Session Chairs: Matteo Bianchi, Charles Dhong, Marcia O'Malley and Tristan Trutna
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2012

8:00 AM *SB08.04.01
Role of Fingertip Friction in the Tactile Perception of Surface Materials Roland Bennewitz, Maja Fehlberg, Kim Michéle Jost, Sairam Saikumar and Victor Infante; Leibniz Inst for New Materials, Germany

Fingertip friction plays a key role in the stimulation of tactile perception upon sliding touch. We present psychophysical experiments with materials, whose tactile perception is dominated by their surface microstructure. Random roughness at the length scale of the finger ridge distance contributes more to the tactile perception of similarity than the resemblance of surface topography [1]. For micro-fibrillar surfaces, tactile perception follows the bending stiffness of fibrils rather than the elastic moduli or the length of fibrils [2]. The perception of frictional strength in sliding touch can be confused if the characteristic length scale of surface microstructure varies [3]. Finally, physiological characterization reveals the soft matter properties of fingertip skin and their influence on tactile perception of materials.

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8:30 AM SB08.04.02
The Role of Rigidity in Soft Robotic Fabrics Rebecca Kramer-Bottiglio[1] and Xiaonan (Sean) Huang[2]; [1]Yale University, United States; [2]University of Michigan–Ann Arbor, United States

Fabrics are breathable, conformable, and compactible interlaced fiber structures, which makes them the perfect material for wearables, among many other everyday applications. Given their ubiquity, the possibility of "roboticizing" fabrics could lead to smart adaptive clothing, self-deploying shelters, and lightweight, stowable, shape-changing machines. Ideally, a robotic fabric's actuation, sensing, and structural support should be provided by fiber-based components, designed to integrate seamlessly with the fabric's soft and conformable nature. Variable-stiffness mechanisms are often used for the structural elements, functioning as "bones" that can be turned on and off as needed. However, many available fiber-based variable-stiffness mechanisms are passively rigid, only allowing the fabric to become soft when powered, and others require bulky external air or power supplies, making them untenable for untethered robots. In this talk, I will present a new electrically-driven variable-stiffness fiber that can provide a rigid load-bearing structure when powered, but remains flexible otherwise. The active variable-stiffness fibers are stable enough for a robotic fabric to lift and locomote with its own battery pack and onboard electronics, enabling a fully untethered locomoting robotic fabric. I will also present new fabric capacitive sensors that exhibit high strains, cyclic stability, and high water-vapor transmission rates, the latter of which allows for sweat evaporation, an important parameter of comfort in wearable applications. Finally, I will speculate on the combination of the fabric sensors with actuated and variable-stiffness fabrics for human motion monitoring and haptic feedback.

8:45 AM SB08.04.03
Enhancing Actuation Response in Haptic Displays Utilizing Nanoparticle-Based Magnetorheological Elastomers Ludovico Cestarollo[1], Shane Smolenski[2,1] and Amal El-Ghazaly[1]; [1]Cornell University, United States; [2]Bowdoin College, United States

Despite the importance of touch for humans, interactive tactile (haptic) displays can still be considered in their infancy. While several actuation techniques have been developed, all these methods still present major drawbacks either in terms of the power demanded for actuation or their large size, thereby discouraging their use in high-resolution haptic displays. *Magnetorheological elastomers* (MREs) constitute an ideal candidate for a low-power and compact solution to be integrated into a programmable haptic interface. MREs are smart composite materials made of a soft elastomeric matrix and magnetic micro-/nanoparticles. Few studies have focused on the actuation of MREs, and those that do, mostly report the use of relatively large magnetic microparticles inside of elastomeric matrices. In contrast, much smaller nanoparticles would be required to fabricate films on the order of hundreds of nanometers in thickness, able to actuate into sharp textures at the microscopic scale. This research project focuses on building *high-resolution* haptic interfaces by developing flexible magneto-responsive thin-films based on magnetic *nanoparticles*. In the future these materials will be integrated into a nonvolatile magnetic control system that can produce local magnetic fields to actuate the film and generate the desired resolution of three-dimensional shapes and textures.

In this study, we fabricated MREs composed of soft, low-remanence ferromagnetic iron nanoparticles with isotropic and anisotropic arrangement in an elastomeric matrix (Ecoflex 00-30) and optimized them by characterizing their magnetic and mechanical behavior. Films with nanoparticle concentrations varying between 2% and 8% by volume were fabricated. All films showed large visible deformations at the millimeter scale at small applied magnetic fields of only 100-300 mT. However, the magnetically-induced deformations increased with the nanoparticle concentration in the films up to 6 vol. % for both isotropic and anisotropic films. Furthermore, isotropic 6 vol. % films exhibited 1.6x the deformation of anisotropic films at the highest applied field (300 mT). These isotropic films were able to achieve deflections of 0.73 mm and 1.6 mm at 100 mT and 300 mT, respectively. Moreover, we characterized the morphology of magnetic particles from SEM cross section images of the optimal 6 vol.% isotropic and anisotropic films. While the isotropic films showed random dispersion of the nanoparticles in the matrix, the anisotropic ones confirmed preferential alignment of the nanoparticles along the magnetization direction. The magnetic hysteresis behavior of isotropic and anisotropic films was measured to visualize the difference in remanent magnetization between the two cases and a small but evident increase in magnetic anisotropy matched the particle arrangement of the anisotropic films.

To compare with the literature, identical MRE films were also fabricated utilizing soft iron microparticles. In comparison with the nanoparticle-based anisotropic MREs, at a field of 100 mT, the analogous microparticle-based films showed 25-30% lower deflection. The latter were only able to match the nanoparticle films' deflection at higher fields of almost 300 mT. This performance difference between nanoparticle and microparticle films was attributed to the increased anisotropic film stiffness resulting from the larger micrometer-size particles. Finally, the optimal nanoparticle-based isotropic MRE was utilized to create an enlarged programmable braille display which can be refreshed real time by actuating the deflection of specific buttons to construct different letters and words. In conclusion, this research showed for the first time the benefits of utilizing nanoparticles to engineer MREs with enhanced magnetomechanical response, enabling the realization of a reconfigurable haptic interface prototype with the potential for scalability and the promise of enabling numerous future haptic innovations.

9:00 AM SB08.04.04
A Monolithic Fabrication Strategy for Millimeter-Scale, Self-Sensing Actuators Hun Chan Lee, Nash Elder, Matthew Leal, Sarah Stantial and Sheila Russo; Boston University, United States

Advances in soft robotic technology helped to overcome many challenges in minimally invasive surgery by improving dexterity, flexibility, and safety. However, there are tradeoffs as well in using soft robots for surgical applications including complicated fabrication and assembly processes, low output force, poor controllability, and limited sensing functionality. The confined, tortuous workspace of minimally invasive surgery adds additional challenges, such as restricting the size of a robot to a millimeter scale and requiring a wide range of motion for navigation. Thus, the fabrication of these millimeter-scale soft robots becomes more delicate and convoluted, resulting in inconsistent fabrication outcomes. The manufacturing and assembly process becomes more onerous as the number of sensing and actuation elements increases. In addition, the control of these soft robots can be complicated due to the nature of their non-linear behavior, requiring computationally expensive control algorithms. Likewise, some aspects of mechanical performances (i.e., output force and torque) are limited due to the use of low elastic modulus materials. Bridging these gaps, we present the design, fabrication, and characterization of programmable composite actuators (PCAs). PCAs implement the concept of using an ionic solution as a working fluid for actuation and as a sensing medium for self-sensing. Unlike other soft robots, which require a manual assembly process to combine two discrete components, an actuator and a sensor, PCAs seamlessly integrate actuators and sensors into a single unit by embedding both self-sensing and actuation capabilities in a monolithic laminate structure. Leveraging a layer-by-layer fabrication method, PCAs are manufactured by stacking and bonding various types of films (i.e., rigid, flexible, soft, adhesive, and conductive films). PCAs include three components: 1) soft, inflatable Teflon balloons, 2) a rigid-flexible origami structure, and 3) conductive electrodes for self-sensing. The soft, inflatable balloons consist of adhesive films and Teflon films whose surface is chemically modified by using hydrogen plasma to promote adhesion. The Teflon films are selectively bonded to create multiple bellow-shaped actuation chambers. By fluidically inflating these chambers, the flat Teflon balloons can be transformed from 2D to 3D bellow shapes, producing motion. Similarly, the rigid-flexible origami structure is fabricated by selectively bonding rigid (i.e., fiber-reinforced epoxy laminate) and flexible (i.e., polyimide) films, and it surrounds the soft, inflatable Teflon balloons. Encompassing the soft, inflatable Teflon balloons, the origami structure helps to increase the output force of the actuator, and it mechanically programs the actuator to produce various types of motion and degrees of freedom in an actuator (i.e., extension, bending, and rotation). The conductive electrodes are composed of copper and graphene films embedded within the actuator to perform as a proprioceptive ionic sensor when the ionic solution is used as a working fluid. Thus, the position of the actuators can be sensed by measuring the change in impedance across the electrodes, which depends on the volume of the balloons. To further understand the performance of these PCAs, they are characterized in terms of the range of motion and output force. In addition, multiple PCAs are combined as a continuum robot to demonstrate their potential usage as a surgical robot for minimally invasive surgery.

9:15 AM SB08.04.05
A Self-Powered, Single Sensor for Both Dynamic and Static Pressure by Mimicking the Sensory Adaptation Behavior of Skin Ey-In Lee and Jin-Woo Park; Yonsei University, Korea (the Republic of)

The tactile sensor can be applied to various technical fields like electronic-skin technology, human-machine interface, prosthetics, and robotics. Particularly, the technology with feedback systems like haptic interfaces necessitates a sensitive, multimodal, flexible sensor for an actuator to give elaborate tactile sensations to the users. Pressure, one of the most important stimuli that the haptic interfaces should acquire, can be divided into two concepts: dynamic pressure and static pressure. To elaborately sense and apply the sensations of the pressure, it is crucial to detect the moment of the pressure application and whether the pressure application is continued. Like as mechanoreceptors of the human skin are divided into fast-adapting mechanoreceptors (Meissner corpuscle, Pacinian corpuscle) and slow-adapting mechanoreceptors (Merkel disc, Ruffini corpuscle), researchers integrate two sensors that detect dynamic and static pressure each into a single platform to discriminate the dynamic and static pressure. However, the integrated sensing system is inconsistent with the direction of the tactile sensing-related technology development that continues to develop as a system containing the sensing ability of various stimuli generated by the humans or external environment and the feedback control to interact with humans. While wearability and implantability of the system are developed for high compatibility with humans, a conventional integrated sensing system with batteries and signal processors is bulky, limits continuous operation with a fixed energy capacity, and restricts practical usage due to frequent charging. Accordingly, the integrated sensing system with energy issues and the volumetric problem is inadequate for human-linked technology. In this work, we propose a self-powered, single sensor with a compact structure using piezoelectricity and ionics as sensing mechanisms with mimicry of the sensory adaptation behavior of the human skin. Piezoelectricity is responsible for detecting dynamic pressure, and ionics is responsible for detecting static pressure and expressing the sensory adaptation behavior. Since the piezoelectric materials can only respond to dynamic pressure, we introduced the ions slower than the piezoelectric charges to sense the static pressure. Since the ions can hold the piezoelectric charges from moving to the electrode, they delay the charges from being measured by the instrument. The static pressure can be detected by analyzing a prolonged piezoelectric voltage output achieved from the introduction of the ions. We utilized the piezoelectric polymer, poly(vinylidene fluoride-*co*-trifluoroethylene) (P(VDF-TrFE)), and ionic liquid, 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) to achieve intrinsic mechanical flexibility and non-volatility of the sensing layer. Electrochemical impedance spectroscopy verified the stable sensor fabrication and the equivalent electrical circuit of the tactile sensor. Emulated systems based on EIS data proved the sensing mechanism and sensory adaptation behavior quantified by the decay constant. With sensory adaptation behavior, the sensitivity of the dynamic pressure increased about 4.4 times, and the sensitivity of the static pressure increased about 4 times. The tactile sensor with sensory adaptation behavior can detect the overlapped stimulus upon sustained pressure with higher sensitivity. The tactile sensor that can elaborately analyze the pressure and sense the overlapped stimulus is vital in a stimuli-flourishing environment where it is more important to detect newly applied stimulus than sustained one.

9:30 AM SB08.04.06
One Pot Multimaterial Photochemistries for Mechanical Gradients in Soft Wearable Tech Thomas Wallin; Reality Labs Research at Meta, United States

Seamless multimaterial construction, particularly joining soft, stretchable tissues with stiff, inextensible structures, is a common motif in animal physiology. Such continuous mechanical gradients remain challenging to reproduce in engineered systems as current resin chemistries typically result in a single fixed set of properties. As an alternative to single-property materials, we introduce a ternary sequential reaction scheme that produces multimaterials by profoundly altering the polymer microstructure from within a single resin composition. In this system, the photodosage during 3D printing sets both the shape and extent of conversion for each subsequent reaction. The different polymerization mechanisms of the subsequent stages allow our single photochemistry to exhibit a diverse range of soft (Young's Modulus, E ~ 400 kPa; ultimate elongation, dL/L0 ~ 300%) and stiff (E ~1.6 GPa; dL/L0 ~ 3%), providing the capability to match the mechanical properties of commercial polymers and biological tissues. Further, we successfully pattern photostable and mechanically robust modulus gradients (d[Er,stiff/Er,soft]/dx > 1000 mm-1) that exceed those found in squid beaks and human knee entheses. We demonstrate the ability to 3D print intricate multimaterial architectures by fabricating a soft, wearable braille display.

9:45 AM BREAK

SESSION SB08.05: Soft Matter I
Session Chairs: Matteo Bianchi, Charles Dhong, Marcia O'Malley and Tristan Trutna
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2012

10:15 AM SB08.05.02
Soft Haptics for Virtual Reality and Tele-Operation Applications Femke van Beek; Eindhoven University of Technology, Netherlands

Humans are experts at using soft touch to efficiently manipulate a vast range of objects in a variety of situations. In several application domains, rigid robotic solutions such as exoskeletons and vibrotactile gloves have been designed in an attempt to tap into this human potential. In our lab, we are exploring soft robotic solutions for creating more comfortable and more compelling haptic displays. With these displays, we hope to enable a soft touch in Virtual Reality and tele-operation applications. In this talk, I will present our work on design, control and attachment strategies of these soft displays. I will also discuss our recent perceptual experiments in which we directly compare task performance of humans wearing rigid and soft haptic feedback displays.

10:30 AM SB08.05.03
Programming Complex Shapes in Soft Electrically-Active Materials Nakhiah Goulbourne; University of Michigan–Ann Arbor, United States

Electrically-activated elastomeric materials hold great promise to bring alive the dream of autonomous life-like soft robots. Fast actuation of materials that match the compliance and rheology of biological materials could enable breakthroughs in realistically mimicking the rippling fin motion of a cuttlefish, the dynamic acrobatics and dexterity of the bat wing membrane during flight, and even simulate the contractions and twists of arteries and the left ventricle of the heart. There have been several soft materials proposed to date ranging from very soft hydrogels to shape memory polymers whose shape change can be triggered by heat, magnetic field, electric field, and light. Of the soft active materials investigated to date, dielectric elastomers have garnered significant interest due to their nontrivial and reversible fast deformations in response to an external stimulus. Another soft elastomer demonstrating large deformations are liquid crystal elastomers via light and thermal actuation near their phase transition temperature, and more recently via electric field when configured as a planar capacitor. We discuss programming complex three-dimensional shapes using soft electrically-active elastomeric materials by controlling the anisotropy and mode of electric activation. The programming is achieved by patterning contractile fibers and selective activation. We introduce a computational model for simulating the shape-changing phenomena. The model is based on a new constitutive formulation within a finite viscoelastic framework. Computational implementation using a finite element user-subroutine allows us to simulate the complex shape response. Several examples of the achievable 3D complex shapes are demonstrated.

10:45 AM *SB08.05.04
Soft Haptic Interfaces and Soft Surgical Robots Sheila Russo; Boston University, United States

Minimally invasive surgical (MIS) procedures, such as interventional flexible endoscopy, present several advantages to traditional surgery including shorter recovery time, less trauma, and lower risk of infections. However, MIS is more technically demanding for the surgeon, entailing limitations in visual (limited field of view, low spatial and chromatic resolution), motor (dexterity), and haptic (reduced perception and tactile information) functionalities.
This talk will highlight our recent work in the design, materials, manufacturing, and development of soft sensing technologies and wearable, textile-based, haptic interfaces that aim at restoring and amplifying sensor and haptic feedback directly to the surgeon's hand to facilitate navigation and improve safety during colonoscopy.
First, a new class of soft surgical robots (i.e., soft reactive skins) will be discussed. Soft reactive skins are thin, conformable robots with distributed sensing and actuation, that can be wrapped around traditional medical instrumentation to augment their functionalities. Our research group (the Material Robotics lab at Boston University) has explored these devices to sense and react to inputs like contact force, bending, shape, and bleeding during colonoscopy.
Second, our progress on soft robotic wearable haptic interfaces will be discussed. The talk will highlight our efforts in materials and manufacturing towards an ergonomic, lightweight, flexible, and comfortable-to-wear design. Through a user study, we assessed the mental workload and benefits of the haptic interface in a simulated colonoscopy scenario. The device is transparent while performing tasks, and could be worn and removed with minimal to no assistance.
The talk will conclude by discussing potential future applications of soft surgical robots and soft haptics in other minimally invasive surgical scenarios, like interventional bronchoscopy and endoscopic brain surgery.

SESSION SB08.06: Soft Matter II

Session Chairs: Matteo Bianchi, Charles Dhong, Marcia O'Malley and Tristan Trutna
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2012

1:30 PM SB08.06.01
Digital Light Processing 3D Printing Dielectric Elastomer Actuator for Haptic Device Peiwen Huang, Hongbo Fu and Pooi See Lee; Nanyang Technological University, Singapore

Haptic devices have attracted attention for application in automotive, telecommunication, braille communication, virtual reality, augmented reality, and medical healthcare. Dielectric elastomer actuators (DEAs), a kind of soft actuator based on electroactive materials, possess great potential for haptic devices because of the advantages of their lightweight, large displacement, fast response, and physical properties similar to skin. However, the force output generated by a single-layer DEA is limited, and can only be used in areas with high haptic sensitivity like the fingertips and the back of the hand. To expand the applicability, stacking multilayer DEA devices is a common approach to obtain larger actuation performance but can be tedious in preparation and are often low in device stability. Moreover, multiple actuators with various shapes and sizes are needed to be integrated into haptic devices for different applications, further extending the fabrication time and incurring difficulty in their fabrication. Hence, there is a compelling need for printing or molding processes that could address these challenges.
In our work, digital light processing (DLP) 3D printing is introduced to print the dielectric elastomer structure and realize the fast fabrication of multilayer cylinder DEAs. The printable elastomer resin is prepared by mixing epoxy aliphatic acrylate (EAA) and an aliphatic urethane diacrylate (AUD)-based material. The printed elastomer has a high dielectric constant of 7.3 and Young's modulus of 800 kPa at 10% strain. The DEAs can be fabricated by injecting carbon grease as the compliant electrodes into the designed cylinder channels made from the resin and sealing the ends with silver paste. The final cylinder DEA has 1 cm in diameter and 1 cm in height. The freestanding multilayer DEA has a blocked force of 120 mN and a free displacement of 50 µm under a voltage of 6 kV. The DEA can also maintain about 40 % actuation performance under a 100 Hz AC voltage, enabling a vibrotactile response perceivable through different body parts other than fingertips. In addition, the DLP 3D printing process allows multiple DEA devices to be prepared at the same time, which largely shortens the manufacturing time and enables the integration of multiple haptic devices. Overall, this process offers new opportunities for the development of haptic devices based on dielectric elastomer actuators.

1:45 PM *SB08.06.02
Stimuli-Responsive, Morphing Liquid Crystal Elastomer Structures and Electronics for Intelligent Systems Xueju Wang; University of Connecticut, United States

Intelligent systems with capabilities of sensing, actuation, and closed-loop control are promising for many applications such as augmented reality, rehabilitation, and soft robotics. In this talk, I will present our work on stimuli-responsive materials, structures, and electronics toward this effort. I will start with our study on liquid crystal elastomers (LCEs), a type of smart material that has capabilities of soft elasticity and large, reversible shape-changing behaviors due to liquid crystal-polymer network couplings. Through introducing a versatile mechanical programming technique, previously inaccessible reconfigurable three-dimensional structures made of LCEs and their magnetic composites are created and their potential applications in soft robotics are demonstrated. I will further present our facile strategy to locally tailor the stiffness and the morphing behavior of these reconfigurable LCE structures by harnessing molecular-material-structure interactions, i.e., locally controlled mesogen alignment and crosslinking densities. Selective photopolymerization of spatially aligned LCE structures yields well-controlled lightly and highly crosslinked domains of distinct stiffness and selective permanent mesogen programming, which enables various previously inaccessible stiffness-heterogeneous geometries, as demonstrated in diverse morphing LCE structures via integrated experimental and finite element analysis. Furthermore, reprogramming of the non-photopolymerized regions allows for reshaping, as shown in a sequentially shape morphing LCE rod and "face". The heterogenous morphing LCE structures have the potential for many applications including in artificial muscles, soft robotics, and many others. In addition, a simple strategy for creating 3D thermochromic LCE structures with synchronous shape-morphing and color-changing capabilities for biomimetic robotics will also be introduced. I will conclude my talk with soft sensing devices for in situ pressure measurements, beyond the actuation capabilities enabled by LCEs. The introduced actuation and sensing strategies and concepts are promising for many intelligent platforms.

2:15 PM DISCUSSION TIME

2:30 PM BREAK

3:00 PM *SB08.06.04
Haptic Biomaterials as Tools for Understanding and Manipulating the Tactile Sense Darren J. Lipomi; University of California, San Diego, United States

Most clinicians would not trade their sense of touch for even the most powerful imaging tool or surgical robot. Indeed, touch has played a critical role in diagnosis and treatment since prehistory, and is central to most branches of internal medicine. Clinicians rely on touch for all procedures performed by hand, e.g., tracheotomy, venous catheterization, routine orthopedic, obstetric, and urological procedures, most surgeries, and many forms of physical therapy. Despite the ubiquity of touch in medicine, haptic technologies are underdeveloped. For example, plastic and rubber models do not come close to mimicking the feel of biological tissue, and they cannot be reconfigured dynamically in a training environment. In robot-assisted surgery, limited forms of kinesthetic feedback have so far not led to improved patient outcomes. In telehealth appointments for individuals located in urban and rural "healthcare deserts"—or for most patients during a pandemic—medical touch is completely absent. Nevertheless, if tactile interaction with a high degree of realism were possible in these scenarios, the value of the technology which enabled it would be immense.

To implement feedback of a visual and auditory nature in a medical context is a simple matter: a digital display can render nearly any image and a loudspeaker can render nearly any sound. Implementing tactile feedback, on the other hand, is far more difficult. Whereas vision and hearing are localized to the eyes and the ears, touch and proprioception involve a range of structures distributed through the body. The reason that virtual medical training and remote care do not include touch is that existing haptic systems are incapable of recapitulating the surface texture and mechanical response of biological structures. This deficiency arises because most haptic systems rely on off-the-shelf mechanical actuators, which are limited to vibration, tingling, and other percussive effects: i.e., inaccurate proxies for sensations produced by soft, hydrated objects. In other words, these devices cannot mimic the texture, softness, wetness, thermal conductivity, adhesion, tack, and other near-surface properties of biological tissue.

Here, we describe several ways in which our group has explored the ways in which materials science can be used to understand and manipulate the tactile sense for applications in healthcare, VR, AR, and assistive devices. In this talk, I will discuss our major outcomes from this area of research, including (1) the development of a new type of conductive polymer that conforms to the skin and can be used to deliver haptic cues to the wearer; (2) elucidation of how the details of contact with the fingertip to materials surfaces contribute to the sense of softness, as well as (3) design rules for haptic surfaces that survive human contact in the real world.

3:30 PM SB08.06.05
Easy Fabrication of Stretchable Waveguide for E-skin Applications Lionel Fliegans, Sylvain Blayac and Marc Ramuz; MINES Saint-Étienne, IMT, France

For many years, a strong research interest has been oriented towards soft electronics for artificial skin applications. However, one challenge with stretchable devices is the limited availability of high performance stretchable electrical conductors and semiconductors that could remained entirely stable while stretched. Moreover, examples of such electronic skin embed excess amount of wires for addressing each sensors (pressure or temperature) in the conventional matrix structure.

Here, we present a new process for fabricating artificial skin consisting of an optical waveguide architecture allowing wide range of sensitivity to pressure [0 to 1KPa - 0.2 kPa $^{-1}$], strain, shear and/or temperature variation [20 to 100°C], in multi-level ultra-stretchable network. The manufacturing process allows for a simple and low cost design of 100% low Young's modulus polymer [<1GPa].
This new type of stretchable optical sensor is highly robust, transparent and present a large sensing area [10 x 10 cm^2] with limited amount of wires. Thus, this optical artificial skin presents far superior mechanical properties compare to current electronic skin.

3:45 PM *SB08.06.06
Transparent Soft Cutaneous Haptics Amir Firouzeh, Ayana Mizutani and Herbert R. Shea; Ecole Polytechnique Federale de Lausanne, Switzerland, Switzerland

Having clickable buttons that appear and disappear at will on any surface transforms how we interact with objects using our fingertips, be they touchscreens, furniture or a pair of binoculars. We report soft, compliant electrostatically driven actuators that pop up from a flat state to a curved shape in a few milliseconds and provide an intuitive click-like response to a user's fingerpress. The devices are completely transparent, allowing them to be mounted on an LCD or OLED display, while still using the multitouch finger position sensing of the display. The devices are HAXELs, a type of electrostatic zipping actuator that displaces fluid to a central elastomer region, creating a raised bump, when a high electric field is applied to electrodes at the devices' periphery. For a 2 cm x 2 cm device, we have strokes of 1.8 mm, and a holding force of 3 N, providing a haptic feel very much like a mechanical keyboard. The arrays are flexible, and can this be used on curved surfaces. Optical transparency is achieved using ITO for the electrodes and transparent polymers and oil for the other layers. We will report device fabrication, scaling, and use for cutaneous haptics, as well as self-sensing, illustrating several use cases.

4:15 PM SB08.06.07
Characterizing Acoustic Wave Propagation in Hydrogels Using Transient Grating Spectroscopy Melanie C. Adams, Allison Chau, Angela A. Pitenis and Bolin Liao; University of California, Santa Barbara, United States

Acoustic and thermal energy transport is critical for a wide range of applications, including biomedical diagnostics (e.g. ultrasound), renewable energy production, and building thermal management. Improving the performance of these technologies requires precise tailoring of acoustic and thermal energy transport, which remains a fundamental challenge. Understanding how to tune these materials and study them in real-time requires methods that can be used in varied environmental conditions. Hydrogels are of interest because they are easily fabricated, tunable, and have environment specific behavior. Our research investigates using transient grating spectroscopy, a method that employs acoustic wave signatures, to mechanically characterize hydrogels and other inhomogeneous materials. We provide a systematic approach across a range of polymer groups, to decompose the effects of crosslinking, swelling, and/or entanglements on Rayleigh wave speeds, which can then be related to a material's elastic modulus. Transient grating also presents a method for dynamic response measurements of hydrogels. Traditional characterization methods, such as indentation, result in large discrepancies in measurements, which indicates that mechanical properties of hydrogels differ significantly in dynamic and static conditions. These differences are the first step to developing models for the direct contribution of poroelasticity and viscoelasticity on hydrogel behavior. This project will show how we can model and subsequently develop hydrogels with the mechanical properties necessary for our desired applications. This work was supported by the UCSB Materials Research Science and Engineering Center (MRSEC) of the National Science Foundation under award No. DMR-1720256 (IRG-3). The development of the transient grating spectroscopy at UCSB is supported by a DURIP grant from the U.S. Army Research Office under the award number W911NF-20-1-0161. Allison Chau acknowledges support from the NSF Graduate Research Fellowship Program under Grant No. 1650114. Angela Pitenis acknowledges funding support from the NSF CAREER award (CMMI-CAREER-2048043).

4:30 PM *SB08.06.08
The Patterns of Skin Deformation That Encode Friction Michael Wiertlewski; TU Delft, Netherlands

Having a secured grip on an object fundamentally depends on controlling the amount of frictional force. Our sensorimotor system excels at estimating the frictional strength of the contact to anticipate the object's slippage, which in turn enables our remarkable dexterity. But how the tactile information about the state of friction is encoded within the mechanical deformation of the fingertips? Using a new setup that can image and modify friction in real-time, we show using that the skin undergoes specific patterns of deformation from the moment the skin first enters in contact with a surface all the way to sliding. The presence of these patterns of deformations is confirmed by a parsimonious model of the skin which captures the interplay of the visco-elastic nature of the skin and the frictional boundary layer.
Our finding suggests that the perceptual system uses these patterns of deformation as matched filters to rapidly estimate the frictional state, independently of knowing whether the contact has a large or small amount of friction.

SYMPOSIUM

April 10 - April 25, 2023

Symposium Organizers
Lihua Jin, University of California, Los Angeles
Jiheong Kang, Korea Advanced Institute of Science and Technology
Jia Liu, Harvard University
Zhiyuan Liu, Chinese Academy of Sciences

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* Invited Paper
\+ Distinguished Invited

SESSION SB09.01: Self-Healing Bioelectronics
Session Chairs: Lihua Jin, Jia Liu and Zhiyuan Liu
Monday Afternoon, April 10, 2023
Moscone West, Level 3, Room 3000

1:30 PM SB09.01.01
Exploiting Supramolecular Chemistry for Self-Healing Organic Semiconductors Megan Westwood, Peter Finn, Lewis M. Cowen and Bob C. Schroeder; University College London, United Kingdom

Material degradation is a primary concern to every material scientist and engineer, not only does degradation lead to failure, but results in the need for repair – a very costly endeavor. It is therefore of interest to develop self-healing materials that will make maintenance redundant. As opposed to inorganic semiconductors, organic semiconducting materials have low Young's moduli, which makes them ideal to be used in wearable electronic devices, which can be directly applied to the human skin.[1] Wearable electronics, however, are particularly susceptible to environmental stresses, such as mechanical damage, chemical attack, temperature fluctuations, and radiation damage. This constant stress can lead to the degradation of the chemical structure, resulting in the degradation and ultimately the loss of the material's physical properties.

Herein, we will discuss our approach to compensate for the loss of physical properties, by developing intrinsically self-healing polymers. This was achieved by exploiting supramolecular chemistry concepts such as intramolecular hydrogen bonds.[2-4] In order to gain a deeper insight into the effects of the hydrogen bonding on the viscoelastic, as well as on the electrical properties of the organic semiconductors, we developed two sets of materials; (1) a conjugated polymer with hydrogen bonding functionality and (2) a composite material comprised of a conjugated polymer embedded in a self-healing polysiloxane matrix. We will discuss the effects of the different approaches on the charge transport and self-healing capabilities and outline how we can take advantage of the observed differences to tune not only the electronic but also the self-healing and mechanical properties of the material depending on the field of application and its specific requirements.

[1] J. Y. Oh & Z. Bao, Advanced Science, 2019, 6, 1900186.
[2] J. Y. Oh et al., Nature, 2016, 539, 411-415
[3] A. Gasperini et al., Macromolecules, 2019, 52, 2476-2486.
[4] J. Ma et al., Nature Communications, 2021, 12, 5210

1:45 PM SB09.01.02
Autonomous Self-Recognition and Healing in Multilayer Soft Electronics Using Orthogonal Dynamic Polymers Christopher B. Cooper and Zhenan Bao; Stanford University, United States

Can we design multilayer electronics that can spontaneously heal themselves after damage? Having this functionality would protect electronic devices from traditional "wear and tear" damages, improving product lifetime, as well as from intense mechanical damage that would otherwise cause product failure. Compared to the self-healing of a single polymer composite, the self-healing of complex, multilayered devices requires simultaneous healing between multiple layers with distinct functions. Currently, this is achieved by manual alignment of the layers after damage. In this work, we demonstrate a multilayer electronic device that can autonomously re-align and heal after damage using orthogonal dynamic polymers. We show that dynamic polymers with controlled orthogonality exhibit significant and predictable variations in interfacial healing dynamics, allowing for autonomous self-recognition. When misaligned after damage, these multilayer structures possess surface tension gradients that drive directional chain diffusion to enable realignment. We experimentally characterize the interface between different orthogonal dynamic polymers and compare our results to coarse-grained molecular dynamics simulations and self-consistent field theory. Using these polymers, we prepare conductive and high dielectric composites to create thin film capacitors that can autonomously heal with thicknesses below 100 microns. We also demonstrate macroscopic self-assembly of these polymers after damage using magnetic composites. This work provides the first proof-of-concept demonstration of autonomously self-healing multilayered devices and opens a pathway for future autonomous self-assembly in multi-component dynamic materials via pattern recognition.

2:00 PM SB09.01.03
Tough, Self-Healing and Somatosensitive Soft Robot Jaehoon Jung and Jiheong Kang; Korea Advanced Institute of Science & Technology, Korea (the Republic of)

The physically compliant and gentle interactivity of soft robots has opened new possibilities of robot tasks like dexterous manipulation, soft material grasping, and human-interactive applications. However, the softness causes mechanical vulnerability to damage like puncture, tendon cuts, degradation, and delamination. To overcome the vulnerability, tough and self-healing elastomers are needed. However, it was very difficult to design tough and self-healing materials for somatosensitive soft robots due to the trade-off relationship between self-healing efficiency and mechanical toughness.
Here, we report a new molecular design of a self-healing elastomer with high mechanical toughness, and its application for a tough self-healing somatosensitive soft robot system. The designed polymer chain has two kinds of hydrogen bonding from isophorone diisocyanate (IP) and 2-ureido-4-pyrimidone (UPy) for self-healability and toughness respectively. Along with the autonomous self-healing at room temperature, the designed polymer shows unprecedented high toughness and high fracture toughness, which protects the soft robots from damage by sharp objects. The self-healing somatosensory system is composed of various stretchable self-healing sensors including temperature, pressure, damage and strain sensors. These somatosensory systems not only allow us to know the unknown environment but also recognize unexpected damage and respond immediately. The first demonstration of the tough self-healing somatosensitive soft robot would allow the autonomous soft robot system to be used in much more dynamic environments for a long time.

2:15 PM *SB09.01.04
Gold Nanowire-Based Electronic Skins and Tattoos Wenlong Cheng; Monash University, Australia

Sensitive, specific yet multifunctional tattoo-like electronics are ideal wearable systems for health monitoring anytime anywhere because they are virtually becoming parts of Human skins offering burdenless "unfeelable" wearing experience. Here, I will present our skin-like, multifunctional gold electronic skins and tattoos using standing enokitake mushroom-like vertically aligned nanowires. Among various materials of choices, gold has advantages of biocompatibity, chemical inertness, facile synthesis/Surface functionalisation and band-gap-matching with a lot of semiconductors materials. In this talk, I will briefly discuss our gold nanowire-based soft biosensing platform for applications in remote health monitoring.

2:45 PM SB09.01.05
Self-Healable and Stretchable Electronic Materials with Liquid Metal Composites Ravi Tutika[1], Aaron Haake[2], Gwyneth Schloer[1], Eric Markvicka[2] and Michael D. Bartlett[1]; [1]Virginia Tech, United States; [2]University of Nebraska–Lincoln, United States

Polymeric electronic materials with liquid metal (LM) droplets can enable new generations of self-healing soft electronics and robotics that can sense, stimulate and control biological systems. However, techniques to control local composite microstructure, which ultimately governs material properties and performance, is lacking. Current approaches to program LM droplet microstructure requires specific materials, lack spatial control, and only allow for programming of inclusions along a single axis. Further, integrating these polymeric electronic materials with current diverse rigid electronic components and materials is a significant challenge due to lack of adhesion control. Here, we introduce a new DIW 3D printing strategy to achieve on-demand programming of LM-composite microstructures throughout a printed part. This on-demand spatial control of LM microstructure (i.e., shape, orientation, and connectivity) has not been demonstrated with currently available casting, stretching, or patterning approaches. By systematically controlling the printing process conditions and LM droplet size, we can transform the initially spherical LM droplets into highly elongated and orientated ellipsoids on demand at any location with very high aspect ratios ≤ 40. The rapid formation of the surface oxide locks these droplets into the programmed shape and allows for systematic control of the LM droplet microstructure. The printed materials are soft (modulus < 200 kPa), highly deformable (>600 % strain) and highly thermally conductive. The initially isolated LM droplets can also be transformed into a connected network, enabling local creation of insulating or electrically conductive regions using a single ink and manufacturing system by controlling the process conditions. Additionally, using a chemical anchoring technique, the fracture energy can be enhanced up to 7800 Jm^{-2} (100x relative to untreated surfaces) which can further be tuned by controlling the liquid metal microstructures. The LM composite system and DIW 3D printing strategy will enable intrinsically stretchable electronic materials with tough bonding characteristics which provides opportunities to address the challenges in the integration of wearable electronics, implantable devices, and artificial skins with natural and engineered soft biological systems.

SESSION SB09.02: Implantable Bioelectronics I

Session Chairs: Lihua Jin, Jiheong Kang, Jia Liu and Zhiyuan Liu
Tuesday Morning, April 11, 2023
Moscone West, Level 2, Room 2022

10:30 AM SB09.02.01
Conformable Wireless Power Transfer System for Implantable Bioelectronics Based on Internal Ion-Gated Electrochemical Transistors Alexander N. Ranschaert and Dion Khodagholy; Columbia University, United States

Implantable flexible bioelectronics allow for high resolution recordings in animal and human models, which is needed for effective monitoring and clinical treatment. Currently, such implanted devices are powered using batteries, supercapacitors or silicon-based wireless solutions that are often bulky, non-biocompatible, non-rechargeable and require a rigid encapsulation. Furthermore, the threshold voltage of silicon-based field effect transistors lies close or beyond hydrolysis potentials, limiting the applicability in biological environments. In this work, we present a fully conformable inductive wireless power transfer system. The receiver coil and rectifier are integrated in the same substrate resulting in a compact design more suitable for surgical implantation. To accomplish this, enhancement mode internal ion-gated organic electrochemical transistors (e-IGTs) are employed, which can work at speeds beyond the limitations imposed by ion drift and mobility by creating local ion reserves inside the channel bulk. This ensures a large design freedom to optimize the operational frequency of the system to MHz ranges and achieve a high efficiency. We show that by carefully controlling the polyethylenimine (PEI) de-dopant concentrations and transistor geometry, the diode characteristic of the e-IGTs can be fine-tuned to avoid the point of hydrolysis and the power transfer efficiency can be optimized. A conformable high-density prototype is then fabricated and tested in-vivo in a freely moving rat to confirm that an implanted device can be efficiently powered over an extended period. This proves that IGTs are extremely versatile with respect to their applicability in bioelectronic devices. The designed wireless power transfer system is attractive in the context of powering bioelectronic devices, such as neural implants to treat epilepsy through responsive neurostimulation. Therefore, IGT-based devices are a promising platform for future high-performance neural implants.

10:45 AM SB09.02.02
Soft, Multichannel, Subcutaneous Electrical Junction for Long Term Ohmic Contact with Implantable Bioelectronics Hyung Joon Shim and Dion Khodagholy; Columbia University, United States

Implantable bioelectronics are becoming an integral part of modern medicine, from drug delivery systems such as insulin pumps to responsive neural interface devices. To minimize the adverse effects of such implants, all components of the device should be soft and conformable, including the access port to the outside world. However, conventional wires or connectors require a permanent transcutaneous portal which increases the risk of infection, inflammation, and mechanical disruption. For this reason, wireless communication is preferred to allow complete implantation of the device without tissue-extruding components. However, the complexity of wireless communication combined with the associated rigid radiofrequency electronics inevitably result in bulkier and higher power consumption implants with limited applicability. Here, we developed a soft, subcutaneous, multichannel polymeric junction as an alternative approach to provide on-demand ohmic contacts with implants for exchange of data and power. Insertion of a patterned needle into this self-healable connector enables transmission of power and multi-channel, high-speed data. When not in use, the connection can be easily removed completely with no exposed components. This access port is made out of a three-dimensional conductive polymer structure sandwiched in an insulating stretchable polymer matrix. The healable properties of the polymers allow repetitive connections for long-term use. The electrical as well as mechanical properties of the synthesized materials were analyzed. The feasibility of the access port for implantable bioelectronics was validated with long-term chronic implantations in freely moving rodents to exchange power and neurophysiological data at the resolution of single neurons. We anticipate this approach will have a broad applicability to a wide range of implants and offer possibilities to improve patient quality of life.

11:00 AM SB09.02.03
Using Electric Fields to Stick Hydrogels to Tissues—A Simple Way to Perform Suture-less Surgical Repairs Leah K. Borden[1,2] and Srinivasa R. Raghavan[1]; [1]University of Maryland, United States; [2]Massachusetts Institute of Technology, United States

We demonstrate electroadhesion, i.e., adhesion induced by an electric field, between cationic hydrogels, animal and plant tissues [1]. When gel and tissue are placed under an electric field (DC, 10 V) for 20 – 60 s, the pair strongly adhere, and the adhesion persists indefinitely thereafter. Applying the DC field with reversed polarity reverses the adhesion. Electroadhesion works with tissues of many mammals (cow, pig, chicken, and mouse), and is especially strong in the case of the aorta, cornea, lung, and cartilage. Electroadhesion is also achieved with plant tissues such as with carrot, onion and strawberries. Only cationic gels can be electroadhered to tissues, which suggests that the tissues have anionic character. These findings show the potential for using electroadhesion in surgery while obviating the need for sutures or staples. Advantages include the ability to achieve adhesion on-command, and moreover the ability to reverse this adhesion in case of error.

We then explore variables that contribute towards adhesion in these diverse types of tissues. For instance, the higher the fraction of anionic polymers (proteins and/or polysaccharides) in the biological material, the higher the electroadhesive strength. Interestingly also, because tissues often have anisotropic structure, adhesion by electroadhesion can be strong in one tissue orientation, but weak or non-existent in the perpendicular orientation. Last, we see that electroadhesion occurs in both soft and hard animal and plant tissues.

[1] L. K. Borden, A. Gargava and S. R. Raghavan
Reversible Electroadhesion of Hydrogels to Animal Tissues for Suture-less Repair of Cuts or Tears.
Nature Communications, 12, 4419 (2021)

11:15 AM SB09.02.04
Smart Multi-Sensory Capsule for Simultaneous Location Tracking and Inflammation Detection Sarath Gopalakrishnan, Sotoudeh Sedaghat, Rithu Thomas, Akshay Krishnakumar, Sina Nejati and Rahim Rahimi; Purdue University, United States

Inflammatory bowel disease (IBD) has gained a lot of attention in recent decades as it is increasingly prevalent in Western countries and steeply emerging in developing countries. IBD affects 7 million people worldwide and is characterized by chronic inflammation of the gastrointestinal tract (GI) which is manifested as Crohn’s disease, ulcerative colitis, and colon cancer if remained untreated. Existing methods widely used in hospitals include a combination of endoscopy, colonoscopy, and imaging studies. Endoscopy and colonoscopy are invasive and expensive and require a technician’s assistance. Similarly, MRI and CT scans require bulky equipment and manual assistance and cannot be made portable or automated.

To address the issues envisaged by these benchtop systems, ingestible capsules have emerged as an ideal portable wireless in-situ monitoring platform to perform around-the-clock measurements using contactless readout units. Although the existing ingestible capsules have gained popularity as miniaturized devices, the state-of-the-art active capsules are designed to sense a single parameter either for location tracking or inflammation detection but not for both parameters simultaneously. Single parameter sensing significantly limits traceability, targeted detection, and accuracy of measurements. Furthermore, the active capsules that contain electronic modules lack suitable sensor interfaces that can establish good contact with the tissues and biocompatible packaging to prevent leakage from the batteries and seepage into the electronics. To address these challenges, we report a multi-sensory smart capsule that can perform both targeted detection of inflammation using Oxidation Reduction Potential (ORP) sensing as well as location tracking of the device inside the GI tract using pH monitoring.

The device consists of a compartmentalized sensor interface, an electronic module, and a biocompatible encapsulation. The sensor interface consists of three compartments which include a pH sensing unit, an ORP sensing unit, and a common reference unit. The pH sensing unit is manufactured by dispensing carbon paste mixed with pH-sensitive ionophores. The ORP sensing unit is formed by dispensing carbon paste sensitive to redox reactions in the environment. The reference unit is made by mixing KCl particles, polyvinyl chloride, and cyclohexanone and is used for both pH and ORP sensors. This multi-sensory compartment is interfaced with the electronic module inside the capsule through reflow soldering. The electronic module consists of a microcontroller unit powered by batteries, separate buffer circuit boards for performing accurate potentiometric readings from the pH and ORP sensors, and an antenna to wirelessly transmit the collected data to an external reader. This heavily miniaturized electronic module of diameter 8 mm is secured inside a biocompatible 3D printed housing of outer diameter 9.5 mm and length 2.5 cm to prevent leakage and seepage.

To investigate the performance of the multi-sensory capsule, extensive characterizations are conducted on the pH and ORP sensors individually as well as collectively. A systematic study reveals that the sensors demonstrate the capability to detect pH within the range of 1-8 and ORP within the range of -500 mV to +500 mV. The capsule can provide successful passage through the GI tract at a polling rate of 30 min with an average power consumption of 110 μAh. As a proof-of-concept, we perform ex-vivo characterization on pig tissues to demonstrate the specificity, power consumption, and traceability of the capsule in a GI-tract surrogate environment. The multi-sensory smart capsule presented here provides a new avenue in addressing the emerging need for accurate IBD detection using a portable, wireless system and can be a successful alternative to the existing medical equipment.

11:30 AM SB09.02.05
4D Printing of Biomimicking Elastomers with Digital Light Processing (DLP) for Personalized Biomedical Device Fabrication Alireza Mahjoubnia and Jian Lin; University of Missouri-Columbia, United States

A real challenge to improving human health and quality of life is the gap between the growth in personalized medicine demand and the lack of cutting-edge biomedical technologies. The fabrication of complex medical devices that could respond to stimulation by biological signals implanted through minimally invasive surgery is facilitated by the innovative and promising 4D printing technique, which can be utilized to simulate numerous dynamic processes of living tissues. However, the 3d printing of biocompatible shape memory polymers (SMPs) that is frequently used produces structures with low printing resolution, unsuitable mechanical properties (relatively low toughness), and undesired transition temperatures (T_{trans}), which complicates implantation procedures. Herein, we demonstrate 4D printing of SMP poly(glycerol dodecanoate) acrylate (PGDA) and Poly(acrylic acid) (PAA) with a T_{trans} in a range of human body temperature(~37°C), making it appropriate for maintaining programmed shape at the room temperature and then shape deployment within the physiological temperature. Introducing the PAA network to PGDA has dramatically increased the toughness of the resulting PGDA-PAA elastomer, while the double crosslinked network has improved its chemical stability. In addition, Young's modulus (E) (40-170 MPa) and toughness (10-20 MJ/m^3) of the printed structures can be decreased by 90 and 25 times, respectively, due to the phase transition of PGDA over its T_{trans}. These mechanical properties make the implantation process more straightforward as it has shown enough stiffness to maintain the programmed shapes when used at room temperature. The low E above T_{trans} will make shape reprogramming easy. The drastic self-driven change of mechanical properties enables printed structures to mimic the natural tissue and maintain robust properties under cyclic deformations suitable for cardiovascular applications. Moreover, the pre-PGDA/Acrylic acid resin used as the ink for digital light processing (DLP) printing possesses suitable rheological properties to allow for the fabrication of a variety of high-resolution complex 3D structures such as "boat," "diamond," and "human hand," with the printing speed of 25-100 mm/h depending on model geometry, and slice thickness. Although printing tubular structures is challenging due to the over-curing of the residual resin inside the channel in vat photopolymerization (VPP)-based 3D printing techniques, we have been able to print sub-millimeter hollow tubes with a wall thickness of 200 mm. The printed 3D structures show shape memory properties, including a large fixity ratio of 98% at room temperature and a significant recovery ratio of 100% at 37°C. Furthermore, cell studies have shown cell viability of over 90%, proper attachment, and proliferation of cells over printed materials. Finally, Abdominal Aneurysm and Left Atrial Appendage were chosen as the target diseases. Devices were individually designed and printed for defects scanned from animal models and tested both in vitro and in vivo. The implantation of personalized devices demonstrated the geometrical and mechanical adaptivity of the printed constructs. This newly developed PGDA-PAA SMP-based 4D printing technology has the potential to pave a new route to the fabrication of shape memory scaffolds for personalized biomedical applications.

SESSION SB09.04: Poster Session I
Session Chairs: Lihua Jin, Jia Liu and Zhiyuan Liu
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SB09.04.01
Electropolymerized Organic Mixed Ionic-Electronic Conductors Arnel Besic and Connor G. Bischak; University of Utah, United States

Organic mixed ionic electronic conductors (OMIECs) are conjugated polymer systems that conduct both ions and electrons. They are promising materials for biosensors, neuromorphic computing platforms, and energy storage devices. An obstacle for these new materials is the lack of understanding of the fundamental processes that underlie operation, namely the coupled dynamics of ion motion, electron transport, and structural changes. This work presents the electropolymerization and characterization of thiophene-based polymers and copolymers. One advantage of electropolymerized materials is that they do not require bulky side chains to dissolve in organic solvents, allowing them to hold more charge per volume. Using electropolymerization, we synthesize several polythiophenes with different side chain chemistries. We investigate ion injection kinetics in these materials using spectroelectrochemistry and find that injection kinetics depend on the identity of the electrolyte. We also characterize their morphology with atomic force microscopy (AFM) and scanning electron microscopy (SEM). Electropolymerized OMIECs may play an important role in the advancement of OMIEC-based technologies due to their unique morphologies and ease of synthesis.

5:00 PM SB09.04.02
Switching Characteristics Enhancement of L-Tryptophan-Based Resistive Random-Access Memory by Plasma Treatment for Bio-Implantable Electronics Moon Ho Lee, Jong Bin An, Seok Gyu Hong and Hyun Jae Kim; Yonsei University, Korea (the Republic of)

Because the COVID-19 pandemic spreads globally, interest in non-face-to-face treatment and bio-implantable electronics has increased. Unlike conventional electronic devices, which are rigid and have harmful properties to the body, bio-implantable electronics must have features that are flexible and harmless to the body. In addition, bio-information real-time sensing is essential for bio-implantable electronics. Among the various components of bio-implantable electronics, such as integrated circuits, displays, and batteries, a non-volatile memory storage device that can maintain data even in the absence of electrical power is one of the most important components. Due to its fast switching speed, simple structure, low power consumption, and low cost, resistive random-access memory (ReRAM) is one of the most promising non-volatile memory devices. However, an inorganic ReRAM has disadvantage such as relatively high fabrication cost and high temperature processes. To overcome these disadvantages, many biocompatible ReRAM devices composed of organic materials such as chitosan, egg albumen, sericin, glucose have been studied.

In this study, L-tryptophan, one of the essential amino acids that humans must ingest, was used as the switching layer of the ReRAM device. L-tryptophan is contained in foods such as milk, cheese, eggs, fish, and peanuts, and it is a precursor to the serotonin and melatonin, which are crucial for preventing insomnia, obesity, and depression. Because L-tryptophan is one of the essential amino acids that humans must ingest, it has been proven to be biocompatible property, thus it should be appropriate to be used as a switching layer material in bio-implantable ReRAM devices. In addition, for excellent memory characteristics the L-tryptophan-based ReRAM device, O_2 plasma treatment was performed prior to top electrode deposition. Through the following process, L-tryptophan-based ReRAM was fabricated. First, 2 × 2 substrates of heavily doped p-type silicon were cut to size. Second, L-tryptophan film was deposited at room temperature using the spin coating method on a cleaned silicon substrate. A 2 wt % L-tryptophan solution was synthesized by dissolving L-tryptophan powder (Sigma-Aldrich) in DI water. Before the top electrode deposition, an O_2 plasma treatment was performed under condition of 100 sccm, 50 W, and 10 min. Finally, a 150-nm-thick aluminum (Al) top electrode was deposited using an electron beam evaporator via a shadow mask.

In general, the resistive switching mechanism of ReRAM is attributed to the migration of oxygen ions in the interface oxide layer created between the top electrode and the organic material. We expect that hydroxyl functional groups in L-tryptophan react with the Al top electrode through redox reactions and the formation of conductive filaments because of oxygen ion migration at the interface between Al/L-tryptophan. Also, O_2 plasma treatment can increase the extra available oxygen ion in the switching layer of ReRAM. To increase these oxygen ions, we confirmed the switching characteristics change of L-tryptophan-based ReRAM after O_2 plasma treatment. The set and reset processes of non-treated and plasma-treated L-tryptophan-based ReRAM are performed at 2.7 V, -3.8 V, and 3.0 V, -2.9 V, respectively. At a read voltage of 0.2 V, plasma-treated L-Tryptophan-based ReRAM exhibited an improved resistive switching window from 10^4 to 10^6, defined as the ratio of high and low resistive, compared to non-treated L-tryptophan-based ReRAM. High-resolution transmission electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS) analyses were performed to investigate the aforementioned Al oxide formation mechanism between the Al top electrode and L-tryptophan interface. Based on its superior switching characteristics, we confirmed that plasma-treated L-tryptophan-based ReRAM could be a candidate for bio-implantable electronics.

5:00 PM SB09.04.03
Photothermal Self-Healing, Magnetically Aligning Wearable Sensor System Jung Wook Kim and Jeong Sook Ha; Korea University, Korea (the Republic of)

Self-healing functionalities are studied actively in fields of stretchable electronics applications to improve the device lifespan, to gain economic feasibility, and ensuring environmental friendliness. However, the synthesis of high-efficient healing materials and specific application of these materials to actual devices are still in progress. In this abstract, we report on the fabrication of magnetic-aligning, light-responsive self-healing devices based on a custom-synthesized polyurethane(PU). Light-responsive self-healing PU was synthesized by reacting poly(tetramethylene ether) glycol, aminopropyl-terminated PDMS and aniline trimer. Aniline trimer inserted PU showed high photothermal property, increasing its temperature over 150°C when 808nm NIR laser is irradiated for several minutes. The glyoxime bond in PU chain dynamically regenerated when heated through NIR laser irradiation, exhibiting self-healing properties. Also, to acquire an automatic self-aligning property of self-healing devices, 5T-magnetized commercial ferrite rubber magnet was diced to 1mm-width rod shape and aligned to form in wanted magnetic flux. After patterning deformable magnet pattern in circular shape, the magnetic aligning layer was deposited into PU layer through liquid-casting method. After several hours of curing process, the magnetic pattern embedded in PU film was formed, showing self-aligning properties through attraction force between damaged magnetic patterns. Finally, the sensor device to measure biosignal and interconnection layer was embedded on polymer surface. The sensor system could be easily self-healed through magnetic-align and laser induced self-healing properties.

5:00 PM SB09.04.04
Optical Detection of Single Brain Cell and Neuron-Related Activities Using 3D Plasmonic Sensing Micro Antenna Array Yuxin Cai and Pengyu Chen; Auburn University, United States

Studies of brain activities have been conducted at the frontmost end of neuroscience. The brain is composed of billions of neurons and is in charge of the central nervous system, yet despite the main biological role of the brain, there still are many unknown structures, functions, and connections remaining unknown to us. Meanwhile, the development of medical and clinical research has been phasing in the *in vitro* inspection of brain cell and neuron-related mechanisms for preclinical studies. Specifically, the *in vitro* exploration of brain and neuron cell activities in preclinical studies has been conducted to mimic the central nervous system response to advanced new medicines or medical technologies and to assist deliver precision treatment for brain diseases.

Parallel to fluorescence methods, localized surface plasmonic resonances (LSPR) has become a particularly interesting technique for studying the chemistry of living cells. LSPR is a label-free, non-invasive technique, confined to subwavelength-size noble metal nanoparticles that possess large optical cross-sections which have been thoroughly studied. The nanoplasmonic structures propose remarkable potential in sensor sensitivity, tunability, miniaturization, and large-scale fabrication, which makes it possible to intrinsically record neural cell activity at a single neuron level by optical means.

Deciphering the mechanisms of brain and neuron-related activities requires the acquisition of detailed information from a wide range of different scales, ranging from neuron networks to single neuron cells. In our study, we directly measured the change of surface electron density on a gold nanoparticle that is induced by the local neural cell's electric field to monitor brain neural activity. A 1 cm^2 area sensing array of 100 um-high and 5 um-diameter antennas was used, which is large enough to analyze the collective behavior while offering high resolution to observe single neural cell activity.

Because of its low cost, easy processability, biocompatibility, and hydrophobic nature, polystyrene is widely used for biomedical research. First, we designed the desired basal face of the 3D structure and a silicone mode will be manufactured through lithography. By precisely manipulating the etching time, the photoresist layer, and the ultraviolet light source, we are able to control the height and shape of the pattern, and finally formed a micro-antenna array mode for unlimited polydimethylsiloxane (PDMS) microwell masks. Then, a polystyrene solution (20% w/v in toluene) will be cast onto the PDMS mask and covered with indium-doped tin oxide (ITO) coated glass. After degassing, processing, and evaporation of the organic solvent, the base layer of our micro-antenna sensing array will be subsequently coated with gold nanoparticles to serve the sensing purpose with the strong plasmonic coupling can be observed by our previous developed LSPR dark-field imaging technique.

Murine hippocampal cell line (H19-7) and dissociated hippocampal neurons were observed on our micro-antenna sensing array. After a common preparation of the sensing array surface, differentiated hippocampal cells and hippocampal neurons were transferred to the sensing surface and further cultured, forming a neuron-network-like *in vitro* cultured specimen and later treated with different formulations. Firstly, the baseline was set when there was rarely any scattered light change captured before any formulation was injected. However, after the formulation injection, spiking activities were spotted under the dark field microscope. According to the references, the shape of the signals is typical of results that would be obtained in extracellular electrode recordings. Within the microfluidic channel designed and applied, it will be easy to use the device to acquire real-time *in vitro* neural cell activity of any formulations of medicine.

5:00 PM SB09.04.05

Ecofriendly Transfer Printing for Biodegradable Electronics Seung-Min Lee[1], Woo-Jin lee[1], Jae-Young Bae[1], Joon-Woo Kim[2], Ju-Yong Lee[1], Jeonghyun Kim[2] and Seung-Kyun Kang[1,1]; [1]Seoul National University, Korea (the Republic of); [2]Kwangwoon University, Korea (the Republic of)

Biodegradable electronics, which serve biomedical sensing and treatment for a certain period yet degrade into biocompatible and bioresorbable byproducts after their usage, have drawn a great interest in the field of minimally invasive implantation and disposable biomedical devices. Although various demonstration of biodegradable electronics including electrical field generators, stimulators, drug delivery systems, and wireless sensors, their fabrication on biodegradable polymer substrates remains as a great challenge. Especially, high resolution photolithography process on typical biodegradable polymers is infeasible owing to their low glass transition temperature and active reactivity to the organic solvents. Therefore, transfer printing of fully formed device to a polymer substrate has been suggested. Early reported transfer printing technique, however, still have limitations as following: 1) contain removal process of a non-biodegradable inter-process layer, 2) limitation in size and resolution 3) risk of shape distortion during the removal process of a sacrificial layer. Here, we propose simple, reusable, and large scale transfer printing method for biodegradable electronics realized with biodegradable materials during the whole process. A delicate control of adhesion between Si wafer and biodegradable metals (Mg, Zn) via formation of a self-assembled-monolayer (SAM) allow serial deposition, photolithography, etching process to fabricate a metal trace on a temporary wafer, but readily released by peeling-off force of a biodegradable polymer stamp. Quantitative analysis of adhesion was conducted using scratch test and thermal conductivity test. Fabrication of temperature sensors, wireless heater, metal-oxide-semiconductor field-effect transistor (MOSFET) using silicon nanomembrane (SiNM) present a wide range application of this method for passive and active devices. Wafer scale fabrication of circuit components including resistors, inductors, and capacitors allow large scale, and mass production. Printed circuit board (PCB) presents the fabrication of high resolution, yet dissolvable integrated circuit board. Wireless hydration sensor for xerostomia diagnosis address the possibility of a real-time monitoring of a salivary level in mouth. A set of transfer printing technique and exemplary demonstrations of various electronics presented in this study provide a novel strategy for simple, large-scale, mass productive, and ecofriendly fabrication of biodegradable electronics.

5:00 PM SB09.04.06
Biodegradable Conductive Conduit and Electroceutical for Accelerating Peripheral Nerve Regeneration Jio Kim and Seung-Kyun Kang; Seoul National University, Korea (the Republic of)

Peripheral nerve injury that completely cut and damaged by traumatic injury causes loss of motor function and/or sensory function. Peripheral nerve generally regenerates naturally in some range, but natural regeneration is limited and functional recovery is incomplete when the nerve defect is longer than 10 mm. An autograft, one of gold standard in clinics, is needed for peripheral nerve amputation patients, however, treatment success rate of autograft does not exceed 50 %. Recent studies propose artificial nerve conduit as a new treatment method that can possibly replace autograft. A conductive nerve conduit that helps electrical signal exchange has been highlighted along with biodegradable nerve conduits. In addition, recent studies have shown that electrical stimulation of peripheral nerves not only accelerates nerve regeneration but also improves functional recovery.
In this study, we introduced electroceutical combined with the biodegradable conductive nerve conduit and electrical stimulator for accelerated regeneration of long defect gap of sciatic nerve in rodent model. We fabricated a composite type of nerve conduit using biodegradable polymer (PCL) and biodegradable metal particles (Mo Nanoparticles). Wireless electrical stimulation was attempted for several days to maximize the nerve regeneration effect. Histological studies show that there is no mechanical or immunochemical damage by biodegradable conductive conduit. In-vivo demonstration for rodent model shows the successful treatment results.

5:00 PM SB09.04.07
Self-Healing Ionic Skins with Moisture Self-Regulation Characteristics for Ultra-Long Ambient Stability Peisheng He, Yu Long, Chao Fang and Liwei Lin; University of California, Berkeley, United States

Vulnerability to mechanical damages and dehydrations limits the operations of conductive hydrogels in ambient conditions. Inspired by the self-healing and water regulation behavior of jellyfish, we designed hydrogel-based self-healable ionic skins that can self-regulate internal moisture level by exploiting the mutually cohesive interactions among water, ions, and zwitterionic polymer networks. The material can sustain in the ambient for an ultra-long period of over 16 months and exhibit high stretchability (>1650% strain) and conductivity (as high as 23.5 mS/cm). Furthermore, after incidental exposures to harsh environments, including heating at 200 °C, freezing and vacuum drying conditions, the hydrogel can self-replenish water content from the ambient moisture and regain most of its conductivity and stretchability. Meanwhile, reversible ionic and hydrogen bonds allow the material to heal from fully cut-through damages repeatedly recouping conductivity (>90%) at room temperature within one minute. Utilizing the ionic skins as building blocks, flexible transparent piezoelecret sensors have been constructed to monitor physiological signals. Additionally, a facile transfer-printing process has been introduced to fabricate a breathing sensing system with self-healable supercapacitor and humidity sensor printed directly on ionic skins. These demonstrations illustrate broad-ranging possibilities of the ionic skin in areas including energy storage devices, wearable sensors, and human-machine interfaces.

5:00 PM SB09.04.08
Preparation-Free Hydrogel EEG Electrodes for Concurrent EEG-fMRI-TMS Yuhan Wen, Nehal Almamun, Michael Lustig and Ana C. Arias; University of California, Berkeley, United States

Transcranial magnetic stimulation (TMS) techniques provide a non-invasive tool to modulate cortical excitability by inducing charges at targeted brain areas and suppressing or enhancing local neural activity patterns. In neurological studies, it can be combined with other multimodal brain recording tools, such as Magnetic Resonance Imaging (MRI) or Electroencephalography (EEG), to provide important insight into how cells and neural circuits interact on a system level. Currently, only separate EEG-TMS and EEG-MRI systems are commercialized and clinically available. However, a concurrent EEG-fMRI-TMS system will allow EEG and fMRI to provide complementary spatial and temporal information of the transient and dynamic TMS-evoked network response and help advance neurological knowledge. One major challenge of such a system is that MRI and TMS environments are harsh on electronics and impose strong EMI due to the large switching magnetic fields in both RF ranges and EEG-relevant domains. Therefore, careful EEG material selection and electrode design are critical to ensure patients' safety, minimize heating, improve EEG signal quality, and reduce interference on MR images and TMS operation.

In this work, we aim to develop preparation-free hydrogel EEG electrodes compatible with concurrent EEG-fMRI-TMS. Biocompatible physically-crosslinked alginate hydrogel and freeze-thawed PVA hydrogel were prepared with varying polymer concentrations, crosslinking densities, and conductive additives. Different conductive additives including salt, PEDOT:PSS, and CNT were tested to enhance the conductivity of the hydrogel. The hydrogel conductivity was characterized with an LCR meter for EEG relevant range (20Hz-2MHz) and a Vector Network Analyzer at MRI-relevant frequencies that are sources of RF noises and major heating. After integration with stencil-printed Ag/AgCl electrodes, we measured the contact impedance on the subjects' forearms. Alginate/CaCl2/Ag/AgCl and PVA/NaCl/Ag/AgCl showed the most comparable performance to the gold standard wet gel and compatibility with MRI and TMS.

To validate the MRI compatibility of the EEG electrodes, we performed common MRI and fMRI sequences (T2*-weighted GRE scan and GRE EPI fMRI

BOLD scan) with the electrodes on the subject's head. No MR image distortions due to the EEG electrodes were observed, and no heating occurred during the sequences. The EEG data were recorded by a commercial MR-compatible amplifier and power unit. RF noises were removed by in-line filtering and the gradient noise can be canceled by synchronization with the scanner clock and signal processing methods. We also characterized artifacts from polarization during biphasic repetitive TMS pulses to test TMS compatibility. The electrodes were submerged in a physiological saline solution, wired out through a twisted pair, and aligned with the TMS coil in the worst-case scenario. Varying TMS intensity from 10% (14A/us) to 50% (70A/us), the hydrogel electrodes showed a settling time of less than 10us after the TMS pulses, and no significant heating was observed. Our results demonstrate that the proposed hydrogel EEG electrodes are safe and suitable for application in harsh MRI and TMS environments with performance comparable to the traditional wet electrode, and without complex skin preparation and clean-up afterward. This work demonstrates an important step towards a fully integrated multimodal concurrent EEG-fMRI-TMS system.

5:00 PM SB09.04.09
Organic Iono-Electronic Composite Materials Towards High-Performance Bioelectronic Devices Camille E. Cunin, Sanket Samal and Aristide Gumyusenge; Massachusetts Institute of Technology, United States

Organic semi-conducting materials with mixed ionic-electronic transport properties have gained a lot of attention over the past few years due to their ability to operate in close contact with the body and accurately transmit physiological signals. By mimicking the function of biological synapses, such bio-inspired conductors have shown great potential for future applications in bioelectronics and health monitoring. However, despite their better mechanical properties, biocompatibility, ease of integration into miniaturized architectures, low-cost production, low-power consumption, and chemical tunability -compared to their inorganic counterparts, organic semiconductors still suffer from a mechanical mismatch at the body-machine interface, poor charge carrier mobility, and low environmental stability. While polymer backbone and side chains engineering are promising chemistry approaches for addressing these limitations, we demonstrated that engineering organic iono-electronic composites (OIECs) further enables a fine tuning of both microstructural and electrochemical properties of conjugated polymers. OIECs were developed by blending an insulating matrix (poly(methyl methacrylate) (PMMA)) with a novel semiconducting polymer (PDPP3T-20gT), made of polar tetraethylene glycol side chains tethered to a backbone of 80% diketopyrrolopyrrole and 20% thiophene derivatives. The influence of the insulator's tacticity (e.g., atactic, isotactic, syndiotactic) was also investigated. Structural changes across blends were characterized using high-precision atomic force microscopy, grazing-incidence wide angle X-ray scattering, and UV-vis spectroscopy. Mixed conduction properties were assessed using transducing devices (organic field-effect transistors (OFETs) and organic electrochemical transistors (OECTs)). We demonstrated that both the semiconductor/insulator ratio and the insulator's tacticity strongly impact the nanostructure and the electrochemical properties of the semiconducting polymer. We showed that developing OIECs adds an extra layer of flexibility for engineering more mechanically compliant, low-cost, and readily processable channel materials for implementation into transducing devices. In conclusion, while engineering backbone and side chains is an efficient strategy to improve mixed ionic-electronic conduction and level up the performances of current organic bioelectronic devices, designing OIECs paves the way for the development of highly compliant materials towards prosthetics, smart electronics, and on-body computing.

5:00 PM SB09.04.10
Quinoxalineimide-Based Conjugated Polymers: Synthesis, Characterization and Field-Effect Transistor Performance Minoru Ashizawa[1], Katsuki Yaginuma[1], Yoshihiro Hayashi[1], Susumu Kawauchi[1], Hiroyasu Masunaga[2], Noboru Ohta[3], Wen-ya Lee[4] and Hidetoshi Matsumoto[1]; [1]Tokyo Institute of Technology, Japan; [2]Jasri, Japan; [3]SPring8, Japan; [4]National Taipei University of Technology, Taiwan

Quinoxalineimide (QI) building units are versatile electron-accepting components that can create n-channel and/or ambipolar polymer semiconductors in organic field-effect transistors. Herein, we report five QI-based copolymers with thienyldiketopyrrolopyrrole (TDPP) counterparts and systematically examine polymer structure-function correlations in terms of charge carrier transport properties. The introduction of two fluorine atoms into the QI moieties of a polymer backbone lowered both the HOMO and LUMO levels, resulting in n-channel dominant ambipolar FET performance with the highest maximum mobilities of 1.45 $cm^2V^{-1}s^{-1}$ for electrons and 0.71 $cm^2V^{-1}s^{-1}$ for holes, which was attributed to improved crystalline ordering. The electronegative triazole- and thiadiazole-fused QI moieties resulted in drastically decreased LUMO levels in the copolymers, with values close to or below -4.0 eV, as required for stable n-channel operation, whereas the HOMO levels remained unchanged because of the quinoidal resonance contribution. As a result, triazole- and thiadiazole-fused QI-based polymers showed near-infrared (NIR) light absorption across the whole NIR-II window (1000-1700 nm) with an optical energy gap of less than 0.8 eV. Investigation of the charge carrier transport properties indicated that both polymers displayed n-channel-dominant and non-off ambipolar behavior. These results suggest that a series of QI electron-accepting units are excellent building blocks for the development of novel n-channel and/or ambipolar polymer semiconductors with a high NIR light response.

5:00 PM SB09.04.11
A Biodegradable Bioinspired Oil-Coated Adhesive Film for Enhanced Wet Adhesion Yeon Soo Lee, Da Wan Kim, Jinhyung Kim, Seung Hwan Jeon, Gui Won Hwang and Changhyun Pang; Sungkyunkwan University, Korea (the Republic of)

Bioinspired and biodegradable polymer-based adhesive films have attracted attention in the medical field because of their stable adhesion performance and ability to decompose in the body without additional surgical procedures. Among biodegradable materials, poly (glycerol sebacate) (PGS) can be applied to softenss-tuned microarchitecture-based adhesive films, because it has bioresorbable and residue-free characteristics. Herein, we presented a bioinspired oil-coated adhesive film fabricated using PGS, which can maintain adhesion on a wet surface by mimicking the toe pad and mucus of a frog. To implement frog-like adhesive architectures, the particular criteria under which PGS can be patterned were presented using simple models based on the degree of esterification and interfacial energy difference. Wet adhesion of our oil-coated film was achieved by replicating the frog-like hexagonal micro-channel and concave cup structures coated with vicious glycerol oil, resulting in a stable residue-free wet adhesion against diverse non-flat soft organ surfaces.

5:00 PM SB09.04.12
Erythrocyte-Camouflaged Biosensor for α-hemolysin Detection Yonghwan Kim and Hyo Gi Jung; Korea University, Korea (the Republic of)

Without appropriate treatment, Staphylococcus aureus (S. aureus) infection can cause life-threatening diseases. However, a rapid and accurate point-of-care test for the infection remains challenging. The bacterium secretes α-hemolysin (Hla), which spontaneously binds to the cell membrane of erythrocyte, and eventually lyses the cell via pore formation. Taking advantage of this phenomenon, we apply the erythrocyte membrane (EM) extracted from human whole blood as a novel bioreceptor for detecting Hla, fabricating erythrocyte-camouflaged biosensors (ECB) by coating EM onto electrochemical impedance electrodes. We verify the existence of EM on the ECB by using confocal microscopy and atomic force microscopy. We demonstrate that ECBs sensitively detect Hla spiked in phosphate buffer saline and human serum. Also, the sensor shows higher sensitivity to Hla than major blood proteins, such as human serum albumin, fibrinogen, and gamma globulin. Finally, we validate the constant sensing performance of ECB with 99.0 ± 5.6% accuracy for 35 days of storage.

5:00 PM SB09.04.13
Near-Field Electromagnetic 3D Printing for Nanomaterials-Based Electronics Samuel Hales[1], Jared Anklam[1], Yang Xin[2], John S. Ho[2] and Yong Lin

Kong[1]; [1]University of Utah, United States; [2]National University of Singapore, Singapore

The inability to selectively anneal printed materials on a broad range of temperature-sensitive constructs has limited the potential functional complexity and performance of 3D printed electronics. Thermal annealing of 3D printed nanomaterials is a critical process that dictates electronic performance by (1) merging otherwise disconnected nanomaterials, (2) reducing defects and interfaces, (3) removing polymeric additives, and (4) improving contact between printed layers. Prior works primarily rely on heating the entire printed object post-printing in a bulk annealing process, which severely limits the possible multimaterial integration and geometrical configurations. Here, we demonstrate the ability selectively and locally anneal 3D printed nanomaterials *in situ* on a broad range of temperature-sensitive substrates, including plant media and low-melting-temperature polymers, by exploiting metamaterial-inspired electromagnetic structures. The demonstrated near-field electromagnetic 3D printing (NFP) enables exceptional control of printed nanomaterial annealing parameters, creating spatially freeform microstructure where the electronic and mechanical properties can be locally programmed in a multimaterial construct. We envision that NFP significantly broadens the possible class of materials compatible with additive manufacturing processes, enabling the creation of hybrid multi-functional constructs and the integration of functional electronics on temperature-sensitive constructs.

SESSION SB09.05: Implantable Bioelectronics II
Session Chairs: Ying Jiang, Lihua Jin, Jia Liu and Zhiyuan Liu
Wednesday Morning, April 12, 2023
Moscone West, Level 2, Room 2022

8:15 AM *SB09.05.01
Recording and Manipulation of Cell Signaling with Multifunctional Fibers Polina Anikeeva; Massachusetts Institute of Technology, United States

In this talk, I will highlight the recent developments in multimaterial fiber technology that enable recording and modulation of signaling in neuronal as well as non-neuronal cells. Although electrogenic cells such as neurons can be manipulated via electrical signals, the ability to manipulate or record from genetically identifiable neuronal subtypes demands optical or chemical techniques. Using multimaterial fiber technology, our group has demonstrated how optical and chemical recording and manipulation methods can be combined with traditional electrical approaches. Additionally, given emergence of evidence supporting the critical role of signaling between neurons and tumor cells in the development of brain cancers, our group has developed interfaces to optically probe signaling in non-electrogenic tumor cells. As the studies of neuron-tumor interactions require non-immunogenic functional interfaces with both neuronal and tumor tissues, my talk will highlight the materials advances aimed reducing the impact of the implantable tools on local biological environments. Together, our advances in multifunctional, non-immunogenic fiber-based probes pave the way toward unraveling the roles of communication between neuronal and non-neuronal cells in the context of health and disease.

8:45 AM *SB09.05.02
Soft and Stretchable Implantable Electrodes to Interface with the Human Brain Nicolas Vachicouras; Neurosoft Bioelectronics, Switzerland

Neural implants aim at restoring lost or impaired functions of the nervous system by electrical stimulation or recording of the brain. Current neural implants suffer from a mechanical mismatch compared to the soft host tissue, as they constrain mechanically the physiological motion of the central nervous system. This mismatch causes poor electrode-tissue contact, leading to unspecific stimulation or recording, as well as chronic scarring. At Neurosoft Bioelectronics, we overcome these fundamental limitations by developing soft and stretchable neural electrodes, using more compliant materials, that seamlessly interface with the brain, promoting the long-term bio-integration of the devices and reducing surgical risks.

Our electrodes are made of a thin-film (<100 nm) of gold evaporated on a low modulus (<1 MPa) silicone substrate, allowing for reversible elasticity while maintaining electrical properties. The electrode sites are coated with a rough platinum-silicone composite, which increases the electrochemical surface area and thus allowing for reduced interfacial impedance.

Neurosoft Bioelectronics has been working on the translation of these materials to the clinic by developing a subdural electrode, SOFT ECoG, to record from and electrically stimulate the surface of the brain.

9:15 AM SB09.05.03
Magnetic-Driven 3D Curvilinear Neural Probe for Minimal Invasive Injury Tao Zou[1,2] and Paddy K. L. Chan[1,2]; [1]The University of Hong Kong, Hong Kong; [2]Advanced Biomedical Instrumentation Centre, Hong Kong Science Park, Hong Kong

Recording and stimulation of neural circuits in-vivo at the cellular level are essential for us to understand the function of brain and establishing a brain-computer interface. Due to the relatively complicated patterning and fabrication steps, the neural probes with multi-function stimulation and large-area coverage are usually based on conventional semiconductors such as silicon. The major drawback of these rigid neural probes is it will inevitably damage parts of the brain and induce immune response lead to lead to glial scars which limits the long-term recording.

In this work, we will present a polymer-based flexible neural probe, based on standard lithography process and 3D printing process. The probe equip with eight closely spaced 30 µm diameter PEDOT:PSS/pHEMA electrode and a soft magnetic polymer fiber shuttle which can be driven by external gradient magnetic field and go into brain with 3D curvilinear path. We designed and fabricated a magnetic actuation platform for controlling the magnetic probe motion and positioning precisely. We also integrated the Fiber Bragg Gratings (FBG) into this neural probe as the feedback of the probe position and shape. In the talk, the operating mechanism and the fabrication process of the magnetic neural probe will also be discussed. This neural probe can minimize the risks of brain damage or glial scaring during neural spike recording and neuron stimulation and have great potential for biomedical applications. As a demonstration, we will also discuss the application of the flexible neural probe in the brain of the rat for the direct neural spike and local field potential sensing.

9:30 AM BREAK

10:00 AM SB09.05.04
Design, Characterization and *In Vivo* Application of Multi-Conductive Layer Organic Electrocorticography Probes Remy Cornuejols[1,2], Amelie Albon[2], Suyash Joshi[3], James Alexander Taylor[3], Martin Baca[2], Pascale P. Quilichini[1], Sofia Drakopoulou[2], Tania Rinaldi Barkat[3], Christophe Bernard[1] and Charles Rezaei-Mazinani[2]; [1]Aix-Marseille Université, France; [2]École des Mines de Saint-Étienne, France; [3]Universität Basel, Switzerland

Biocompatible and plastic neural interface devices allow for minimally invasive recording of brain activity. Increasing electrode density on such devices is essential for high resolution neural recordings. Superimposing conductive leads on devices can help multiplying the number of recording sites while keeping probes width small and suitable for implantation. However, because of leads' vertical proximity, this can create capacitive coupling (CC) between overlapping channels, which leads to crosstalk. In our study, we present a thorough investigation of CC phenomenon in multi gold layer thin-film MEAs with a Parylene C (PaC) insulation layer between superimposed leads. We also propose a guideline on the design, fabrication and characterization of such type of neural interface devices for high spatial resolution recording. Our results demonstrate that the capacitance created through CC between superimposed tracks decreases non-linearly then linearly with insulation thickness. Moreover, CC creates a high pass filter between superimposed leads, with maximum gain and cutoff frequency depending not only on device geometry but also on the recording equipment. We identified that there is an optimal PaC insulation thickness that leads to a drastic reduction of CC between superimposed gold channels, while not significantly increasing the overall device thickness. Finally, we show that double gold layer electrocorticography probes with this optimal insulation thickness exhibit similar performances *in vivo* when compared to single layer devices. This confirms that these probes are adequate for high-quality neural recordings.

10:15 AM SB09.05.05
Implantable Bioelectronics with Shape Actuation for Minimally Invasive Electrocorticography Lawrence Coles[1], Ben Woodington[1], Domenico Ventrella[2], Alberto Elmi[2], Maria L. Bacci[2], George G. Malliaras[1], Damiano G. Barone[1] and Christopher Proctor[3]; [1]University of Cambridge, United Kingdom; [2]Università di Bologna, Italy; [3]University of Oxford, United Kingdom

The development of innovative neural interface devices would allow for novel approaches to diagnose, monitor, and treat neurological conditions and impaired neural-mediated motor function. Electrocorticography (ECoG) is an implanted neural interface technique that has been developed to record brain activity using large-area electronic arrays placed on the cortical surface and is used as a diagnostic tool in Epilepsy and Parkinson's monitoring, and brain-computer interfaces for prosthesis control. There has been extensive investigation into flexible ECoG devices, with a variety of substrate materials and electrode designs, however, the implantation of these devices is very invasive due to the size of craniotomy required.

This project aims to design shape-morphing ECoG neural implants that can be implanted with minimally invasive surgical techniques, whilst still retaining the large area mapping and spatial resolution of existing ECoG technologies. We have developed a microfluidics-based soft-robotic ECoG design that allows us to deploy a folded thin-film ECoG with a small burr-hole craniotomy onto the cortical surface, before deploying the full large bioelectronic array onto the cortex using fluidic actuation. The application of soft-robotic technologies in shape-morphing implants is an emerging field, applying the use of soft polymeric materials to form actuators that enable the shape actuation of these devices post-implantation. This approach to shape-morphing bioelectronics using soft, compliant materials also allows the large bioelectronic arrays to match the surrounding soft environment of human tissue mechanically.

The ECoG designs were tested in porcine models, with the integration of x-ray opaque PDMS markers allowing the expansion of the devices to be tracked with real-time fluoroscopy. This demonstrated that soft-robotic technologies would be a feasible approach for delivering larger ECoG designs to the cortical surface with a burr-hole craniotomy. By reducing the invasiveness of flexible ECoG sensors, this innovation allows for the reduction of both surgical risk and cost, increasing the availability of these sensors for clinical applications.

10:30 AM SB09.05.06
Spatially Controlled, Bipolar, Cortical Stimulation with High-Capacitance, Mechanically Flexible Subdural Surface Microelectrode Arrays Ilke Uguz and Ken Shepard; Columbia University, United States

Most neuromodulation approaches rely on extracellular electrical stimulation with penetrating electrodes at the cost of cortical damage. Surface electrodes patterned on thin-film plastic substrates, in contrast, can be subdurally implanted and adhere to the pial surface in chronic settings minimizing the mechanical compliance mismatch between probe and neural tissue. However, surface stimulation strategies are challenged by the lack of proximity to axonal processes, leading to poor resolution. Here, we examine how these constraint can be overcome by using high-density (40-µm pitch), high-capacitance (>1 nF), single neuronal resolution poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) electrodes in a bipolar stimulation configuration to shape the charge injection. We tune the surface electrode array to be optically transparent to allow concurrent calcium imaging for mapping immediate neural response to stimulation pulses at depth. This allows us to generate synaptic activation maps and to determine stimulation mechanisms. In addition, we pattern the flexible arrays using dry etching techniques to shape the functional front. This way we generate devices both in the form of surface arrays and implantable probes which can be inserted inside the brain aided by temporary, rigid carriers to generate a three dimensional neural interface. The resulting stimulation effects are captured with both two-photon imaging and simultaneous recording from depth electrodes. We demonstrate the ability to stimulate at depths up to 300 micrometer with lateral resolutions of better than 100 micrometer. We have also been able to show that single-units recorded form the surface correspond to activity from L2/3 pyramidal neurons. By integrating Polydimethylsiloxane microfluidic channels and release sites on the array, we show that the surface stimulation is not influenced by surface apical dendrites through selected drug release between the stimulation electrodes. These studies highlight the bidirectional interfacing possibilities that exist with high-quality, micron-scale surface electrodes for emerging neuro-technologies that rely on surface electrodes.

10:45 AM *SB09.05.07
Translational Neuroelectronics Dion Khodagholy; Columbia University, United States

Our understanding of the brain relies on discoveries in neuroscience and neurology fueled by sophisticated bioelectronics enabling visualization and manipulation of neural circuits at multiple spatial and temporal resolutions. In parallel, to facilitate clinical translation of advanced materials, devices, and technologies, all components of bioelectronic devices have to be considered. Organic electronics offer a unique approach to device design, due to their mixed ionic/electronic conduction, mechanical flexibility, enhanced biocompatibility, and capability for drug delivery. We design, develop, and characterize conformable, stretchable organic electronic devices based on conducting polymer-based electrodes, particulate electronic composites, high-performance transistors, conformable integrated circuits, and ion-based data communication.

These devices established new experimental paradigms that allowed monitoring of the emergence of neural circuits during development in rodents and elucidated patterns of neural network maturation in the developing brain. Furthermore, the biocompatibility of the devices also allowed intra-operative recording from patients undergoing epilepsy and deep brain stimulation surgeries, highlighting the translational capacity of this class of neural interface devices.

In parallel, we are developing the fully-implantable, conformable implantable integrated circuits based on high-speed internal ionic gated organic electrochemical transistors that can perform the entire chain of signal acquisition, processing, and transmission without the need of hard Si-based devices. This multidisciplinary approach will enable the development of new devices based on organic electronics, with broad applicability to the understanding of physiologic and pathologic network activity, control of brain-machine interfaces, and therapeutic closed-loop devices.

11:15 AM *SB09.05.08
Tissue-Adhesive Hydrogel Biointerfaces for Sutureless Implantable Electronics Mikyung Shin; Sungkyunkwan University, Korea (the Republic of)

Soft and stretchable bioelectronics have been attractive due to mechanical modulus matching to biological tissues. Nevertheless, there still have remained challenges to optimize biotic-abiotic interfaces for long-term and reliable bidirectional electrical stimulation and signal recording. Herein, we propose a hydrogel biointerface with wet-resistant tissue adhesiveness – which is inspired by mussel byssal threads, enabling immediate fixation of implantable electronics on nerve and cardiac tissues without any sutures. Firstly, adhesive and strain-gradient artificial epineurium is presented for efficient nerve-to-nerve connection and regeneration, implementing further stable neural interfacing. Secondly, a strain-adaptive fiber-interlocked bioelectronic patch is introduced for efficient cardiac interfacing even in freely moving animals. Such patch-type devices containing tissue adhesive hydrogel interfaces would be promising for developing sutureless bioelectronics.

11:45 AM SB09.05.09
From 2D to 3D Flexible Intraretinal Implants—Towards a New Generation of Visual Prostheses Viviana Rincón Montes[1], Marie Jung[1,2], Jamal Shihada[1,2], Lina Koschinski[1,2], Tibor Lohmann[2], Frederic K. Balcewicz[2], Sven Ingebrandt[2], Frank Müller[3], Peter Walter[2] and Andreas Offenhaeusser[1,2]; [1]Institute of Biological Information Processing (IBI-3) Bioelectronics, Forschungszentrum Jülich, Germany; [2]RWTH Aachen University, Germany; [3]Forschungszentrum Jülich GmbH, Germany

The development of visual prostheses that stimulate the retina electrically has allowed significant advances toward the restoration of useful vision in the daily life of blind patients with retinal degenerative diseases. Nonetheless, such improvements are still rudimentary and the efficiency of retinal implants did not meet the expectations of patients, to the point that commercially available retinal implants were withdrawn recently from the market [1]. To further develop the field of retinal-based visual prosthetics, it is of vital importance to better understand the physiology of healthy and diseased retinas and to improve the efficiency of retinal implants upon electrical stimulation. To this end, feedback about electrical activity in the retina is desirable. Given the above, our research consortium has proposed the development of a bidirectional communication strategy. The idea is that the implant comes in close contact with vital neurons inside the retina to perform simultaneous electrical stimulation and recording of the retina. It thereby allows optimization and acknowledgment of the efficiency of the electrical stimulation process for the restoration of vision.
To this end, we developed a bidirectional microelectrode array (BiMEA), comprising flexible (parylene-C-based) penetrating multi-shank and multi-site neural probes for retinal applications with iridium oxide or PEDOT: PSS electrodes [2-4]. 2D intraretinal probes were first developed, allowing an *in vitro* proof of concept with explanted rodent retinas that showed the feasibility of an intraretinal bidirectional prosthetic device. Here, we showed the capability of intraretinal recording while capturing distinct neuronal responses upon electrical stimulation on both, healthy and diseased retinas. Excitatory and inhibitory, as well as monotonic, non-monotonic, and saturated neural responses were captured when charges between 0.2 nC – 2.5 nC were applied. Furthermore, our devices showed a small acute insertion footprint in explanted retinas when using miniaturized probes (7 µm-thick, 50 µm-wide, and 140/180 µm-long), thereby reducing the acute insertion trauma area by 2-fold when compared to silicon Michigan-like arrays (20 µm-thick, 60 µm-wide, 312 µm-long). Moving even one step forward, we designed, developed, and tested *in vitro* 3D flexible penetrating retinal implants for the first time. The latter allowed the recording of physiological responses of light-adapted retinas. Paving the way toward *in vivo* applications, intraretinal probes were validated in cadaveric animal models, exposing the feasibility of implanting such probes with an open-sky surgery for a future acute *in vivo* validation of the BiMEA concept.
References:

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SESSION SB09.06: Unconventional Polymeric Bioelectronics
Session Chairs: Ying Jiang, Lihua Jin, Jiheong Kang, Jia Liu and Zhiyuan Liu
Wednesday Afternoon, April 12, 2023
Moscone West, Level 2, Room 2022

1:30 PM *SB09.06.01
Development of Semiconducting Polymers for Organic Electrochemical Transistors Iain McCulloch; University of Oxford, United Kingdom

Organic electrochemical transistors (OECTs) have been shown to be promising devices for amplification of electrical signals and selective sensing of ions and biologically important molecules in an aqueous environment, and thus have potential to be utilised in bioelectronic applications. The sensitivity, selectivity and intensity of the response of this device is determined by the organic semiconducting polymer employed as the active layer. This work presents the design of new organic semiconducting materials which demonstrate good OECT performance, through operation in accumulation mode, with high transconductance and low operating voltage.
We discuss here the design, synthesis and performance of novel intrinsic semiconducting polymers for efficient accumulation mode OECT devices. Key aspects such as ion and charge transport in the bulk semiconductor and operational voltage and stability of the devices are addressed in order to elucidate important structure-property relationships. A range of new semiconducting polymers, designed to exhibit facile electrochemical doping of either holes or electrons, facilitate ion penetration and migration, as well as have aqueous compatibility are reported. Optimisation of a series of polymer parameters including electrochemical doping, charge carrier mobility and capacitance are discussed.

2:00 PM SB09.06.02
Characterization of the 3D Neuronal Network Read-Out Platform with an Improved Ratio of Measurable Neurons Using Alginate Patterning on Microelectrode Array for Precise Network Analysis Dongjo Yoon and Yoonkey Nam; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The In vitro biological neuronal network model has been widely used as a tool to improve understanding of neuronal networks by lowering the complexity of the native brain. Among them, the three-dimensional (3D) neuronal network model embedded in the extracellular-based matrix (ECM) is known to be closer to the gene expression and functional activity of the native brain than the flat cultured neuronal network. With these advantages, the 3D neuronal network model has been developed into models with various structures, such as modular structures and layer-by-layer structures. Microelectrode array (MEA) device has the advantage of being able to track the network activity for a long time with high-temporal resolution and has been used to measure the functional activity of a 3D neuronal network. However, signal measurement of the 3D neuronal network models had a limitation in that most of the neurons could not be measured by electrodes because neurons were randomly distributed in 3D space and far from electrodes. 3D MEAs which have electrodes in 3D have been developed, but there are still many neurons that cannot be measured compared to the total neurons in the network.

In this study, we introduce an engineered 3D neuronal network model in which neurons are located only on electrodes. This model can be used as a 3D neuronal network read-out platform to read most of the neurons in the 3D network. In order to develop this 3D network structure, we used the previously reported alginate patterning technique on flat MEA (electrode diameter: 30 μm, interval: 200 μm). Alginate hydrogel was biocompatible and neuron-repulsive so that neurons can be attached to the desired region (diameter: 100 μm) on microelectrode. Then, collagen type 1 (Col1, 1.0 mg/mL) which is ECM-based hydrogel was covered on the cultured cells at 3 days in vitro (DIV). For stable adhesion of Col1, a polydimethylsiloxane (PDMS) sheet (outer diameter: 7 mm, inner diameter: 4 mm, thickness: 200~250 μm) was attached to the bottom of the MEA, and a nylon mesh (Outer diameter: 4 mm, inner diameter: 50 mm) was inserted in the middle.

We investigated the morphological characterization of our model through immunostaining and confocal microscope (LSM880, Zeiss) imaging. It was confirmed that somas were maintained only in the originally placed area even after 3 weeks. Neurites grew more densely in space over 5, 7, and 14 DIV. The neurite density decreased as the height increased, but on the top interface, the neurites were concentrated. There are also dendrites and synapses in 3D space. We verified that our model was formed as a 3D neuronal network through morphological characterization.

In addition, we measured spontaneous activity for 10 to 28 DIV. The 2D neuronal network produced without covering Col1 was compared as a control group. The ratio of the active channel (firing rate > 0.1 Hz) and the amplitude of spikes were similar without significant differences from the 2D network. It was confirmed that the process of covering Col1 had no adverse effect at the electrode-neuron interface. The array-wide firing rate, burst rate, burst duration, percentage of burst spikes, and network synchronization index increased until 19 DIV and were maintained thereafter. As the result of the peristimulus time histogram (PSTH) through electrical stimulation, the 3D network showed a longer reaction during 200-400 msec compared with the 2D network which had 50 msec. It is inferred that more diverse paths are formed by the synapses in 3D space than the 2D network, so the synaptic reverberation is maintained long.

Our platform was able to successfully measure the activity of biological 3D neuronal networks and alginate patterns covered with Col1 maintained the position of all neurons on the electrode for 4 weeks. It can be used as a 3D neuronal network read-out platform to measure the signals from most neurons in the network for precise network analysis.

2:15 PM SB09.06.04

Photobiocatalytic Hydrogen Production from Water Using Conjugated Polymer Nanoparticle-Recombinant *Escherichia coli* Biohybrid Systems
Ying Yang[1], Reiner S. Sprick[2], Lu-Ning Liu[1] and Andrew I. Cooper[1]; [1]University of Liverpool, United Kingdom; [2]University of Strathclyde, United Kingdom

In the pursuit of systems with high solar-to-fuel conversion efficiencies, different strategies have been employed to interface synthetic and biological components. Semi-artificial photosynthesis is aimed to combine the light-absorbing ability of synthetic materials and efficient metabolic pathways in biological systems. As such, it has attracted significant interest over the last 10 years for solar-to-chemical energy conversion. With the development of new photocatalysts, especially organic photocatalysts in the last five years, this presentation will discuss the potential of conjugated polymers, rather than traditional inorganic semiconductors, as photosensitiser materials in biological hybrid systems.

This polymer-microorganism biohybrid system - the first report of polymer/*Escherichia coli* (*E. coli*) system for hydrogen production - not only offers the ability to tune the materials' photophysical properties but also to explore structure-activity relationships, especially for possible electron/energy transfer involved. In this work, nanoparticles of a series of linear polymers with different backbone structures were assembled with recombinant *E. coli* cells. Confocal fluorescence microscopy and scanning electron microscopy confirmed the successful assembly which is driven by hydrophobic and electrostatic interactions. Under simulated solar light irradiation, there a more than 10-times performance improvement for hydrogen production of polymer/*E. coli* biohybrid systems compared with the polymer sample, was observed, while no detectable hydrogen was generated from the bacteria sample. Trends within the series of hybrid systems could be explained by differences in the physical interactions between synthetic materials and microorganisms, energy level alignments, and kinetics. Further insights into the fundamental processes of these biohybrid systems were gained through a range of techniques, including time-correlated single photon counting, transient absorption spectroscopy, and metabolic analysis.

2:30 PM BREAK

3:00 PM SB09.06.05

Molecular Design and Degradation Lifetimes of Semicrystalline to Near-Amorphous Degradable Semiconducting Polymers Jerika A. Chiong and Zhenan Bao; Stanford University, United States

Transient electronics have received widespread interest for their potential applications in reducing electronic waste and improving human health through implantable devices. Synthetic polymers serve as an attractive platform for the development of degradable electronic components due to their ability to be rationally tuned by molecular design for exploration of desired mechanical, electronic, and degradation properties. Although there has been much development on biobased and biodegradable insulating polymers for substrate and dielectric components in recent years, there are only several existing degradable semiconducting materials. As a result, the degradation behavior of semiconducting polymers in relation to molecular design as well as morphological and electronic properties has not been properly studied. Herein, we prepare imine-based semiconducting polymers with tuned polymer architectures, ranging from semicrystalline to near-amorphous morphologies, for the systematic exploration of the impact of several molecular design parameters on the degradation lifetimes of these polymers. To rationalize differences in electronic performance and degradation behavior, we characterize the polymers' optical and morphological properties by ultraviolet-visible (UV-vis) spectroscopy, grazing-incidence X-ray diffraction, and atomic force microscope. By monitoring degradation via UV-vis, gel permeation chromatography, and NMR, we discover that polymer degradation in solution is heavily aggregation and hydrophilicity dependent. Additionally, the aggregation-dependence of these degradable polymers rely heavily on the solvent used, with a fivefold difference in degradation time depending on solvent. We develop a new method for quantifying the degradation of polymers in the thin film and observe that similar considerations used for designing high-performance semiconductors impact the degradation of imine-based polymer semiconductors. This study provides crucial principles for the molecular design of degradable semiconducting polymers, and we anticipate that these findings will expedite progress toward implantable electronics with targeted, controlled lifespans.

3:15 PM SB09.06.06

A Comparative Study of *In Situ* and *Ex Situ* Synthesized Conductive Polymers on Natural Lipid Bilayers Diana Priyadarshini; Linköping University, Sweden

Seamless integration between biological systems and electrical components is essential for enabling a twinned biochemical-electrical recording and therapy approach to understand and combat neurological disorders. Employing bioelectronic systems made up of conjugated polymers, which have an innate ability to transport both electronic and ionic charges, provides the possibility of such integration. In particular, translating enzymatically polymerised conductive wires, recently demonstrated in plants and simple organism systems, into mammalian models, is of particular interest for the development of next generation devices that can monitor and modulate neural signals. As a first step toward achieving this goal, enzyme-mediated polymerisation of two thiophene-based monomers was recently demonstrated on a synthetic lipid bilayer supported on a Au surface. In this paper, a comparative study of in situ vs. ex situ synthesized conductive polymers is conducted on Au supported bilayer substrates made up of natural lipids. Microgravimetric studies of these polymer films provide insights into their interactions with a lipid bilayer model that mimics the cell membrane. Moreover, resulting electrical and viscoelastic properties of these self-organising conducting polymers suggest their potential as materials to form the basis for implantable neural devices targeting novel therapeutic approaches.

3:30 PM *SB09.06.07
Macromolecular Bioelectronics Helen Tran; University of Toronto, Canada

Next-generation electronics will autonomously respond to local stimuli and be seamlessly integrated with the human body, opening the doors for opportunities in environmental monitoring, advanced consumer products, and health diagnostics for personalized therapy. For example, biodegradable electronics promise to accelerate the integration of electronics with health care by obviating the need for costly device-recovery surgeries that increase infection risk. Moreover, the environmentally critical problem of discarded electronic waste would be relieved. The underpinning of such next-generation electronics is the development of new materials with a wide suite of functional properties beyond our current toolkit. Organic polymers are a natural bridge between electronics and soft matter, where the vast chemical design space allows tunability of electronic, mechanical, and transient properties. Our research group leverages the rich palette of polymer chemistry to design new materials encoded with information for self-assembly, degradability, and electronic transport. In this talk, I will share an overview or projects underway in our group.

SESSION SB09.07: Wearable Bioelectronics I

Session Chairs: Lihua Jin, Jiheong Kang, Jia Liu, Zhiyuan Liu and Jin Young Oh
Thursday Morning, April 13, 2023
Moscone West, Level 2, Room 2022

8:30 AM SB09.07.01
New Semiconducting Polymers for Bioelectronic Applications Christian Nielsen; Queen Mary University, United Kingdom

Semiconducting materials have long played a pivotal role in the development of organic electronic applications such as OLEDs and OFETs. More recently, semiconducting polymers have made their entry into the new field of bioelectronics, where electronic materials are interfaced with a biological milieu. In my talk I will discuss our recent work on new semiconducting materials for organic bioelectronic applications with an emphasis on the development of efficient mixed ionic and electronic conductors for biosensing applications. Our work encompasses both small-molecule and polymeric semiconductors with tailored properties for mixed conduction, while we are also actively developing both p- and n-type mixed conductors with examples of both classes of materials discussed in my talk.

8:45 AM SB09.07.02
Strong and Tough Conductive Organo-Hydrogels via Freeze-Casting Assisted Solution Substitution Wei Zhai, Xinyu Dong, Xiao Guo, Quyang Liu, Yijing Zhao and Haobo Qi; National University of Singapore, Singapore

High strength, toughness, and conductivity are among the most sought-after properties of flexible electronics. However, existing engineering materials find it difficult to achieve both excellent mechanical properties and high conductivity. To address this challenge, this study proposes a facile yet versatile strategy for preparing super-tough conductive organo-hydrogels via freeze-casting assisted solution substitution (FASS). This FASS strategy enables the formation of organo-hydrogels in one step with exquisite hierarchical anisotropic structures coupled with synergistic strengthening and toughening effects across multiple length scales. As an exemplary material, the prepared polyvinyl alcohol (PVA) organo-hydrogel with solvent content up to 87 wt% exhibits a combination of high strength (6.5 MPa), high stretchability (1710% in strain), ultra-high toughness (58.9 MJ m^{-3}), as well as high ionic conductivity up to 6.5 S m^{-1} with excellent strain sensitivity. The exceptional combination of mechanical properties and conductivity makes the PVA organo-hydrogel a promising flexible electronics material. In addition, the FASS strategy can also endow hydrogels with multi-functions, including thermo-healability, freezing tolerance and shape recoverability, and can be applied to various hydrogel materials, such as carboxymethyl cellulose, sodium alginate, and chitosan. Hence, this work provides an all-around solution for preparing advanced strong and tough conductive soft materials for a multitude of applications.

9:00 AM SB09.07.03
Intrinsically Conducting Polymers Self-Adhesive to Dry and Wet Skins as Compliant Dry Electrodes for Long-Term Motion-Robust Epidermal Biopotential Monitoring Jianyong Ouyang; National University of Singapore, Singapore

Epidermal biopotential monitoring such as ECG, EMG and EEG can provide vital health information, and they are popularly used in clinic. However, they cannot be used for long-term healthcare monitoring because of the conventional electrodes. Wearable dry electrodes are needed for long-term biopotential recordings but are limited by their imperfect compliance with the skin, especially during body movements and sweat secretions, resulting in high interfacial impedance and motion artifacts. Here, I will report compliant dry electrodes made of an intrinsically conductive polymer that can have excellent self-adhesiveness to both dry and wet skins, high mechanical stretchability, high conductivity, and good biocompatibility. They can show much lower skin-contact impedance and noise in static and dynamic measurement than the current dry electrodes and standard gel electrodes, enabling to acquire high-quality ECG, EMG and EEG signals in various conditions such as dry and wet skin and during physical movements. Hence, these dry electrodes can be used for long-term healthcare monitoring in complex daily conditions.

9:15 AM *SB09.07.04
Mechanically Transformative Electronics as Bio-Interfaces Jae-Woong Jeong; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Conventionally, electronics are constructed with invariant form factors to serve targeted applications. For example, recent soft wearable and implantable electronics are designed to allow dynamic accommodation of applied stress to maximize user comfort and biocompatibility when integrated with the body. In contrast, the traditional consumer electronics are made flat and stiff to offer solid interfaces for easy user handling and interaction. However, the fixed mechanical properties of both types of electronics make them highly target-specific, limiting their broad use in a more compliant manner.
To overcome the fundamental limitation of these current electronics, we developed a new class of device systems, referred to as ‘transformative

electronics', that can reconfigure their shape, flexibility and stretchability for desired purposes. Transformative electronics are realized by integrating flexible, stretchable electronics with a variable-stiffness platform built using a composite of liquid metal gallium and soft elastomer. Utilizing temperature-triggered solid-liquid phase transition of gallium, these electronics can make on-demand conversion between the rigid and the soft modes, thus leveraging advantages of both forms of electronics. We have investigated applicability of this novel technology to promote interfaces between electronics and biological organs. For example, for the skin, we developed a transformative wearable system capable of rapid reversible mechanical switching, which allows the user to utilize it as both a rigid handheld electronic device and a flexible skin-mounted biosensor for improved versatility. For interfaces with internal organs such as the brain and the blood vessel, we employed the property of the gallium-based devices that can tune their stiffness and shape based on body temperature (above 30 °C). Based on this, we established neural probes and intravenous needles that softens upon penetration into tissue, which can significantly reduce inflammatory response in the injected site compared to the rigid devices with similar dimensions. Our proof-of-concept experiments and studies prove the potential of transformative electronics for biological interfaces, which may open new opportunities for diverse applications including wearables, implantables, robotics, and prosthetics.

9:45 AM SB09.12.05
Fabrication of Soft Biobatteries for Powering a Biomedical Sensor Patch Mahya Karamimosammam[1,2], Doris Danninger[1,2], David Schiller[1,2] and Martin Kaltenbrunner[1,2]; [1]Johannes Kepler University Linz, Austria; [2]Linz Institute of Technology, Austria

Many modern medical therapeutic and diagnostic operations are assisted by electronic devices. However, integrating these devices into biomedical systems attached to human organs or skin relies on their flexibility and biocompatibility to adapt to living tissues and deformations. Besides, environmental pollution caused by the rapid increase in tech wastage and improper disposal of them makes degradable electronics indispensable. Addressing these requirements necessitates the development of new materials and methods for fabricating a new generation of soft bioelectronics. Consequently, the fabrication of power sources that withstand the high-power demand of modern bioelectronic devices is of crucial importance. We introduce a new approach for fabricating not only biocompatible but wholly biodegradable batteries as entirely stretchable systems. Here, a concept for merging intrinsically stretchable gels with engineered stretchability through kirigami patterning for the realization of high-power biodegradable batteries with reversible elasticity of up to 35% for uniaxial strain and 20% for biaxial strain is demonstrated. A combination of molybdenum metal foils, a molybdenum trioxide paste, and magnesium metal foils as electrode materials provide a peak power output of 196 μW cm^{-2} and an energy density of 1.72 mWh cm^{-2}. A biomedical sensor patch on the skin for monitoring sodium levels in sweat is powered by biodegradable batteries. An adjustable pathway for high-power biodegradable batteries that enable unbound soft electronics in a sustainable future is offered by this concept.

10:00 AM BREAK

10:30 AM SB09.07.06
Adhesive-Free Hydrogel Bioelectronics Enabled by a Template-Directed Assembly of Metallic Nanofibrous Network Jooyeun Chong and Jiheong Kang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Over the past decade, conductive hydrogels have received great attention as tissue-interfacing electrodes due to their soft and tissue-like mechanical properties. However, a trade-off between robust tissue-like mechanical properties and good electrical properties has prevented the fabrication of a tough, highly conductive hydrogel and limited its use in bioelectronics.
Here, I present a new synthetic method for the realization of highly conductive and mechanically tough hydrogels with tissue-like modulus. I employed a template-directed assembly method, which enables the arrangement of a disorder-free, metallic nanofibrous conductive network inside a highly stretchable hydrogel network. The resultant hydrogel exhibits exceptionally high conductivity (247 S/cm), high stretchability (>600%), and tissue-like Young's modulus (35 kPa). Furthermore, it can provide tough adhesion (800 J/m2) with diverse dynamic wet tissue after chemical activation. In addition, its biocompatibility in vivo was confirmed, which makes our hydrogel an ideal bio-interfacing electrode for bioelectronics. For the first time, this hydrogel enables suture-free and adhesive-free, high-performance hydrogel bioelectronics. I successfully demonstrated ultra-low voltage neuromodulation and high-quality epicardial electrocardiogram (ECG) signal recording based on in vivo animal models. This template-directed assembly method provides a new platform for hydrogel interfaces for various bioelectronic applications. I will discuss the details of the synthesis of T-ECH and its application for adhesive-free hydrogel bioelectronics.

10:45 AM SB09.07.07
A Highly Stable Electrode with Low Electrode-Skin Impedance for Wearable Brain-Computer Interface Huiliang Wang; The University of Texas at Austin, United States

To date, brain-computer interfaces (BCIs) have proved to play a key role in many medical applications, for exam- ple, the rehabilitation of stroke patients. For post-stroke rehabilitation, the BCIs require the EEG electrodes to precisely translate the brain signals of patients into intended movements of the paralyzed limb for months. How- ever, the gold standard silver/silver-chloride electrodes cannot satisfy the requirements for long-term stability and preparation-free recording capability in wearable EEG devices, thus limiting the versatility of EEG in wear- able BCI applications over time outside the rehabilitation center. Here, we design a long-term stable and low electrode-skin interfacial impedance conductive polymer-hydrogel EEG electrode that maintains a lower imped- ance value than gel-based electrodes for 29 days. With this technology, EEG-based long-term and wearable BCIs could be realized in the near future. To demonstrate this, our designed electrode is applied for a wireless single- channel EEG device that detects changes in alpha rhythms in eye-open/eye-close conditions. In addition, we vali- date that the designed electrodes could capture oscillatory rhythms in motor imagery protocols as well as low- frequency time-locked event-related potentials from healthy subjects, with better performance than gel-based electrodes. Finally, we demonstrate the use of the designed electrode in online BCI-based functional electrical stimulation, which could be used for post-stroke rehabilitation.

11:00 AM SB09.07.08
An Integrated ECoG and Depth Electrodes for Signal Monitoring and Deep Brain Stimulation Treatment of Epilepsy Na Xiao[1,2,3], Tao Zou[1,2], Gary Kwok Ki Chik[1,2], Chung Tin[3] and Paddy K. L. Chan[1,2]; [1]The University of Hong Kong, China; [2]Advanced Biomedical Instrumentation Centre, Hong Kong; [3]City University of Hong Kong, Hong Kong

Epilepsy is a central nervous system disorder in which brain activity becomes abnormal, causing seizures or periods of unusual behavior, sensations, and sometimes loss of awareness and even sudden death. It affects more than 65 million people worldwide. Deep brain stimulation (DBS) has been approved to be effective means of seizure control for patients with drug-resistant seizures. However, traditional metal neural probes used for monitoring the neural signal and delivering electrical stimulation have significant disadvantages in poor conformability, risk of tissue damage, long-term stability issue and etc. Soft-material based electrode array has emerged as a promising alternative to metal probes for their small size, biocompatibility, and more importantly, their flexibility and conformability.
Here we designed a multifunctional device that has 16-channel ECoG electrodes and 16-channel depth electrodes for both neural signal monitoring and real-time DBS delivery. The electrodes were fabricated with gold as conducting layer and parylene as the supporting layer, coated with PEDOT:PSS to

reduce the impedance and increase the charge injection capacity and pHEMA to enhance the bio-compatibility. Our device allows multiscale electrophysiological recording in vivo. In the experiment, the ECoG electrodes were placed on the surface of the brain cortex for sensing the ECoG signals and the depth electrodes were implanted into the hippocampus region to record the single neuronal spike and local field potential (LFP), as well as deliver electrical stimulation. The results show that we were able to acquire high-quality ECoG, LFP and spikes signals from both acute and chronic epileptic rat models under anesthesia or awake. We also showed that the electrical stimulation delivered to the hippocampus region through our device effectively suppressed the seizures in these animals.

11:15 AM *SB09.07.09
Wound-Integrated Bioelectronic Sensors with Polymeric Electronics John S. Ho; National University of Singapore, Singapore

Monitoring surgical wounds is essential to prevent infection and other complications. However, current clinical monitoring is typically limited to indirect observations or costly diagnostic investigations that often fail to detect complications before they become severe. In this talk, I will describe wound-integrated bioelectronic sensors based on polymeric electronic materials that provide continuous wireless monitoring of both surface wounds and deep surgical sites. First, I will introduce multifilament surgical sutures functionalized with a conductive polymer that can be operated via radiofrequency identification and used to monitor physicochemical states deep in the body. Next, I will discuss a wireless and battery-free sensors that provides smartphone-based detection of wound infection using a bacteria-responsive DNA hydrogel. In vivo experiments in both small and large animal models highlight the ability of these sensors to integrate seamlessly with wounds and enable the early detection of complications. Wound-integrated bioelectronic sensors may facilitate post-surgical monitoring in a wide range of interventions and improve clinical outcomes.

SESSION SB09.08: Wearable Bioelectronics II

Session Chairs: Lihua Jin, Jia Liu, Zhiyuan Liu and Jin Young Oh
Thursday Afternoon, April 13, 2023
Moscone West, Level 2, Room 2022

1:45 PM SB09.08.01
Stretchable Semiconductor Metallization for Skin-Like Organic Transistors Jin Young Oh, MinWoo Jeong, Jun Su Kim, Tae Uk Nam and Ngoc Thanh Phuong Vo; Kyung Hee University, Korea (the Republic of)

Despite recent remarkable advances in stretchable organic thin-film field-effect transistors (OTFTs), the development of stretchable metallization remains a challenge. In this talk, I present a highly stretchable and robust silver (Ag) metallization on an elastomeric semiconductor film based on metal-polymer intermixing. Ag atoms have a high diffusivity in polymers, which results in the formation of intermixing layer consisted of Ag nanoclusters and polymer chains during thermal evaporation, providing strong adhesion to the metallized Ag film. The Ag metallization maintains a high conductivity ($>10^4$ S/cm) even under 100% strain and successfully preserves its conductivity without delamination even after 10,000 stretching cycles at 100% strain and several adhesive-tape tests. Moreover, a native silver oxide layer formed on the intermixed Ag clusters facilitates efficient hole injection into the elastomeric semiconductor, which transcends previously reported stretchable source and drain electrodes for OTFTs.

2:00 PM SB09.08.02
Conducting Polymers for Neurostimulation Gerwin Dijk, Adam Marks and Alberto Salleo; Stanford University, United States

Microelectrodes for high resolution neurostimulation enable therapies and treatments for a variety of neurological disorders and diseases. To enhance the electrochemical interface and ensure sufficient charge injection capabilities, microelectrodes are commonly coated with organic mixed ionic-electronic conductors (OMIECs) that provide a volumetric interaction with the electrolyte. Despite the accelerated development of a large variety of OMIECs, PEDOT:PSS is almost exclusively used as an electrode coating material and is favored for its commercial availability, electrical conductivity, stability and processability. Other OMIECs with different electronic-ionic transport and coupling properties have been characterized and benchmarked for organic electrochemical transistors by determining the product of the electronic mobility and the volumetric charge storage capacitance (μC^*), however, remain largely unexplored in the context of neurostimulation.

In this work, we investigated various OMIECs for neurostimulation applications. The materials are examined with electrochemical methods and pulse experiments to determine typical performance parameters such as the electrode impedance, charge injection limit and stability. Furthermore, the observed performance parameters are linked to the OMIEC specific transport and electronic-ionic coupling properties. The results reveal which OMIEC properties are crucial for optimal performance of microelectrodes and provide guidelines that aid the development of OMIECs for electrical stimulation applications.

2:15 PM SB09.08.03
Long-Term Comfortable Skin Electrodes Based on Conductive Microfiber Mesh and Ion Gel Composites Jongwon Lee and Myung-Han Yoon; Gwangju Institute of Science and Technology, Korea (the Republic of)

With the development of Internet of Things and artificial intelligence technologies, various machines have become an inseparable part of human life. Accordingly, while the importance of interaction via information transfer between machines and humans has increased, the development of suitable skin electrodes have received considerable attention. However, most of commercial skin electrodes exhibit uncomfortable fit and unfavorable look for long-term usage. Herein, we report on a novel gas-permeable highly-transparent skin electrode based on the composite made of grid-type PEDOT:PSS microfiber mesh and PVA-PAA nanofiber ion gel which were prepared by self-fusion and electrospinning, respectively. The fabricated composite skin electrodes showed thin nominal thickness, good optical transparency, and high gas permeability which afforded users comfortable fits. Furthermore, they showed low electrochemical impedance, thus, excellent performance in terms of electromyography recording comparable to those of commercial Ag/AgCl electrodes. We expect that the present gas-permeable highly-transparent skin electrode based on grid-type PEDOT:PSS microfibers will spur the development of many different types of user-friendly human machine interfaces which require both electrochemical performance and aesthetic aspects, particularly, for skin/face attachment.

2:30 PM BREAK

3:30 PM SB09.08.05
Connecting Nanoscale Heterogeneity and Bulk Performance in Organic Mixed Conductors for Bioelectronics Seth Jackson, Garrett W. Collins,

Arnel Besic and Connor G. Bischak; The University of Utah, United States

Developing the next generation of bioelectronics interfaces requires understanding the underlying structure-function relationships in polymeric materials that dictate device performance. Organic mixed ionic-electronic conductors (OMIECs) have emerged as promising materials for bioelectronics and biosensors. The performance of these materials depends on a complicated relationship between ion motion, electron transport, and structural dynamics. Here, we interrogate coupled ionic-electronic-structural dynamics in OMIECs using a suite of spectroscopic and electrochemical methods. We show that structural changes in OMIECs are often complex, resulting in disorder-to-order transformations upon repeated electrochemical cycling. We also demonstrate that heterogeneity at the nanoscale impacts OMIEC performance and map the distribution of ions in OMIECs using nanoscale infrared imaging with photoinduced force microscopy. Our results demonstrate the need to understand structural heterogeneity and dynamic processes at the nanoscale in OMIECs to develop design principles for next-generation materials.

3:45 PM SB09.08.06
Stretchable, Skin-Adherent Piezoelectric Patch with Hierarchically Bio-Inspired Architectures for Energy Amplification Seung Hwan Jeon[1], Hyunseng Kim[2], Da Wan Kim[1], Chang Kyu Jeong[2] and Changhyun Pang[1]; [1]Sungkyunkwan University, Korea (the Republic of); [2]Jeonbuk National University, Korea (the Republic of)

Recently, the piezoelectric energy harvester with advantages including high-power density, simple design, and high scalability under low strain changes has emerged as an alternative to supply electrical energy to intelligent technologies such as wearable healthcare electronics, robots, and biomedical devices. However, the low adhesion between the wearable energy harvesting device and the biological skin interface has limited its ability to generate electrical energy from physical movements of the body. Here, we report a Stretchable skin-adherent piezoelectric patch with a hierarchically designed octopus-beetle inspired array (HOBA). HOBA is composed of adhesion layer, stretchable electrode, and piezoelectric energy composite. Each layer is based on a polymer material, which helps HOBA to be monolithic and has excellent mechanical stability between layers. The adhesion layer has high normal adhesion and shear adhesions in rough skin. Stretchable electrodes with a wrinkle structure show stable electrical conductivity even in omnidirectional stretching and bending. The energy composite layer is based on a lead-free material that can be used on the human body and has a constant power density of 1.52 W/cm^3 in repeated bending (150°). Finally, our energy patch shows potential for use as a self-powered sensor for monitoring muscle movement and finger movement for medical applications.

SESSION SB09.09: Poster Session II
Session Chairs: Lihua Jin, Jia Liu and Zhiyuan Liu
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SB09.09.01
Enhancing Ion Injection Kinetics in Organic Mixed Ionic-Electronic Conductors by Balancing Crystalline and Amorphous Regions Seth Jackson and Connor G. Bischak; The University of Utah, United States

Organic mixed ionic-electronic conductors (OMIECs) have emerged as promising materials for an array of next-generation devices, including bioelectronics interfaces, neuromorphic computing platforms, and energy storage modules. To advance these technologies, we need to uncover the structure-function relationships in OMIECs that underlie device performance. Here, we study poly(3-hexylthiophene) (P3HT), a common conjugated polymer, and how its crystallinity affects ion injection kinetics by blending a regioregular (RR) P3HT and a regiorandom (RRa) P3HT. Using steady-state and time-resolved spectroelectrochemistry, we show that a 75:25 RR:RRa blend of P3HT has faster ion injection kinetics than that of pure RR P3HT and pure RRa P3HT, indicating a potential "Goldilocks ratio" between crystalline and amorphous polymer content that maximizes ion injection kinetics. We also find using steady-state spectroelectrochemistry that positively charged holes initially dope crystalline regions of the polymer before doping the amorphous regions. Using grazing incidence wide-angle x-ray scattering (GIWAXS), we see the negatively charged ions enter the polymer film at the same potential the positively charged holes form. Taking a closer look at the time-resolved spectroelectrochemistry results, we notice a hysteresis effect in doping and dedoping P3HT, signifying that doping and dedoping are occurring through different pathways. We image the distribution of ions in the P3HT films using nanoscale infrared imaging with photo-induced force microscopy (PiFM) of an infrared-active ion. From these images, we see an increase in ion heterogeneity in the blended P3HT films as we increase the crystalline content. Overall, these results highlight the importance of balancing crystalline and amorphous regions in organic mixed conductors to enhance ion injection kinetics and the importance of connecting bulk performance with nanoscale heterogeneity.

5:00 PM SB09.09.02
Ultrasoft Stretchable Electronics for Stable and Imperceptible Integration with Soft, Dynamic Bio-Tissues Yang Li, Nan Li, Yahao Dai and Sihong Wang; The University of Chicago, United States

Interfacing electronics with the human body as wearable or implantable devices provides a large collection of functions in health monitoring, disease treatment, and even basic biological studies. To achieve seamless and compatible interfacing, it is imperative to minimize the mechanical mismatch between electronic devices and human skin/tissue. Hydrogels and ultrasoft silicones have been utilized due to their extraordinary performance in stretchability and softness. However, building complex electronics on top of such ultrasoft materials remains challenging because of the mismatched mechanical properties with highly rigid, electrically functional materials, which further introduces problems to the interface, as well as the fabrication process. To achieve stretchable electronic devices with ultralow Young's modulus, here, we present a generalizable soft interlayer design that can effectively solve the challenge of using existing electrically functional materials with high modulus to build the tissue-level-modulus devices (e.g., transistors, active matrix, sensors) with high stretchability. When the soft interlayer is inserted in between the high-modulus functional layers and ultrasoft substrate, interfaces within the device are improved by decreasing the modulus mismatch and enhancing interfacial toughness. We successfully demonstrated stretchable conductive interconnections with high stretchability and ultralow modulus based on conventional high modulus materials (CNTs, AgNWs and PEDOT: PSS composite). Also, a transistor device with Young's modulus of 6.7 kPa is fabricated, which can be stretched up to 100% strain. Furthermore, a 5x5 transistor array device on patterned soft interlayer and hydrogel substrate can even achieve a lower modulus of 3.6 kPa, which is 3 orders of magnitude softer than previously reported stretchable transistor arrays on SEBS substrate. Benefiting from the tissue-level softness, our electronic devices demonstrate highly stable and imperceptible integration with soft bio-tissues with nonzero Gaussian surfaces. Besides, combined with the high stretchability, the ultrasoft electronic devices further promote concurrent deformation on bio-tissues, causing less immune response when implanted.

5:00 PM SB09.09.03
Probing the Initial Steps in Electrochemical Doping of Organic Mixed Conductors with Photoluminescence Quenching Garrett W. Collins and Connor G. Bischak; University of Utah, United States

Organic mixed ionic-electronic conductors (OMIECs) are conjugated polymers that conduct electrons and ions. Due to their mixed conductivity, OMIECs are promising materials for many applications, including bioelectronics, electrochemical energy storage, neuromorphic computing, and supercapacitors. OMIECs function through electrochemical doping, in which an electrical charge is injected into the polymer matrix, and a complementary ion from an adjacent liquid electrolyte enters the polymer matrix to compensate for the electronic change. As OMIECs become more prevalent, new characterization techniques are needed to understand their structure-function relationships. Photoluminescence measurements as a function of voltage are much more sensitive to small concentrations of dopants, as well as changes in the polymer morphology associated with ion intercalation and hydration, compared to other characterization methods. We performed *in situ* photoluminescence measurements on two different polythiophenes with ethylene glycol-based side chains, poly(3-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}thiophene-2,5-diyl) (P3MEEET) and poly(3-{[2-(2-methoxyethoxy)ethoxy]methyl}thiophene-2,5-diyl) (P3MEEMT). Potassium salts of bromide (KBr), chloride (KCl), perchlorate ($KClO_4$), bis-(trifluoromethanesulfonyl)imide (KTFSI), and hexafluorophosphate (KPF_6) were the electrolytes of choice, as they span the Hofmeister series. It was found that as the voltage increases, the photoluminescence of the OMIEC is quenched due to the presence of polaron-ion pairs in the material. Results indicate that the voltage at which quenching first occurs depends on the identity of the ion and the polymer side chains. These changes in photoluminescence are compared to other processes that occur during electrochemical doping, such as absorption spectroelectrochemistry, electrochemical quartz crystal microbalance (EQCM), and *in situ* grazing incidence wide-angle X-ray scattering (GIWAXS), to determine how photoluminescence quenching correlates to other dynamic processes in OMIECs.

5:00 PM SB09.09.04
Direct Electrical Biointerfacing with Adhesive and Stretchable Polymer Semiconductors Nan Li and Sihong Wang; University of Chicago, United States

Polymer semiconductors have shown distinct promise for merging human-machine interface, owing to their solution processability and soft mechanical nature. Organic electrochemical transistors (OECTs) as an advanced type of sensing devices, are highly desired for direct electrical biointerfacing due to their low operation voltage, high sensitivity and signal-to-noise ratio. To interface with wet and dynamically moving tissues, for example, heart, brain, or sciatic nerve, conventional suturing causes tissue/device damage and cannot achieve good conformability; having the adhesive property will ease the attachment process and help achieve a conformable contact and high spatial sensing resolution. So far, however, to the best of our knowledge, none of the existing high-performance polymer semiconductors are adhesive owing to a number of challenges, which prevent OECTs from achieving direct and conformable electrical interfacing with wet and dynamically moving biotissues.

Here, we develop an intrinsically adhesive and stretchable semiconducting polymer by creating a rationally designed polymer network with interpenetrating semiconducting polymers and adhesive brush polymers to realize both high normalized maximum transconductance (~100 siemens per centimeter) and good adhesion on wet biotissues (interfacial toughness ~35 joules per square centimeter). Benefiting from the brush polymer design, the semiconducting polymer network possesses soft and viscoelastic mechanical properties (Young's modulus ~10 kilopascal) comparable to biotissues, moderate water absorption (30 %), controllable swelling (<10 %), and abundant tissue-reactive groups (-COOH and -NHS), which synergically contribute to the adhesion on wet tissue surfaces. In addition, the semiconducting material shows abrasion-resistance and high stretchability above 100 % strain, which lead to the robust electrical performance. Also, the material presents good biocompatibility owing to low mechanical strain. Furthermore, enabled by the compatibility of the adhesive polymer with solution processing, we fabricated an intrinsically adhesive and stretchable OECT with the adhesive semiconducting polymer as both the active channel and gate and further demonstrated its use for monitoring electrophysiological signals consistently and reliably on wet heart surfaces even under perturbation scenarios.

5:00 PM SB09.09.05
Conductive Hydrogel Nerve Guidance Conduits with NGF-Gradient for Peripheral Nerve Repair in Diabetics Yuting Cai and Zhengtang Luo; The Hong Kong University of Science and, Hong Kong

Owing to hyperglycemia and microvascular complications, diabetics suffer from segmental axon demyelination and slow repair of injured nerves and result in motor function loss, muscle paralysis, and even life-long disability. Besides, autologous nerve transplantation which is the gold choice for repair is bothered by the poor size match between the donor and the acceptor and limited source of the donor. Therefore, multifunctional nerve guidance conduits for diabetics are proposed as an alternative. This study demonstrates a graphene-based nerve guidance conduit by integrating natural double network hydrogel and a neurotrophic concentration gradient. Wet-adhesive design of conduit can not only wrap and adhere to the injured nerve rather than suture, but also provide protection for the injured nerve and accelerate regeneration. The novel design of GelMA/silk fibroin double network hydrogel plays quadruple role for rapid setting/curing, strong mechanical-supporting, superior biocompatibility, and sustainable growth factor delivery. Additionally, encapsulated graphene mesh not only can enhance the mechanical strength of tube but also promote the regeneration of peripheral nerve and muscle fibers. Importantly, silk tapes achieve long-term and tough adhesion with wet surface via constructing the mechanical interlocking followed by covalent bonds. The histological staining reveals that conduits with gradient concentration of netrin-1 have better performance than uniform concentration for axon extension, remyelination, and angiogenesis which may cause by chemotaxis phenomenon. All in all, the new guidance conduit with gradient netrin-1 and adhesive design can enormously promote repair of peripheral nerve and prevent the atrophy of muscles for diabetics.

5:00 PM SB09.09.06
Ultra-tough, Highly Conductive and Electrochemically Stable Solid Electrolytes for Accurate Detection of Mechanical Motion Minsu Kim, Jeong-hui Kim, Kyung Gook Cho and Keun Hyung Lee; Inha University, Korea (the Republic of)

As a promising candidate of next-generation solid-state electrolytes for electrochemical devices, polymer gel electrolytes face two important challenges: insufficient mechanical toughness and low ionic conductivity compared to liquid electrolytes. To overcome these limitations, various methods of solidifying ionic liquids and fabricating the tough ionogel electrolytes have been suggested. Herein, we report the fabrication of physically crosslinked ionogels by utilizing phase separation of a semicrystalline homopolymer swollen in ionic liquids. The crystalline domains that serve as the network junction points were formed by solvent exchange and dissipates enormous energy upon application of external stress. The ionogels exhibited excellent mechanical properties including very high toughness (~ 46.24 MJ m^{-3}), and stretchability (~ 2135 %). Simultaneously, the ionogels possessed outstanding electrochemical performance, including high ionic conductivity (as high as 20 mS cm^{-1}) and wide electrochemical windows (~ 3 V). By using the ultra-tough ionogels as a piezoelectric sensing element, stretchable strain sensors were successfully fabricated to accurately detect mechanical movements of automobile parts. Overall, these results provide a new direction to fabricate tough ionogels for widespread electrochemical/electronic device applications.

5:00 PM SB09.09.07
Hydrogel Based Anisotropic Conductive Film (H-ACF) for Versatile Electrical Interfacing in Soft Electronics Yurim Lee, Yejin Jo and Jungmok

Seo; Yonsei University, Korea (the Republic of)

Electronic packaging, which attaches electronic elements to the substrate and connects the circuits, has developed from soldering to anisotropic conductive film (ACF). ACF is a mixture of conductive particles and an adhesive for making electrical connections only in the vertical direction. Thus, it prevents short-circuiting with neighboring circuits and can form a more concentrated electrical connection to circuits compared to the previous packaging technology. However, the conventional ACF has a limitation in that it is inappropriate for interconnecting elastic material, which has become more problematic as soft electronics have received attention as an interface to connect electronic devices to the human body. Because the electrical connection between integrated circuits (ICs) embodied on the flexible printed circuit boards (FPCBs) and soft electronics is necessary to perform the advanced function. Therefore, more investigations have been demanded to develop advanced ACF that is capable of electrically connecting various materials like stretchable polymer and moist hydrogel to electronics.
In this study, a hydrogel-based anisotropic conductive film (H-ACF) is designed for material-independent interconnection between electronic parts. H-ACF is composed of stacked poly (vinyl alcohol) (PVA) with conductive particles and tannic acid (TA) layers. PVA is non-toxic and one of the well-used hydrogel adhesives. So, it serves as the primary adhesive containing conductive particles. TA enhances hydrogel mechanical properties by acting as a crosslinker of PVA. Also, TA makes the film to adhere to the substrate regardless of the surface properties due to its abundant hydroxyl groups.
Based on these features of the components, H-ACF enables rapid (>1 min) and strong bonding (<1.5 MPa), which is essential for consistent connection even in harsh conditions with mechanical. Also, H-ACF can allow bonding between bumps on rigid PCBs and soft stretchable materials including polydimethylsiloxane (PDMS) and hydrogels. Particularly, the hydrogel can be adhered to the H-ACF by entangling the chains with the linkers of the film, which enables a heat-free bonding process. We confirmed that H-ACF has comparable electrical performance with conventional ACF, which is explained by low connection resistance and excellent insulation value.

5:00 PM SB09.09.08
Ionically Conductive, Soft Neural Interface for Non-Faradaic Neurostimulation Bokyung Kim[1], Joo Sung Kim[1], Junho Kim[2], Jun Woo Lim[3], Dong Jun Kim[1], Jihong Kim[1], Jae Hyun Jeong[3], Sung-Min Park[2,2] and Do Hwan Kim[1,1]; [1]Hanyang University, Korea (the Republic of); [2]Pohang University of Science and Technology, Korea (the Republic of); [3]Soongsil University, Korea (the Republic of)

Despite extensive clinical and biomedical research, optimal treatment of prominent neurological disorders is not fully established. Deaths per neurological disorder have perpetually increased, becoming a global burden today. Implantable neural prostheses with enormous potentials, such as spinal-cord stimulators, deep-brain stimulators, and vagus nerve stimulators are used for the effective therapeutic approaches in this field. Most stimulating metal electrodes in direct contact with the neural system use platinum or iridium oxide, which have low bulk resistance and high charge injection capability. However, conventional metal electrodes are prone to the mechanical mismatch of the neural interface between hard solid metal and soft tissue. Research on implantable neurostimulators using soft conductors based on conducting polymers and hydrogels is surging to overcome this limitation. However, both the faradaic charge injection in the conducting polymers, which results in the gas evolution, and ion diffusion in hydrogels, which leads to loss of biomolecule, cause neurological disorders.
In this talk, we propose a soft ionic neural interface design for highly stable neuromodulation using a non-faradaic charge injection mechanism. The ionic neural interface serves as a bioadhesive, based on biocompatible multi-crosslinked membrane–ionogel assembly (McMiA) soft electrodes. Importantly, we incorporated a crosslinked graphene oxide (X-GO) membrane and a crosslinked biopolymeric ionogel (X-BI) conductor onto metal electrode-coated flexible substrates. Contrary to conventional bioelectronics neural interfaces, the ionic neural interface allows neurostimulators to provide a non-faradaic charge injection because of the wide electrochemical potential window without undesirable electrochemical reactions even under high voltage conditions. In addition, the distorted ion-diffusion pathway of the GO membrane prevents ion exchange at the neural interface in physiological-relevant conditions. Our results corroborate the biological signaling processes starting from the sciatic nerve using Myoblast fusion in cultured muscle cells. Eventually, we developed a peripheral neurostimulator based on the ionic neural interface to control overactive bladder syndrome and performed proof-of-concept tests using a rat model. We believe that our bioadhesive ionic neural interface can provide a direct connection between the fields of electronics and biology for the design of next-generation implantable devices.

5:00 PM SB09.09.09
Electrically Induced Bursting of Aqueous Capsules Made from Biopolymers— 'Switching On' the Release of Payloads Wenhao Xu, Ankit Gargava and Srinivasa R. Raghavan; University of Maryland, College Park, United States

The use of electric fields to stimulate the delivery of drugs or other active ingredients is of great interest for wearable electronics and other applications. Most attempts at electrically induced delivery with soft materials in water have focused on electronically conducting polymers (e.g., polypyrroles) or conductive nanocomposites (e.g., polymers with carbon nanotubes). Here, electrical responses are induced even in structures made from nonconducting biopolymers that are widely available, biocompatible, and biodegradable. The materials studied here are spherical capsules created from the anionic polysaccharide alginate by cross-linking with cations like Ca^{2+} or Cu^{2+}. When these capsules are placed in an aqueous solution and subjected to an electric field (direct current) of ≈8 V/cm, they deform within a couple of minutes and then burst and disintegrate into pieces within ≈5 min. Capsules across a range of length scales (200 μm to 2 cm) respond in the above manner, and the electroresponse persists even if the capsules are embedded in a nonionic gel matrix. This electroresponse is due to electrophoretic migration of charged species (ions and/or polyelectrolyte chain-segments) within (or out of) the capsules. In an alginate capsule, the cations are induced to migrate away from the positive electrode, which creates a weakly cross-linked region of the capsule that swells appreciably. This anisotropic swelling continues until the capsule eventually bursts. Applications for electroresponsive capsules that highlight the spatial and temporal accuracy possible with an electrical stimulus are discussed. The bursting of capsules can be used to release solutes loaded inside these structures. Also, even the deformation of intact capsules can be used to create electrically actuatable valves, where a liquid flows out through the valve only when a capsule plug is dislodged.

5:00 PM SB09.09.10
The Effect of Polyethylene (glycol)diacrylate Post-fabrication Rest Time on Compressive Properties Ozlem Yasar and Najvan Kased; City University of New York, United States

Tissue Engineering has been studied to develop an alternative way to organ transplantation. Choosing the right type of biomaterials, cell sources, growth factors, and engineered scaffolds determine the success rate of Tissue Engineering. In this research, poly(ethylene glycol) diacrylate (PEGDA) is used to fabricate the scaffolds as it is a biocompatible and biodegradable material, and its porous microstructure help cells to breathe.

In this research, we studied how the mechanical properties of different concentrations of PEGDA change with the post-fabrication ageing time. Cylindrical PEGDA samples were prepared at 20%, 40%, 60%, 80%, and 100% concentrations and cured under UV light. After the solidification process, the weight of each sample was monitored every 0, 2, 4, 6, and 24 hours post-fabrication ageing time until the mechanical testing. Compressive elastic modulus and strength were calculated and statistically analyzed. Our results indicated that the water content of each PEGDA group constantly decreased over time, however, this loss significantly affected the elastic modulus and strength only after 6 hours in some PEGDA concentrations.

In recent years, tissue engineering has been utilized as an alternative approach for the organ transplantation. The success rate of tissue regeneration is influenced by the type of biomaterials, cell sources, growth factors and scaffold fabrication techniques used. The poly(ethylene glycol) diacrylate (PEGDA) is one of commonly used biomaterials because of its biocompatibility, ease of use, and porous microstructure. The mechanical properties of PEGDA have been studied to some extent by several research groups. However, the stability of the mechanical properties with time has not been investigated.
In this research, we studied how the mechanical properties of different concentrations of PEGDA change with the post-fabrication ageing time. Cylindrical PEGDA samples were prepared 20%, 40%, 60%, 80%, and 100% concentrations and cured under the UV light. After the solidification process, weight of each sample was monitored in every 0, 2, 4, 6, and 24 hours post-fabrication ageing time until the mechanical testing. Compressive elastic modulus and strength were calculated and statistically analyzed. Our results indicated that the water content of each PEGDA group constantly decreased by time, however, this loss significantly affected the elastic modulus and strength only after 6 hours in some PEGDA concentration.

5:00 PM SB09.09.11
Amphiphilicity-Driven Polymer Assembly Enables Performance Enhancement in n-Type Organic Electrochemical Transistors Dahyun Jeong[1], Il-Young Jo[2], Seungjin Lee[1], Ji Hwan Kim[2], Youngseok Kim[2], Donguk Kim[1], John R. Reynolds[3], Myung-Han Yoon[2] and Bumjoon Kim[1]; [1]Korea Advanced Institute of Science and Technology (KAIST), Korea (the Republic of); [2]Gwangju Institute of Science and Technology (GIST), Korea (the Republic of); [3]Georgia Institute of Technology, United States

A series of naphthalene diimide-based polymers incorporated with branched oligo(ethylene glycol) (OEG) side chains are developed to enable eco-friendly-processed, high-performance n-type OECTs. The OEG side chains afford processability in ethanol/water solvents. Importantly, taking advantage of the amphiphilicity of OEG-based polymers, ethanol/water solvents selectively solvate hydrophilic OEG side chains, while producing tight π–π stacks of hydrophobic backbones. This enables highly edge-on-oriented polymer packing, and thus excellent lateral charge transport. In particular, the fine-tuned OEG side chains of P(NDIMTEG-T) provide compact backbone packing, effective polaron generation, and superior electrochemical stability. The resultant OECT shows the best electrical/electrochemical performance, represented by a figure-of-merit (μC^*) of 0.56 F V^{-1} cm^{-1} s^{-1}. This study demonstrates the aqueous processing in OECTs and the design rule of n-type organic mixed ionic-electronic conductors.

5:00 PM SB09.09.12
Cellulose/Chitosan Composite Aerogel Based Triboelectric Nano-Generator for Harvesting Mechanical Energy Shadman Sakib; UTRGV, United States

Triboelectric nanogenerators have garnered much attention over recent years as the world continues advancing toward it's goals of green renewable energy and a more cohesive relationship with our environment. Every day small amounts of energy are lost in the form of mechanical energy as we move throughout our daily lives, triboelectric nanogenerators seek to use some of this otherwise lost mechanical energy for the purpose of powering small devices which would otherwise have to be powered using more costly and unsustainable sources of energy. Ideally these nanogenerators would be made of readily available, inexpensive, and safe natural materials which possess high mechanical and triboelectric properties. The goal of this research is to fabricate an aerogel made of cellulose and chitosan and reinforced with natural nanofiber materials for an increased level of mechanical strength and durability. While also generating enough electricity to power a small device or sensor. Currently it has been difficult to generate sufficient power via biiopolymer-based trio electric nano generators. Challenges in our research have been producing an aerogel which can produce a significant electrical charge through the triboelectric effect to harness mechanical energy as well as have the aerogel be durable and flexible enough to endure the daily wear and tear it must face as part of a person's clothing to make effective and practical nanogenerators which will power small embedded biosensors.
In our triboelectric layers high charge density is desired. This can be achieved with a combination of high surfac area(provided by porous nano fiber mats) and dopants with high electropositive and high electronegative charge affinities. We envision the sliding contact to be the main method for charge generation in this context. The high structural strength and flexibility will be provided by a porous, flexible aerogel/xerogel complex matrix structure. Medical applications for these (TENGs) are the goal of this research, the fruits of this research will go into producing TENGs for small medical devices which would otherwise have to be charged or be powered by external batteries which currently makes them expensive and impractical. Expecting mothers with high risk pregnancies have a very big concern when it comes to their fetuses and every minute counts especially when it comes to them. For these special cases a way to constantly monitor vital signs for their fetuses is crucial especially if something happens and there is a need for corrective action or a physician intervention. Our device would be flexible, safe and accurate to be embedded in everyday garments and used as a self powered tool to monitor their fetus's health in real time and be able to alert the mother when things are starting to get serious and their is an urgent need for medical attention.

5:00 PM SB09.09.14
Hole-Limited Electrochemical Doping in Conjugated Polymers Scott T. Keene[1], Joonatan Laulainen[1], Raj Pandya[1], Maximilian Moser[2], Christoph Schnederman[1], Paul Midgley[1], Iain McCulloch[2], Akshay Rao[1] and George G. Malliaras[1]; [1]University of Cambridge, United Kingdom; [2]University of Oxford, United Kingdom

Organic mixed ionic electronic conductors (OMIECs) have recently risen as a promising material choice for bioelectronic devices due to their low impedance, soft mechanical properties, and ability to transduce ionic signals to electronic currents. These materials properties have enabled the development of high-performance devices for electrophysiological recordings, chemical sensing, cell monitoring, energy storage, and neuromorphic devices. The unique behaviour of OMIECs arises from ion intercalation through the bulk of the material which can modify the oxidation state, and therefore charge carrier concentration, of the conjugated polymer backbone.

While the mixed conductors enabling these technologies are widely used, the dynamic relationship between ionic and electronic motion is generally poorly understood, hindering the rational design of new materials. In most semiconducting electrodes, mixed transport is assumed to be limited by motion of ions due to their large effective mass compared to electrons/holes. Here, we show that this basic assumption does not hold for conjugated polymer electrodes. Using *operando* optical microscopy to differentiate between ionic and electronic transport, we reveal that electrochemical doping in a state-of-the-art polythiophene is limited by hole transport. This hole transport-limited regime leads to substantially slower switching speeds than expected for electrochemical devices using otherwise high-performing materials. Structural characterisation reveals that the timescale of hole-limited doping can be controlled by the degree of heterogeneous disorder in the polymer microstructure. The hole-limited doping revealed in this work enables a deeper understanding of mixed conduction and informs the design of new mixed conducting polymers.

5:00 PM SB09.09.16
Capillary Force-Assisted CNT Microstructuring for Biomedically Applicable Flexible Microelectrode Array Kwangjun Kim[1], Minwook Kim[1], Hyunmin Baek[1], Hyeonhee Roh[2], Maesoon Im[2] and Jong G. Ok[1]; [1]Seoul National University of Science and Technology, Korea (the Republic of); [2]Brain Science Institute, Korea Institute of Science and Technology (KIST), Korea (the Republic of)

Interconnecting technologies for sensing neural signals are investigated with microscale needle or rod-shaped electrode array foams. In this regard, the first point is to design an electrode whose shape can be easily integrated with biological organs. Flexibility and electrical conductivity are the second and third requirements, respectively, to facilitate structural and electrical connections between the device and the biological organs. In many previous studies, the devices are made by using the top-down process for feasible fabrication, array formation, and device packaging, but in this case, high mechanical stiffness of materials (Si, SiC) is involved. Alternatively, a microelectrode array could be fabricated by developing specific novel approaches, in which case the inferior reproducibility is pointed out as a bottleneck. Addressing these issues, we have developed carbon nanotube (CNT) microstructures for flexible microelectrode arrays that can be readily fabricated by chemical vapor deposition (CVD) and densification process; the CMS (CNT microstructure) once reliably grown by CVD can be shaped into mechanically robust and electrically conducting microelectrodes through the capillary force-assisted densification postprocess. Essentially, CMS growth technology on micropatterned catalyst layer was optimized; a stable CMS growth with appropriate CNT density on a micropatterned catalyst layer was realized by the control of catalyst thickness and CVD parameters. Next, a densification process is conducted for the needle-like shaping of CMS, which could make feasible biological integration (e.g., tissue implantation). With an exposure of CMS to acetone vapor under specific conditions, intrinsic nanopores inside the CMS can be considerably reduced to densify the structure with slenderized shape. Here the acetone vapor flow was controlled by adjusting temperature, while the CMS deformation characteristics were qualitatively investigated. Furthermore, in order to improve the mechanical properties and the electrical properties of densified CMS, additional structural and electrical reinforcement by using reductive Ag ion ink was conducted. The Ag ink consists of silver cations and their compounds. With direct contact with the densified CMS, Ag ink is absorbed into the intrinsic nanopores some of which are still present inside. Subsequently, with simple thermal annealing at a mild temperature, a silver particle is formed on and inside the CMS. The Ag particles bind the adjacent CNT pillars, which further improves the mechanical stiffness and the electrical conductivity of the CMS. Finally, the PDMS-hexane mixture was permeated into each structure: as-grown, densified, and Ag-reinforced CMS structure, to convert the entire structure into a flexible platform. The polymer mixture is gradually filled up from the side of the CMS array structure. Right upon contact to the CMS array, the polymer mixture was permeated into individual CMS pillars by the capillary force. Thereafter, the CMS array is completed as a flexible microelectrode array by curing at 80°C for a sufficient time and separating it from the substrate. Since then, microelectrode arrays based on as-grown/densified/Ag-reinforced CMS have been quantitatively investigated in terms of their strength and elastic properties through compression tests. As a result, sufficient mechanical stiffness and elastics for stable biological integration were confirmed. These structures can be used for sensing biological signals through implantation, attachment, and other connecting methods.

Acknowledgment
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5:00 PM SB09.09.17
Direct-Print-Enabled Customizable Neural Interfaces with Single-Cell and Single-Cell-Type Resolutions Pingyu Wang[1], Eric Wu[1], Hasan Ulusan[2], Andrew J. Phillips[1], Madeline R. Hays[1], Alexandra Kling[1], Eric T. Zhao[1], Sasidhar Madugula[1], Ramandeep Vilkhu[1], Andreas Hierlemann[2], Guosong Hong[1], E.J. Chichilnisky[1] and Nicholas Melosh[1]; [1]Stanford University, United States; [2]ETH Zürich, Switzerland

Advanced silicon processing has enabled neural sensing or modulation at an unprecedentedly large scale and a spatial resolution matching that of the neuron density. However, most planar and rigid silicon electronics have limited access to regions within neural tissue, and it still remains challenging to scalably obtain high-density neural activities in 3D. There has been progress in bridging the geometrical gap between silicon electronics and neural tissues, but the demonstrated penetrating electrodes have low spatial density and their fabrication processes can damage sensitive silicon electronics.
Here, we leveraged the state-of-the-art 2-photon polymerization technology to directly build high-density penetrating microelectrode arrays onto silicon electronics. We demonstrate with an array consisting of 6,600 electrodes pitched at 35 microns and with varying heights. The customizability of the process allows tailoring of array shape and spatial density to target different tissue shape or neuron density. As a proof-of-principle demonstration, we recorded retinal ganglion cell activities *ex vivo*, and were able to distinguish the neural activities with single-cell and single-cell-type resolution. We believe this technology will be crucial for next-generation neural interfaces that enable communication with neural circuits using their natural neural codes.

SESSION SB09.10: Organic Biosensor I
Session Chairs: Lihua Jin, Jiheong Kang and Bao-Nguyen Nguyen
Friday Morning, April 14, 2023
Moscone West, Level 2, Room 2022

8:30 AM SB09.10.01
Engineering of Conjugated Polymers for Sensing Applications in Organic Electronics Raymundo Marcial Hernandez[1], William G. Neal[1], Sofia Giacalone[1], Peter Gilhooly-Finn[1], Dilara Meli[2], Ruiheng Wu[2], Jonathan Rivnay[2], Matteo Palma[1] and Christian Nielsen[1]; [1]Queen Mary University of London, United Kingdom; [2]Northwestern University, United States

Organic semiconductors have gained attention due to their versatility in various organic electronic applications. Polythiophenes like Poly(3-hexylthiophene) (P3HT) are polymers that have been extensively investigated as reference materials due to their attractive properties such as flexibility, biocompatibility, lightweight, stretchability, solvent processing and charge-carrier mobilities in organic field-effect transistors (OFETs). Despite the promising results obtained in OFETs, the implementation of conjugated polymers in other applications such as organic electrochemical transistors (OECTs) has been limited due to the hydrophobic nature of the material. In this talk, we will discuss the development of new synthetic paths and methodologies to increase the interaction between the semiconductor layer and the aqueous electrolyte solution used in many sensing applications. Along with new synthetic routes the effects of side chain engineering over the polymer backbones have also been investigated. In particular, we have extensively studied the exchange of the conventional alkyl side chains for polar chains in various ratios to understand its effects on chemical and electrochemical doping processes, conjugated polymer nanoparticle formation, and mixed ionic and electronic conduction properties relevant for bioelectronic applications.

8:45 AM SB09.10.02

Sensitive Immuno-Biosensors Based on Different Bioreceptor Layers and Organic Electrochemical Transistor (OECT) Configurations Yunjia Song; Johns Hopkins University, United States

Electronic biosensors based on conjugated polymers have been developed in recent decades because of the ease of attaching receptor functional groups and modulating electronic properties [1]. Organic electrochemical transistors (OECTs) have been recognized as an emerging platform technology for biosensing because of their architecture, flexibility, and amplification capability [2]. A typical OECT structure consists of two metal electrodes (source and drain) and one gate electrode immersed in an electrolyte. The gate electrode is electrically coupled to the organic semiconducting layer (usually conjugated polymer layer), which covers the channel region between the source and drain, through the electrolyte.
In this presentation, we will first discuss the properties of different polymers as bioreceptor layers. Poly 3-(3-carboxypropyl) thiophene-2,5-diyl (PT-COOH) and hydroxylated polythiophene (PT-OH) can be both bioreceptor layer as well as channel region material, which show different sensing properties as well as stability. PT-COOH can be a good biomolecule receptor layer on the channel of organic electrochemical transistor (OECT) devices; it shows the ability to immobilize multiple types of biomolecules and transduce the interaction between biomolecules into electrical signals. Myelin basic protein, SARS-CoV-2 spike glycoprotein S1, and their antibodies were alternately used in the attached molecule form as receptors and analytes. The sensitivity was indicated by the change of currents as well as threshold voltages.
Besides the typical OECT configuration, we also developed a dual gate functionalization organic electrochemical transistor (D-OECT) configuration. D-OECT connects two OECT devices in series, while the biomolecule interaction happens on the gate electrode. The gate electrodes were connected in series through buffer solutions, so the solution-electrode interfaces had opposite polarities. We proved that the D-OECT configuration has the ability to increase the accuracy of antibody-antigen interaction detection, and further decrease or eliminate the effect of ions in the buffer solution.

1. Song, Y.; Lamberty, Z. D.; Liang, J.; Aller Pellitero, M.; Wagner, J. S.; Jumai'an, E.; Bevan, M. A.; Frechette, J.; Arroyo-Currás, N.; Katz, H. E. Nanoscale Bioreceptor Layers Comprising Carboxylated Polythiophene for Organic Electrochemical Transistor-Based Biosensors. ACS Appl. Nano Mater. 2021, 4 (12), 13459–13468. https://doi.org/10.1021/acsanm.1c02949.
2. Song, Y.; Zhang, H.; Mukhopadhyaya, T.; Hall, A. S.; Katz, H. E. Sensitive Organic Electrochemical Transistor Biosensors: Comparing Single and Dual Gate Functionalization and Different COOH-Functionalized Bioreceptor Layers. Biosensors and Bioelectronics 2022, 216, 114691. https://doi.org/10.1016/j.bios.2022.114691.

9:00 AM SB09.10.03
Near-Amorphous Semiconducting Polymers with Non-Covalent Interactions Xiaozhou Ji, Hao-Wen Cheng and Zhenan Bao; Stanford University, United States

High-performance semiconducting polymers with high charge carrier mobility and stretchability are desired for skin-like organic electronics. For conventional semi-crystalline semiconducting polymers, crystalline regions with π-π interactions are critical for interchain charge transport to endow good mobility, while it decreases mechanical stretchability. Near-amorphous polymers with high mobility, such as poly(indacenodithiophene benzothiadiazole) (IDTBT), brings in a new strategy of high-performance stretchable polymer semiconductors. The good charge carrier mobility is attributed to its rigid and coplanar backbone structure. Previously, various structural modifications on IDTBT have been studied, while most led to decreased mobility. In this work, non-covalent interactions, including S-F, S-O, and S-N, are introduced in IDTBT to further modify the backbone conformation and improve mobility performance. IDTBT derivatives are synthesized with optimized polymerization. The energy-favored backbone conformations are evaluated by computational simulation. The non-covalent interactions also influence energy levels, aggregation behaviors, and thin film morphology of IDTBT derivatives, which are related to their charge transport properties. High hole-mobility is obtained in top-gate bottom-contact field-effect transistors (FETs) for IDTBT with non-covalent interactions, which is further investigated with the low activation energy and disorder level. Stretchable FET devices are fabricated with the high-mobility IDTBT derivative and demonstrate good performance under strains.

9:15 AM SB09.10.04
Topological Supramolecular Network Enabled High Conductivity, Stretchable Organic Bioelectronics Yuanwen Jiang; University of Pennsylvania, United States

Intrinsically stretchable bioelectronic devices based on soft and conducting organic materials have been regarded as the ideal interface for seamless and biocompatible integration with the human body. First, compared to rigid inorganic materials, soft organic electronic materials do not suffer from the inherent trade-off between overall system stretchability and device density. Therefore, high-resolution mapping/intervention can be realized with conformal biointerfaces. Second, the high volumetric capacitance of conducting polymers (CPs) can reduce the electrode-tissue interfacial impedance, especially at physiologically relevant frequency ranges (<10 kHz), which allows high recording fidelity and efficient stimulation charge injection. However, the electrical conductivities of existing stretchable CPs are too low once they are micro-fabricated into bioelectronic devices. As a result, rigid metal interconnects are still required, which greatly diminished the advantages of soft CPs.

We describe here a rationally designed topological supramolecular network to simultaneously enable three significant advancements in bioelectronics. These are (i) biocompatible and stretchable CPs with high conductivity, (ii) direct photo-patternability down to cellular level feature sizes, and (iii) high stretchability maintained after micro-fabrication with no crack formation under 100% strain, which are all essential for low-impedance and seamless biointegration. The unprecedented performances of the conducting polymer with 2 orders of magnitude improvement in the conductivity under strain allow us to realize previously inaccessible applications including (i) high resolution recording of muscle signals from both human palm and highly malleable and soft-bodied octopus, and (ii) localized neuromodulation through delicate brainstem for precise controls of individual muscle activities down to single nucleus level.

9:30 AM *SB09.10.05
Hyperconnective 3D Polymeric Nanofiber Networks for Tissue-Mimetic Soft Electronics Lizhi Xu; The University of Hong Kong, Hong Kong

Microfibrillar networks are essential structures in natural biological tissues, which exhibit a combination of mechanical flexibility, fracture resistance, and mass permeability to enable many important physiological functions. Inspired by natural soft tissues, we exploit biomimetic nanofiber composites as building blocks for the construction of a variety of bio-integrated soft devices. In this presentation, I will introduce our recent works on nanofiber-enabled polymer soft bioelectronics including the following examples: (1) Electroconductive hydrogels and devices involving framework-assisted assembly of conducting polymers; (2) Rugged and breathable kirigami electronics from hyperconnective nanofiber aerogels; and (3) Theoretical understanding and microstructural engineering of biomimetic 3D nanofiber networks. These works address the fundamental microstructural mismatches between electronic devices and biological soft tissues, paving the way for the development of advanced wearable human-machine interfaces, implantable electronics, tissue engineering platforms, and other biomedical systems.

References:

1. H. He, H. Li, L. Xu* et al., manuscript submitted (2022)
2. H. Liu, H. Li, Z. Wang, L. Xu* et al., Advanced Materials 2207350 (2022).
3. H. He, X. Wei, Y. Lin*, L. Xu* et al., Nature Communications 13, 4242 (2022).
4. H. Li, L. Xu* et al., Advanced Functional Materials 32, 2202792 (2022).

10:00 AM BREAK

SESSION SB09.11: Organic Biosensor II
Session Chairs: Ying Jiang, Lihua Jin, Jia Liu and Zhiyuan Liu
Friday Afternoon, April 14, 2023
Moscone West, Level 2, Room 2022

1:45 PM SB09.11.01
Ion Selective-OECTs for Blood Testing and *In Vivo* Sensing Xiang Meng[1] and Paddy K. L. Chan[1,2]; [1]The University of Hong Kong, China; [2]Advanced Biomedical Instrumentation Centre, China

Organic electrochemical transistors (OECTs) have received extensive attention owing to their ability to translate and amplify ion signals to electron signals recently. Compared to other types of transistors, in the operation of OECT, the ions from the electrolyte permeate into the channel and form a mixed of ionic-electronic conducting materials while a gate voltage (V_g) is applied. This phenomenon causes a volumetric change of the channel doping state, with significant modulations of source-drain current (I_{ds}) at low V_g (below 1V) and very high signal amplification (transconductance values can reach tens of mS). Furthermore, the promising biocompatibility allows the OECTs to be one of the most attractive candidates in biophysical and biochemical sensors for a large variety of targets. These sensors usually have high sensitivity and on-site amplification.

To date, there is a significant need for miniaturized ion sensors for monitoring of ion concentrations in health care applications. Portable and disposable ion sensors could monitor electrolyte levels in human blood or cerebral fluid, which can reflect the health conditions of the patients or neuron activities. In this talk, we will report an ion selective membrane-functionalized OECTs for specific ion detection. Compared to the OECT state-of-the-art, our sensor exhibits high performance, sensitivity of 126 μA/dec, response time of 1.9 s, dynamic range of 10^{-4} to 1 M, excellent stability, reversibility and accuracy. Furthermore, calibrations for Na^+ within the physiological range (110 mM – 160 mM) with blood serum show highly sensitivity of 498 μA/dec. While this investigation focused on Na+ as the target analyte, this platform can be adapted to sense variety of ionic species by simply tuning the ISM composition with the appropriate ionophore molecule. The advances in device architecture can further miniaturize devices and enable device placement in an implantable neural probe, while maintaining the ion sensing capability, i.e., a change of I_{ds} from 20 μA to 5 μA is observed when ion concentration changes from 1 mM to 100 mM. We expect the IS-OECT integrated neural probe to pave the way toward the design and fabrication of a new generation of multifunctional bioelectronics devices.

2:00 PM *SB09.11.03
Plant Bioelectronics for High Resolution Monitoring and Electronic Control of Plant Processes Eleni Stavrinidou; Linkoping University, Sweden

The climate change and growing population calls for plants with increased tolerance to biotic and abiotic stress and plants with higher productivity. In my group we are developing organic bioelectronic technologies for sensing and actuation in plants that overcome limitations of conventional methods used in plant science but also enable new possibilities for plant interface. In my talk I will present our recent advancements of interfacing bioelectronic tools with plant model systems. With miniaturized OECTs and polymeric electrodes we monitor with high resolution sugar dynamics in trees and stress induced responses in Arabidopsis plants. Furthermore, we developed a flexible organic electronic ion pump for controlled delivery of phytohormones in the vasculature enabling activation of long distance responses related to stress tolerance. Finally, I will present a novel bioelectronic platform for stimulation of plant growth. Our results highlight the potential of bioelectronics in elucidating and enhancing plant processes but also for their application in agriculture.

2:30 PM BREAK

3:00 PM SB09.11.04
AC Amplification Gain in Organic Electrochemical Transistors (OECTs) for Impedance-Based Single Cell Sensors Filippo Bonafè, Francesco Decataldo, Isabella Zironi, Daniel Remondini, Tobias Cramer and Beatrice Fraboni; University of Bologna, Italy

Research on electrolyte-gated and organic electrochemical transistor (OECT) architectures is motivated by the prospect of a highly biocompatible interface capable of amplifying bioelectronic signals at the site of detection. Despite many demonstrations in these directions, a quantitative model for OECTs as impedance biosensors is still lacking. We overcome this issue by introducing a model experiment where we simulate the detection of a single cell by the impedance sensing of a dielectric microparticle. The highly reproducible experiment allows us to study the impact of transistor geometry and operation conditions on device sensitivity. With the data we rationalize a mathematical model that provides clear guidelines for the optimization of OECTs as single cell sensors, and we verify the quantitative predictions in an in-vitro experiment. In the optimized geometry, the OECT-based impedance sensor allows to record single cell adhesion and detachment transients, showing a maximum gain of 20.2±0.9 dB with respect to a single electrode-based impedance sensor.

References:
Bonafè, F. *et al.* AC amplification gain in organic electrochemical transistors for impedance-based single cell sensors. *Nat Commun* **13**, 5423 (2022).

3:15 PM SB09.11.05
Phase Separation in Organic Mixed Ionic-Electronic Conductors and Their Interface with Bioelectronics—A Multiphysics Approach Xiaokang Wang and Kejie Zhao; Purdue University, United States

Organic mixed ionic-electronic conductors (OMIECs) are ideal material candidates for bioelectronics owning to their unique capability of mixed conduction and biocompatibility. When integrated to organic electrochemical transistors (OECTs), they enable interaction between electrochemical devices and living matter, such as transmitting and accepting neuron signals and monitoring sweat as a skin sensor. Of all types, two-phase OMIECs exhibit exceptional performance due to their high stretchability and balanced ionic-electronic conduction. However, the electron-conducting phase may segregate from the ion-conducting phase in a two-phase OMIEC, changing the conducting path and eventually leading to degraded performance and dysfunction of the devices. In this work, we study the mechanics and electrochemistry of a two-phase OMIEC channel undergoing phase separation in an OECT model. The computational model captures the concurrent transport of charge carriers, mechanical swelling, and phase separation in the OMIEC and replicates the transfer curves of an OECT which agree well with the experiments. More specifically, we reveal the origin of the volumetric capacitance as the accumulation of charge carriers at the two-phase interfaces. We examine the parametric space to elucidate experimental observations such as the molecular size-dependent conductivity and substrate-dependent phase separation. The swelling behavior and the transfer curves of OECTs under stretched, free, and constrained states are compared, demonstrating the effects of deformation on the phase dynamics and the electron-conducting behavior. This work provides a theoretical basis for the mechanics and electrochemistry of two-phase OMIECs for biological interfaces and sheds light on synthetic and processing principles.

3:30 PM SB09.11.06
Strain-Insensitive Intrinsically Stretchable Transistors and Circuits Weichen Wang; Stanford University, United States

Intrinsically stretchable electronics can form intimate interfaces with the human body, creating devices that could be used to monitor physiological signals without constraining movement. However, mechanical strain invariably leads to the degradation of the electronic properties of the devices. Here we show that strain-insensitive intrinsically stretchable transistor arrays can be created using an all-elastomer strain engineering approach, in which the patterned elastomer layers with tunable stiffnesses are incorporated into the transistor structure. By varying the cross-linking density of the elastomers, areas of increased local stiffness are introduced, reducing strain on the active regions of the devices. This approach can be readily incorporated into existing fabrication processes, and a strain insensitivity of less than 5% performance variation when stretched to 100% strain. We also show that it can be used to fabricate strain-insensitive circuit elements, including NOR gates, ring oscillators and high-gain amplifiers for the stable monitoring of electrophysiological signals.

3:45 PM SB09.11.08
Complementary Internal Ion-Gated Organic Electrochemical Transistors (C-IGT) Duncan Wisniewski and Dion Khodagholy; Columbia University, United States

To understand and modulate neural network processes, bioelectronic devices capable of forming physiologically safe circuits to capture, amplify, process, and stimulate neural activity are required. Because signals of communication between neurons can be read out from minute changes in the ionic flux within brain tissue, organic mixed-conducting-based transistors that transduce ions to electrons can most effectively convert physiological signals to those suitable for input to electronics. These transistors can be fabricated to form conformable systems using scalable microfabrication processes to enable complex computational functions. Because most integrated circuits are currently designed based on complementary transistors (N and P-type), development of the combination of equal performance N and P-type IGTs would permit seamless integration with pre-existing designs. Here we demonstrate a method to create transistors with N-type function, transistor action in the first quadrant and resistor like in the third quadrant, from P-type materials which usually express the opposite behavior, modulating in the third quadrant and acting as a resistor in the first quadrant. These opposing behaviors enabled a complementary logic device with an output voltage range similar to the input voltage dynamics. Additionally, similar channel material and geometry resulted in equal impedances between the two transistors yielding a higher power efficiency. To accomplish this, we created geometrically asymmetric transistor design for optimal complementary performance. An array of devices with different source, gate, and drain sizes were analyzed to determine design rules N and P type performance. Channel material additives were evaluated to find the best formula for creation of both types of transistor for use in complementary devices. Transistors were characterized in terms of asymmetry, voltage required for complementary operation, speed, and gain. Using designs informed by the characterization of channel asymmetry we then fabricated all logic gates to demonstrate digital operations. These complementary IGT designs which can be fabricated with both N and P type single channel materials have a broad range of applications in bioelectronics including wearable electronics, neural interfacing, and therapeutic implants.

SESSION SB09.12: Virtual Session I
Session Chairs: Lihua Jin, Jiheong Kang, Jia Liu and Zhiyuan Liu
Tuesday Morning, April 25, 2023
SB09-virtual

8:00 AM SB09.12.01
Nanostructures of PEDOT Derivatives Decorated on the Channel Layer of Organic Electrochemical Transistor Influences the Sensitive Detection of Sweat Cortisol. [a] Jayakrishnan Aerathupalathu Janardhanan[1], Ying-Lin Chen[2], Chun-Ting Liu[3], Hsueh-Sheng Tseng[2], Po-I Wu[2], Jia-Wei She[1], Yu-Sheng Hsiao[2] and Hsiao-hua Yu[1]; [1]Academia Sinica, Taiwan; [2]National Taiwan University of Science and Technology (NTUST), Taiwan; [3]National Taiwan University, Taiwan

Nanostructures of conducting polymers are versatile candidate for the development of biosensors. Electrochemical polymerization is a simple and efficient technique to engineer such conducting polymer nanostructures as bioelectronics interface (BEI) platform. This study highlights the influence of functionalized poly (3,4-ethylenedioxythiophene) (PEDOT) nanostructures decorated on the channel layer of an organic electrochemical transistor (OECT) for the detection of sweat cortisol-an adrenocorticosteroid stress hormone. Our design of novel OECT cortisol immunosensor highlight an active channel area decorated by poly(EDOT-COOH-co-EDOT-EG3) nanotube embedded upper layer engineered from two monomers such as EDOT-COOH and EDOT-EG3 by template free electrochemical polymerization and PEDOT: polystyrenesulfonate (PSS) under layer for the sensitive detection of sweat cortisol. The molecular design provides an easy access of antibody conjugation by 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide/N-hydroxysulfosuccinimide (EDC/Sulfo-NHS) coupling chemistry through carboxylic acid side chain and EDOT-EG3 is best known to reduce non-specific binding of biomolecules. The electropolymerization parameters were optimized for channel morphology of the OECT device together with the output characteristics and electrical properties of the device, pH of the electrolyte solution and monomers feed ratios prior to the immobilization of anti-cortisol antibody. Cortisol antibody was covalently attached inside the channel layer by EDC/Sulfo-NHS coupling chemistry. OECT device having channel area without any nanostructures were also engineered to get insight into the influence of nano topology of the channel area for enhanced analyte detection. Cortisol antibody immobilization on the channel layer was confirmed by different spectroscopic techniques such as Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and Quartz Crystal Microbalance (QCM) technique. QCM experiments revealed that the polymer nanotube embedded active channel area of the device displayed enhanced immobilization of cortisol antibody compared to the active channel area without any nanostructures. The real time detection of cortisol ranging from 1fg /mL to 1 μg/mL were investigated by the newly engineered OECT device. The OECT cortisol immunosensor embedded with nanotubes on the channel area showed enhanced detection limit of 0.0088 fg/mL with good linearity (R^2 =0.9566). In addition, the device displayed excellent selectivity to cortisol with the other structurally similar interfering compounds such as cholesterol, corticosterone, prednisolone and cortisone. Predominant selectivity to cortisol was observed for OECT device with nanotube channel layer compared with the OECT device having channel layer without any nanostructures. Moreover, the newly designed OECT cortisol immunosensor showed rapid response towards 100 ng/ mL cortisol spiked artificial sweat, highlighted the clinical practicality of the novel OECT device towards wearable sensors for future healthcare applications.

References

[a] Aerathupalathu Janardhanan, Jayakrishnan; Chen, Ying-Lin; Liu, Chun-Ting; Tseng, Hsueh-Sheng; Wu, Po-I; She, Jia-Wei; Hsiao, Yu-Sheng and Yu, Hsiao-hua, Sensitive Detection of Sweat Cortisol Using an Organic Electrochemical Transistor Featuring Nanostructured Poly(3,4-Ethylenedioxythiophene) Derivatives in the Channel Layer, **2022**, *Anal. Chem.* 94, 7584–7593.

8:15 AM SB09.12.02
Thermal-Drawn Fiber-Based Multiplexed Electrochemical Sensor for Sweat Sensing Applications Jingxuan Wu[1], Yuichi Sato[2] and Yuanyuan Guo[2,3,4]; [1]Graduate School of Engineering, Tohoku University, Japan; [2]Frontier Research Institute for Interdisciplinary Sciences (FRIS), Tohoku University, Japan; [3]Graduate School of Biomedical Engineering, Tohoku University, Japan; [4]Graduate School of Medicine, Tohoku University, Japan

The sweat, representing the most easily accessible body fluids, contains important biomarkers, including electrolytes and metabolites that are directly associated with our health status. Recently, a significant amount of research effort has been devoted to developing sweat sensors for wearable applications. However, photolithography or printing techniques are often the mainstream of the fabrication process, resulting in sweat sensors based on 2D planar structures with limited surface area for body contact. The strict definition for wearable sensors is the ones that we wear daily, which are clothes. In this study, we developed a flexible fiber with all-in-one multiplexed sensing capabilities, which has a footprint of 750 µm × 370 µm to 1100 µm × 550 µm and can be weaved into textile for on-body sweat sensing. Such fibers were fabricated by the scalable and versatile thermal drawing process that has been conventionally used in the telecommunication industries to produce optical fibers. Here it has been adopted to fabricate multiplexed electrochemical sensing fibers. The fiber is composed of two polymer electrodes based on carbon black loaded polyethylene (CPE) and stainless-steel wires right beneath them, an internal microfluidic channel between the electrodes, which then were further encapsulated within the polycarbonate (PC) cladding. To realize the longitudinal functions, we used laser machining techniques to expose the CPE within the PC cladding at the designated positions along the length of the fiber. The exposed electrodes were further modified with sensing materials, such as gold nanoparticles (AuNP)s as well as ion-sensitive membranes (ISM) for either direct monitoring of uric acid oxidation or sensing Na+ concentration. In addition, the pseudo reference electrode (p-RE) based on Ag/AgCl was also incorporated into the fiber by integrating Ag/AgCl ink, NaCl-containing hydrogel buffer zone and membrane passive layers, to realize all-in-one electrochemical sensing. We carefully characterized the electrochemical functions of each component. First, the electrode modified with AuNPs exhibits a high sensitivity of 0.82 ± 0.08 nA/µM towards UA in the physiological ranges of 0 to 500 µM. Secondly, Na+ ion-sensitive electrodes (ISE) achieved via the ISM showed sensitivity to Na+ of up to 55.2 ± 0.8 mV/decade, close to the theoretical Nernstian value of 59.2 mV/decade. In addition, p-RE had excellent stability, which had no response in NaCl solution with varying concentrations (- 4.0 ± 0.5 mV/decade). Lastly, we integrated all the functions within a single fiber as an all-in-one sensor and characterized its performance in the artificial sweat. It exhibited UA sensitivity of 0.62 ± 0.1 nA/µM and Na+ sensitivity of 43.1 ± 3.5 mV/decade, the performance of which can meet requirements for on-body applications. Additionally, we also showed the proof-of-concept of the fluid delivery capability of its internal microfluidic channels, for washing and resetting the sensor surfaces. In summary, the thermally drawn fibers and textiles-based multiplexed electrochemical sensing system shows great promise in its future deployment as wearable clothes for monitoring important physiological signals in sweat and beyond.

8:30 AM SB09.12.03
Flexible Microneedle Patch for Wound Oxygenation and Biofilm Eradication Akshay Krishnakumar, Sina Nejati and Rahim Rahimi; Purdue University, United States

In the United States alone, chronic non-healing wounds impact more than 6 million people each year and constitute a major social issue. These wounds are further colonized by bacteria developing intricate biofilms which builds up barriers against antibiotics, impede tissue oxygenation (hypoxia) and wound healing. Clinical experts frequently utilize wound debridement and forceful mechanical abrasion procedures to manage and remove biofilms from wound surfaces which are extremely nonselective and painful. Local tissue oxygenation and delivery of antimicrobial species into the wound bed would effectively discriminate the biofilm growth and enhance the host wound healing simultaneously. Henceforth, we have developed a flexible polymer composite microneedle array that can overcome the physicochemical barriers (i.e., bacterial biofilm) present in chronic nonhealing wounds and co-deliver oxygen and bactericidal agents. The polymeric microneedles were developed *via* a facile UV polymerization process using polyvinylpyrrolidone and calcium peroxide onto a flexible fiber mat substrate for conformable attachment onto different locations of the human body surface. Dry heat autoclave parameters were experimented to sterilize the microneedles effectively without compromising its performance characteristics. The bactericidal properties of these microneedles were studies using gram negative *Pseudomonas* Aeruginosa as they are commonly observed to form biofilms. Additionally, microneedles exposed to human dermal fibroblast cells exhibited high levels of cytocompatibility and less than 10% apoptosis. Skin irritation and compatibility of the microneedle structures will be experimented on *in-vivo* animal models. Finally, the efficacy polymeric microneedles to collapse the biofilm formation and wound healing would be investigated in *in-vivo* rat models after inducing a biofilm on the wound model.

SYMPOSIUM

April 11 - April 25, 2023

Symposium Organizers
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Peter Liaw, University of Tennessee

Eun Soo Park, Seoul National University
Cem Tasan, Massachusetts Institute of Technology

* Invited Paper
\+ Distinguished Invited

SESSION SF01.01: Overview of High Entropy Alloys
Session Chairs: Peter Liaw and Eun Soo Park
Tuesday Morning, April 11, 2023
Marriott Marquis, B2 Level, Golden Gate C2

10:30 AM *SF01.01.02
Fracture and Damage-Tolerance in *fcc* and *bcc* High-Entropy Alloys Robert O. Ritchie[1,2], Andrew M. Minor[1,2], Mark Asta[1,2], Mingwei Zhang[2], Punit Kumar[2], Flynn Walsh[1,2], Madelyn I. Payne[1,2], Wenqing Wang[1,2] and David Cook[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Face-centered cubic (*fcc*) medium- and high-entropy alloys (M/HEAs) can display exceptional combinations of strength, tensile ductility and fracture toughness, properties that can be further enhanced at cryogenic temperatures. Body-centered cubic (*bcc*) refractory HEAs, conversely, can display exceptional strength and compressive ductility at elevated temperatures, but are often compromised by poor lower-temperature behavior. We examine here the damage-tolerance of these two classes of multiple principal-element alloys, and show that whereas some of the *fcc* HEAs exhibit among highest fracture toughness values on record, the *bcc* HEAs can display extremely low toughness (and ductility) when subject to tensile loading. The *fcc* M/HEAs are also examined under extreme conditions of ultrahigh strain rates and liquid helium temperatures. We further examine the role of short-range order (SRO) in these two alloy classes, theoretically using DFT-based Monte-Carlo and Molecular Dynamics simulations and experimentally using energy-filtered TEM and 4D-STEM techniques. Whereas atomistic simulations predict the existence of SRO in *fcc* and *bcc* HEAs, together with its influence on plastic deformation behavior, *e.g*., slip behavior, dislocation mobility, *etc*., direct experimental evidence is difficult. We discuss some of the complicated aspects of defining the nature of the local order and its potential role on mechanical properties of *fcc* HEAs; however, studies for the *bcc* systems show an influence of SRO on dislocation motion but this is diminished at the high temperatures where these alloys are expected to perform. Our overall emphasis is on defining the origins of damage-tolerance in both *fcc* and *bcc* medium- and high-entropy alloys and how SRO can affect the mechanistic sequence of processes that underly their strength, ductility, and toughness.

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*funded by the Department of Energy, Office of Science (Basic Energy Sciences), Materials Sciences and Engineering Division.

11:00 AM *SF01.01.04
Prospects for BCC Refractory High-Entropy Alloys Given Their Phase Stability and Mechanical Properties Easo P. George[1,2]; [1]The University of Tennessee, Knoxville, United States; [2]Ruhr University Bochum, Germany

Refractory high-entropy alloys (RHEAs) are high-entropy alloys in which the constituent elements are refractory elements. Their high melting points make them attractive as next-generation high-temperature materials because of their potential for applications beyond state-of-the-art Ni-base superalloys. However, before that potential is realized, a few critical aspects of RHEAs need to be clarified, including the following: (1) are their tensile creep properties in fact superior to those of leading superalloys, (2) do they possess a minimal level of tensile ductility at room temperature to withstand normal handling and accidental drops, and (3) do they undergo phase transformations (microstructural instabilities) and the associated degradation of mechanical properties under expected service conditions. In this talk I will address these points by presenting our experimental and thermodynamic simulation results on model RHEAs of the VNbMoTaW and TiZrHfNbTa systems and their lower-order subsystems (quaternary, ternaries, etc.). Our results show that, the latter alloys, although relatively ductile at room temperature, have a long way to go before they can be creep-competitive with Ni-base superalloys at elevated temperatures. The former alloys are brittle at room temperature, and there is insufficient tensile creep data to judge whether they will be creep-competitive with Ni-base superalloys. Additionally, many of these RHEAs undergo phase decompositions when subjected to the expected thermal cycles of engine components such as turbine blades, which would further deteriorate the already marginal ductility and toughness of these alloys. By systemic investigation of pseudo-binary subsystems of these model quinary alloys, we attempt to understand the key factors responsible for the observed phenomena and provide suggestions for improvement of their physical and mechanical properties.

SESSION SF01.02: Structural/Mechanical Properties I
Session Chairs: Haruyuki Inui and Robert Ritchie
Tuesday Afternoon, April 11, 2023
Marriott Marquis, B2 Level, Golden Gate C2

1:00 PM *SF01.02.01
Short Range Order and the Evolution of Deformation Mechanisms in the CrCoNi Medium Entropy Alloy Mingwei Zhang[1,2], Flynn Walsh[2,1], Yang Yang[3], Madelyn I. Payne[1,2], Punit Kumar[2], Mark Asta[1,2], Robert O. Ritchie[1,2] and Andrew M. Minor[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]The Pennsylvania State University, United States

This talk will describe our recent results utilizing energy filtered diffraction, 4D-STEM and in situ TEM nanomechanical testing and ex situ nanoindentation that provide insight into multiscale deformation phenomena in the CrCoNi medium entropy alloy. Using energy-filtered TEM and HRSTEM techniques it is possible to directly image, and therefore quantitatively assess, SRO and its effect on mechanical properties. In order to understand the effect of SRO in terms of the evolution of plasticity at different stages, the technique of 4D-STEM was used during in situ deformation and fracture experiments. 4D-STEM can provide both real-space imaging and diffraction analysis during *in situ* testing, making it possible to perform strain mapping via diffraction pattern analysis during in-situ deformation in a TEM. The diffraction patterns are used to identify defects and map relative strain, while the images formed by using virtual apertures provide microstructural context for the analysis. Our results from electron microscopy are then correlated with mechanical testing including nanoindentation to examine how SRO evolves with different processing conditions. Lastly, we will consider the role of both SRO and planar defects in the both the mechanical response as well as structural determination via electron diffraction as a function of heat treatment in the CrCoNi MEA.

1:30 PM *SF01.02.02
Dislocation Pathways in Refractory Multi-Principal Element Alloys Daniel S. Gianola; University of California, Santa Barbara, United States

Emerging classes of structural materials proposed to meet the demands of aggressive applications share a common theme: complexity across a large range of length scales. A common denominator is the intentional design of disorder in these new materials. In load-bearing materials, this disorder can manifest as topological disorder as found in glassy materials, or chemical disorder as found in compositionally-concentrated alloys. Of particular interest from the latter class, refractory multi-principal element alloys (MPEAs) are promising candidates for structural applications demanding mechanical robustness at temperatures exceeding the capacity of state-of-the-art superalloys. While excellent high temperature strength has been demonstrated in many refractory MPEAs, a fundamental understanding of (i) the nature of dislocation pathways in the BCC versions of these chemically complex alloys, (ii) their ability to enable macroscopic ductility, and (iii) the role of interstitial species such as oxygen is still in its infancy. This talk will detail a study of a ternary MPEA, MoNbTi, and its binary derivative, NbTi, through a combination of *in situ* dislocation observations, microstructural investigations, and atomistic calculations. Our results highlight multi-planar, multi-character dislocation slip in MoNbTi at low homologous temperature, *encouraged by the substantial dispersion in the glide resistance for dislocation due to the atomic-scale chemical fluctuations*. The ability of dislocations to choose the easy gliding direction and plane enables an excellent combination of strength and homogeneous plasticity in this alloy. We further compare the mechanical response of MoNbTi to its binary counterpart NbTi, to which we also incorporate oxygen to study the influence of interstitials on phase evolution and concomitant changes in dislocation slip behavior. The presence of oxygen mediates spinodal decomposition, leading to compositional fluctuations comprising length scales and interfacial regions that alter the pathways for dislocation glide.

2:00 PM SF01.02.03
Investigating the Origin of Diffuse Scattering and Extra Reflections in Electron Microscopy Studies of FCC High/Medium Entropy Alloys Mingwei Zhang[1,2], Flynn Walsh[2], Madelyn I. Payne[2], Punit Kumar[1,2], Robert O. Ritchie[1,2], Mark Asta[1,2] and Andrew M. Minor[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

The observation of diffuse superlattice intensities in many FCC high/medium entropy alloys by transmission electron microscopy has been attributed to the presence of chemical short-range order (CSRO). Namely, streaking, 1/3<422>, and 1/2<311> peaks were observed under electron diffraction along [110], [111], and [112] zone axes, respectively. However, displacive planar defects in FCC crystals (i.e., stacking faults or nanotwins) can produce the exact set of those peaks, making the interpretation ambiguous. In addition, our theoretical predictions of ordering reveal discrepancies between predicted superlattice peaks and observed ones. In this presentation, we discuss the origin of extra electron reflections in FCC concentrated solid solutions using the insights from our recent experiments and simulations as well as the implications on the mechanical properties. We will compare our TEM analysis of diffuse scattering and superlattice peaks with both diffraction contrast and high resolution electron microscopy imaging of defect structures.

2:15 PM SF01.02.04
Defect Interactions in High Entropy Alloys and Development of *In Situ* Atomic Scale Defect Spectroscopy Farida Selim[1], Maciej Oskar Liedke[2], Maik Butterling[2], Andreas Wagner[2], Djamel Kaoumi[3], Geoffrey Beausoleil[4], Khalid Hattar[5], Adric Jones[1], Matthew Chancey[6], Peter Hosemann[7], Blas P. Uberuaga[6] and Yongqiang Wang[6]; [1]Bowling Green State Univ, United States; [2]Helmholtz-Zentrum Dresden-Rossendorf, Germany; [3]North Carolina State University, United States; [4]Idaho National Laboratory, United States; [5]Sandia National Laboratories, United States; [6]Los Alamos National Laboratory, United States; [7]University of California, Berkeley, United States

Defects in materials form, interact, and evolve at the atomic level. The measurements and analysis of their atomic level generation and evolution can reveal the mechanisms of defect interactions which dictate the macroscopic material properties and strength. This work investigates atomic scale defects in high entropy alloys (HEAs) using positron annihilation spectroscopy (PAS). I will present several examples that reveal how ion irradiation induced defects interact with the original microstructure and intrinsic defects in HEAs and the strong impact of the nature of chemical disorder on atomic scale defect interactions and evolution during the growth process and under irradiation. Then I will describe the recent development of the first in-situ PAS (iPAS) with high energy irradiation in the world at the ion beam materials laboratory at the Los Alamos National Laboratory and discuss how it can advance our understanding of the physics of defects in HEAs. Further, Early tests of the in-situ system will be presented to demonstrate its unique capabilities.
This work was funded as part of FUTURE (Fundamental Understanding of Transport Under Reactor Extremes), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. It was also supported by the National Science Foundation (NSF) under grant number DMR-2005064.

2:30 PM SF01.02.05
Processing Pathways for Chemical Short-Range Order in Equiatomic CoCrNi Alloy Sakshi Bajpai, Calvin H. Belcher, Benjamin E. MacDonald, Timothy Rupert, Enrique Lavernia and Diran Apelian; University of California, Irvine, United States

Historically, the defining feature of complex concentrated alloys (CCAs) has been a primary phase with random atomic distribution of multiple principal elements in the lattice. Our understanding of this distribution has evolved in recent years with modeling and experimental observation of certain CCAs exhibiting preferential arrangement of atoms within a very short distance (~5-10 nm) in the crystal lattice. This phenomenon is known as chemical short-range ordering (CSRO). To date, it is not apparent how CSRO influences the bulk mechanical properties of CCAs, which may have important implications on the industrial application of CCAs. Can CSRO be manipulated via processing, for example, remains an unanswered question. In this work, the effect of processing pathways on the formation of CSRO in the equiatomic CoCrNi alloy is investigated. Heat treatments with variable temperatures, time, and cooling rates are conducted to systematically probe for the onset of CSRO formation. The variation in the microstructure, such as twin density and grain size, with different heat treatments is taken into consideration to isolate the impact of CSRO on the bulk and nano-level mechanical properties of the CoCrNi alloy. Nano-indentation, Vickers micro-hardness, and tensile testing are used for this purpose. Furthermore, the characterization of CSRO in various heat-treated CoCrNi alloys is done. Trends in behavior are discussed in the context of CSRO as well as the impact on processability to consider future steps toward commercially viable CCAs.

2:45 PM SF01.02.06
***In Situ* TEM Observation of High Entropy Alloy Silicadation and Diffusion Behavior** Chih-Lin Chiu, An-Yuan Hou and Wen Wei Wu; NationalYang Ming Chiao Tung University, Taiwan

High entropy alloy (HEA) has been widely used in the engineering applications due to its high hardness and outstanding corrosion resistance. Previous study reported how the metal elements affected the electrochemical performance and mechanical property of HEA. However, the research of HEA in the field of semiconductor Si is rarely discussed. In this study, $Al_{0.5}CoCrFeNi_2$ was deposited on silicon substrate by sputter. The dynamic synthesis process of high entropy silicide (HES) has been observed by *in-situ* transmission electron microscopy (TEM). During the heating process, Fe, Co and Ni atoms diffused into silicon substrate at 500 degree celsius, Cr would then react with FeCoNi silicide at 700 degree celsius. In addition, the participation of Al in the reaction was observed. Furthermore, HES was found to possess low resistivity, implying a potential candidate for the contact material of complementary metal oxide semiconductor(CMOS). This study demonstrates the formation mechanism of HES, providing a new material for future semiconductor industry.

SESSION SF01.03: Structural/Mechanical Properties II
Session Chairs: Jurgen Eckert and Andrew Minor
Tuesday Afternoon, April 11, 2023
Marriott Marquis, B2 Level, Golden Gate C2

3:15 PM *SF01.03.01
Effects of Short-Range Ordering on Mechanical Properties of Single Crystals of the Equiatomic CrCoNi Medium-Entropy Alloy Haruyuki Inui, Le Li, Zhenghao Chen and Kyosuke Kishida; Kyoto University, Japan

The plastic deformation behavior of single crystals of the FCC equatomic CrCoNi medium-entropy alloy has been investigated in a temperature range of 10-1273 K, paying special attention to possible variations in mechanical properties with heat-treatment that may cause short-range ordering of the constituent elements. Deformation occurs via slip of the {111}<110> system exclusively in the whole temperature range regardless of different heat treatments. The CRSS values increase with decreasing temperature, especially below room temperature, so that the concept of 'stress equivalence' is obeyed. This is a clear indication that the strength of these alloys should be described by a mechanism based on solid-solution hardening. Dislocations are smoothly curved in the slip plane without any preferred line orientation, indicating no significant anisotropy in the mobility of edge and screw segments. Planar ½<110>{111} dislocations dissociate widely into Shockley partials for all alloys investigated, indicating the low stacking fault energy of 13 ± 3 mJ/m^2 for CrMnFeCoNi and CrCoNi, respectively. The CRSS values extrapolated to 0 K for polycrystals of equiatomic quinary, quaternary and ternary alloys are reported to be well scaled with the mean-square atomic displacement from the regular FCC lattice points (calculated based on density-functional theory). This seems also the case for the CRSS values at 10 K for single crystals of CrCoNi and its related quaternary (CrFeCoNi) and quinary (CrMnFeCoNi) alloys. Deformation twinning occurs on the conjugate system in the form of the Lüders type deformation in the later stage of deformation at low temperatures in all of the three alloys. No significant variation of the CRSS values, twinning stress and the stacking-fault energy was noted upon the formation of short-range order by heat-treatment.

3:45 PM *SF01.03.02
Effects of Nitrogen on the Plasticity of Co-Rich Complex Concentrated Alloys Hyunseok Oh; Massachusetts Institute of Technology, United States

Introducing interstitial elements in complex concentrated alloys (CCAs) has received considerable attention due to its effectiveness in changing plasticity mechanisms, resulting in superior mechanical properties. However, fundamental investigation of the effects of interstitial elements is challenging because of the complex chemical interactions among interstitial elements, substitutional elements, and defects. Here, we present the effects of dilute nitrogen on defect evolution in Co-rich complex concentrated alloys with low (negative) stacking fault energies. We will systematically discuss the possible effects of nitrogen: solute pinning, short-range ordering or clustering, stacking fault energies, and segregation.

4:15 PM SF01.03.03
Investigation of Hydrogen Behavior and Hydrogen Embrittlement Mechanisms of FCC-BCC Dual-phase High-Entropy Alloys with Controlled Phase Fraction and Stability Sang Yoon Song[1], Dae Cheol Yang[1], Han-Jin Kim[2], Sang-In Lee[2], Hyeon-Seok Do[3], Alireza Zargaran[3], Byeong-Joo Lee[3] and Seok Su Sohn[1]; [1]Korea University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of); [3]Pohang University of Science and Technology, Korea (the Republic of)

Hydrogen embrittlement (HE) has been considered a serious issue as it deteriorates the strength and ductility of metallic materials. Among various kinds of alloys, the face-centered cubic (FCC) + body-centered cubic (BCC) dual-phase alloys are known to be susceptible to hydrogen environments due to the inherent characteristic of the BCC structure stemming from a high diffusivity of hydrogen. Thus, it is reasonable to believe that reducing the fraction of BCC would improve the resistance to HE in the FCC-BCC dual-phase alloys. However, most of these alloys accompany the transformation-induced plasticity (TRIP), indicating that the FCC phase also contributes to the HE susceptibility through undergoing martensitic transformation. This suggests that it is hard to readily estimate the HE susceptibility of the FCC-BCC dual-phase alloys as both the phase fraction and stability have critical roles on the HE susceptibility. Therefore, it is necessary to reveal each effect of FCC and BCC phases on HE phenomenon and to conduct a systematic study by controlling phase fraction and stability. In this study, four model VCrFeCoNi high-entropy alloys are designed to form FCC-BCC martensite whose phase fraction and stability are largely controlled. Among them, two alloys possess a single FCC phase, while the others consist of FCC and as-quenched BCC martensite. As the Ni content decreases, the thermal and mechanical stabilities of FCC reduce, resulting in the increased BCC fraction and sensitivity to deformation-induced martensitic transformation. For the four model alloys, the HE susceptibility is evaluated by slow strain rate tests (SSRTs) for the specimens H pre-charged via electrochemical cathodic methods. These four alloys showing different HE susceptibility are subjected to detailed analysis of hydrogen diffusion, trap behavior, hydrogen-affected brittle zone, and hydrogen-induced cracking. The initial as-quenched martensite provides diffusion paths for hydrogen, while the deformation-induced martensite possesses an inherently high concentration of hydrogen, leading to dominant roles in crack propagation behaviors. This work suggests the guidance for microstructural designs to enhance the resistance to HE for the metastable FCC-BCC dual-phase alloys.

4:30 PM SF01.03.04
Compositive Role of Refractory Element Mo in Improving Strength and Ductility of Face-Centered-Cubic Complex Concentrated Alloys Tae Jin Jang[1], You Na Lee[1], Yuji Ikeda[2], Fritz Körmann[3], Ju-Hyun Baek[4], Hyeon-Seok Do[5], Yeon Taek Choi[5], Hojun Gwon[5], Jin-Yoo Suh[4], Hyoung Seop Kim[5], Byeong-Joo Lee[5], Alireza Zargaran[5] and Seok Su Sohn[1]; [1]Korea University, Korea (the Republic of); [2]University of Stuttgart, Germany; [3]Max-Planck-Institut für Eisenforschung GmbHdisabled, Germany; [4]Korea Institute of Science and Technology, Korea (the Republic of); [5]Pohang University of Science and Technology, Korea (the Republic of)

Complex concentrated alloys (CCAs) containing multiprincipal elements have been investigated extensively for the last two decades due to the potential for extended mechanical properties from their wide range of compositional space. Particularly, CCAs having a face-centered-cubic (FCC) structured solid-solution containing various 3d-transition metal elements exhibit improved mechanical properties attributed to their enhanced solid solution strengthening, grain boundary strengthening, and strain hardening capability. Due to their distinctive mechanical properties, great efforts have been conducted to demonstrate the origin of improved mechanical properties. Most of these investigations, however, have been focused on the FCC CCAs composed of 3d-transition metal elements. The addition of other elements with a larger atomic size compared to 3d-transition metal elements usually forms secondary phases. Especially, even a small addition of Mo in FCC CCAs generally causes the formation of topologically close-packed phases such as m and s phases, inducing embrittlement of the alloys. Therefore, it is a lack of systematic study on the effect of refractory element Mo on the mechanical response in single-phase FCC CCAs. In this study, three alloys with different Mo content of the CoNiMo system were fabricated, which is predicted to maintain a single FCC with a wide range of Mo content. Interestingly, solid-solution strengthening and grain-boundary strengthening improve simultaneously with increasing Mo content. In particular, the highest Mo alloy exhibits a high yield strength of ~1 GPa attributed to their significant solid-solution strengthening of 229 MPa and Hall–Petch coefficient of 1028 MPa×mm$^{1/2}$. The effect of Mo element on solid-solution strengthening is demonstrated via increasing lattice distortion with increasing Mo content computed by *ab initio* calculation. The improved grain-boundary strengthening is also correlated to lattice distortion, and grain-boundary segregation of Mo leads to a further increase of the Hall–Petch coefficient. In addition to the strengthening contributions, the addition of Mo contributes to improving the strain hardening capacity, which is crucial for sustaining plastic deformation. The transition of dislocation and deformation twin substructures depending on the decrease of stacking fault energy on increasing Mo content makes the dislocation glide more difficult and leads to a higher strain hardening capability of the alloys.

SESSION SF01.04: Structural/Mechanical Properties III
Session Chairs: Hyunjoo Choi and Simon Schweidler
Wednesday Morning, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate C2

8:30 AM *SF01.04.01
High-Throughput Methods Combined with AI for the Development of High-Entropy Materials Simon Schweidler[1], Leonardo Velasco[2], Pascal Friedrich[1], Anurag D. Khandelwal[1], Ben Breitung[1], Jasmin Aghassi-Hagmann[1] and Horst Hahn[1]; [1]Karlsruhe Institute of Technology, Germany; [2]Direccion Academica Universidad Nacional de Colombia Sede de La Paz, Colombia

High-entropy materials offer a huge research area for new material compositions and potential applications, e.g. in the field of rechargeable batteries, electrochemical catalysis, hydrogen storage or supercapacitors.[1] In particular, the combinatorial complexity of several elements in a single-phase structure, can lead to unexpected and unpredictable material properties, which may affect potential application areas. Exploring the vast compositional space of high-entropy materials in a conventional approach, i.e., one experiment at a time is prohibitive in terms of cost and time. Consequently, the development of high-throughput experimental methods supported by machine learning and theoretical predictions will facilitate the search for multicomponent materials in their compositional diversity.
Therefore, this talk will focus on the establishment of automated high-throughput methodologies in the field of synthesis and characterization of metallic and non-metallic (ceramic) high-entropy materials, enabling the creation of material libraries.[2,3] This facilitates the analysis of material properties in terms of composition or morphological and structural differences. Machine learning-based data analysis and theoretical approaches also provide opportunities for the virtual development of novel materials for both functional and structural applications.

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2. Velasco, L.; Castillo, J.S.; Kante, M. V.; Olaya, J.J.; Friederich, P.; Hahn, H. Phase–Property Diagrams for Multicomponent Oxide Systems toward Materials Libraries. *Adv. Mater.* **2021**, *33*, doi:10.1002/adma.202102301.
3. Schweidler, S.; Schopmans, H.; Reiser, P.; Boltynjuk, E.; Olaya, J.J.; Singaraju, S.A.; Fischer, F.; Hahn, H.; Friederich, P.; Velasco, L. Synthesis and Characterization of High-Entropy CrMoNbTaVW Thin Films Using High-Throughput Methods. *Adv. Eng. Mater.* **2022**, *2200870*, 1–7, doi:10.1002/adem.202200870.

9:00 AM SF01.04.03
Old Materials, New Life—Using diffusion-Controlled Synthesis for Discovery of Novel Alloy Systems Annica Wetzel, Ozlem Ozcan, Yasemin Yesilcicek and Julia Witt; Federal Institute for Materials Research and Testing (BAM), Germany

Multi principal element alloy (MPEAs) concept allows us to rethink how we develop application-tailored, sustainable materials. The vast composition space leads to nearly indefinite material combinations and will facilitate finding Pareto optimal materials with lower CO_2 footprint and avoidance of critical minerals as design criteria. To probe this large compositional space efficiently, the use high-throughput screening methods is inevitable. Diffusion-controlled synthesis of gradient materials is the optimal technique for screening complex compositional materials that would otherwise require comprehensive modelling or experimental efforts.

In this study, we have used a series of diffusion couples of pure metals and alloys with the aim to create a materials library with correlated data on composition and microstructure. With future recycling prospects in mind, and possible applications of Cu containing alloys in electrocatalytic carbon dioxide reduction and antimicrobial alloys we have generated diffusion couples of brass ($Cu_{63}Zn_{37}$) and bronze ($Cu_{89}Sn_{11}$) with either pure metals (Fe, Ni, etc.) or with binary or ternary alloys (FeNi, FeNiCr etc.). For different diffusion times and temperatures, we calculated diffusion constants for the material combinations. Following a detailed characterisation of the gradient materials, we have investigated general and local corrosion properties, electrocatalytic activity for oxygen evolution reaction (OER) and carbon dioxide reduction reaction (CRR) as well as mechanical properties (hardness, elastic modulus) on single-phase alloys synthesized in bulk by means of vacuum arc-melting based on the selected local compositions.

In most cases, due to the short diffusion times, the contact between the diffusion couples lead to two separate diffusion zones and thus, different alloy families on both sides. Especially with ternary alloys, interesting selective diffusion processes and unexpected repulsion effects were observed. The presentation will provide an overview of the gradient materials with a focus on the functional properties of single-phase alloy families derived from them.

9:15 AM SF01.04.04
A Map of Single-Phase High-Entropy Alloys Wei Chen[1], Antoine Hilhorst[1], Stéphane Gorsse[2], Pascal J. Jacques[1] and Geoffroy Hautier[3,1]; [1]Université

Catholique de Louvain, Belgium; [2]CNRS, University of Bordeaux, France; [3]Dartmouth College, United States

High-entropy alloys (HEAs) with five or more elements mixed at equal or near-equal compositions in a single crystalline phase have been the focus of much research as they exhibit unusual functional and mechanical properties. Yet, only a limited number of single-phase HEAs have been identified experimentally, highlighting the difficulty of experimental screening and, more fundamentally, the effects beyond the high-entropy criterion for the stabilization of HEAs. Here, through an ab initio driven thermodynamic model, we navigate the vast chemical space of equimolar quinary alloys from the combination of 40 metallic elements. In particular, the enthalpic contribution to the HEAs is described by a simple regular solution model for which the interactions are limited to binary terms and are obtained with density-functional theory. Within this model, the Gibbs free energy of any random solid solutions can be evaluated efficiently as a series of precomputed binary interactions in addition to the ideal configurational entropy. The thermodynamic stability of HEAs is then determined through the convex hull construction which directly compares the free energy of the system in the solid-solution phase versus any linear combination of its subsystems including intermetallic phases. Applying our model to the 658,008 possible equimolar quinary alloys, we find that 35,506 alloys can be stabilized in a single-phase solid solution at near-melting temperature, significantly expanding the scope of chemistry known to the HEA community. In line with the prevalence of BCC HEAs in the literature, the majority (75%) of our predicted HEAs are BCC HEAs, the stabilization of which originates from a combined effect of the high melting point of the constituent BCC elements, which are typically refractory, and a favorable mixing of elements on a BCC lattice. We show that the high melting point is in fact the main driving mechanism for the formation of single-phase HEAs. We further demonstrate the power of our method by predicting the existence of two new HEAs, i.e., the BCC AlCoMnNiV and the FCC CoFeMnNiZn, which have been synthesized and confirmed experimentally. The series of the Al- and Zn-containing HEAs show that non-refractory and cost-effective HEAs with a relatively low melting point can be stabilized by the subtle enthalpic competition between intermetallics and solid solutions. The discovery of a new BCC alloy and a FCC alloy analogous to the Cantor alloy but with an unusual element (Zn) is a compelling demonstration of how our approach can suggest unexpected chemistries and new avenues to the development of HEAs.

9:30 AM SF01.04.05
Investigation on Gradient Fe-Ni-Cr-Mn Alloy Using Diffusion Multiples Yasemin Yesilcicek, Annica Wetzel, Julia Witt, Christiane Stephan-Scherb and Ozlem Ozcan; Bundesanstalt für Materialforschung und Prüfung, Germany

The high-throughput synthesis and characterization of potential material combinations plays an important role in accelerating the development of new materials. Diffusion controlled synthesis of gradient alloys is widely used to create phase diagrams, and it is also one of the most effective combinatorial approaches for rapid realization of potential material combinations.
This study focuses on the synthesis and investigation of the quaternary multi-principal-element alloy (MPEA) FeNiCrMn by means of diffusion multiples, the correlation of their microstructural and chemical characterization data with their application relevant properties like local mechanical and corrosion properties. A diffusion system was set up by combining an equimolar ternary alloy (FeNiCr) with a single diffusing metallic component (Mn) with the highest interdiffusion coefficient. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were used to collect microstructural and compositional information which were correlated to local mechanical properties studied with nanoindentation. Local corrosion properties were investigated by means of Atomic Force Microscopy (AFM) and Scanning Electrochemical Microscopy (SECM). We have observed that a >50 µm deep homogeneous diffusion zone was formed the thickness of which scales with the duration of the thermal treatment. Beyond the Mn-concentration gradient in the FeNiCr matrix, a distinct Cr-rich secondary phase, characterized by high hardness and elastic modulus values appeared. We synthesized MPEAs with selected compositions from the diffusion zone as well as the Cr-rich phase as bulk alloys for electrochemical corrosion studies under different environmental conditions. The presentation will summarize the results of our correlative study on the mechanical properties and corrosion resistance of the quaternary multi-principal-element alloy (MPEA) FeNiCrMn family.

SESSION SF01.05: Physical, Chemical and Functional Properties
Session Chairs: Daniel Gianola and Yu Zou
Wednesday Morning, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate C2

10:30 AM *SF01.05.01
Thermal Stability and Mechanical Properties of Nanostructured High-Entropy Alloys Yu Zou; University of Toronto, Canada

In my presentation, I will talk about a few strategies for the fabrication of nanostructured HEAs – magnetron co-sputtering and electrodeposition. Such nanostructured HEAs exhibit high yield strengths and thermal stability compared to conventional binary alloys. I also demonstrate that such nanostructured HEA films show substantially enhanced stability for long-duration conditions. Nanostructured HEAs combining these properties represent a new class of materials in small-dimension devices potentially for high-stress and high-temperature applications.

11:00 AM *SF01.05.02
Strengthening of Al Matrix Composites by High Entropy Phases Hyunjoo Choi; Kookmin University, Korea (the Republic of)

Aluminum matrix composites (AMCs) have been extensively studied in future mobility industries because of their excellent mechanical properties and elastic modulus. Although carbon-based or ceramic materials have been used as reinforcement for AMCs, their poor wettability with aluminum should be overcome to develop high-strength lightweight composites.
This study employs high entropy alloys (HEAs) as reinforcement AMCs. HEAs have superior stiffness and strength as well as good wetting ability with aluminum. Two different types of composites are suggested in this study. First, sub-micron sized HEA particles, produced by thermal plasma treatment, were dispersed in aluminum powder. The composite powder was consolidated using hot rolling. Second, gas-atomized HEA powder and Al powder were simultaneously additive manufacturing using a multi-nozzle direct energy deposition (DED) printer. The effect of HEA phases on the strengthening of the Al matrix will be discussed.

11:30 AM SF01.05.03
Laser Annealing-Induced Generation and Phase Transformation of High Entropy Metal Alloy and Ceramic Nanostructures Amber Y. Li and Kwan W. Tan; Nanyang Technological University, Singapore

Metal-based inorganic nanomaterials made up of dissimilar elements have large functional potentials in various fields and applications such as catalysis, sensors and bioengineering. The control of crystal phase and composition of multicomponent nanoparticles is a powerful and effective strategy to introduce new unique physicochemical properties, functionalities and applications. Here we describe a millisecond laser annealing approach that provides control of crystal phases, compositions and functional properties of five-elemental multicomponent nanoparticles of metal alloys, oxides, and nitrides. Laser irradiation of an identical five-metal salt precursor mixture for different laser heating times (from 0.25 to 250 milliseconds) allows control of supercooling kinetics and reaction pathways toward multicomponent alloy nanoparticles have single and multiphasic solid solution characteristics, compositions and new physiochemical properties. In addition, laser annealing of a five-component nitride-former precursor mixture at different laser power levels provides selectivity in the formation of multicomponent tetragonal rutile oxide nanoparticles and phase transformation into cubic rock salt nitride nanoparticles. The method is highly generalizable and further provides access to multidimensional mesoporous metal nitride nanostructures. The resultant high entropy alloy nanoparticles enable various applications, including growth of high-quality carbon nanotubes, stable and efficient hydrogen evolution reaction as well as antimicrobial properties against E. Coli species.

11:45 AM SF01.05.04
Complex Roles and Structures of Short-Range Order in Si-Ge-Sn Medium-Entropy Alloy Xiaochen Jin, Shunda Chen, Christopher Lemkan and Tianshu Li; George Washington University, United States

Short-range order (SRO) has been recently demonstrated to play a crucial role in modulating a wide range of physical properties in medium-entropy alloys (MEAs) and high-entropy alloys (HEAs). However, there is a lack of general understanding of SROs in both their structural diversity and impact of properties in complex concentrated alloys. In this regard, our recent theoretical study[1] already demonstrated two distinct types of SROs, which carry different energies, distinct degrees of local ordering, and dissimilar electronic structures, can coexist across a wide range of compositions in Si-Ge-Sn MEAs. In further examining the structures and properties of these alloys, we combine first-principle calculations with Monte Carlo sampling, and further develop a highly-accurate, machine-learning interatomic potential. Our study shows electronic, optical, and thermal transport of Si-Ge-Sn alloys can be significantly modulated and engineered through tuning SROs. We further propose an extended descriptor of SRO, by taking into account both its distribution and higher-order effect.

This work is supported by Department of Energy through DE-SC0023412.

1. Jin, X., Chen, S. & Li, T. Coexistence of two types of short-range order in Si–Ge–Sn medium-entropy alloys. *Commun Mater* **3**, 66 (2022).

SESSION SF01.06: Refractory High Entropy Alloys
Session Chairs: Satish Rao and Cem Tasan
Wednesday Afternoon, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate C2

1:00 PM *SF01.06.01
High-Throughput Design of Refractory Multi-Principal Element Alloys Katharine Flores; Washington University in St. Louis, United States

The design of high entropy alloys often focuses on identifying near-equiatomic solid solution alloys; expanding these to include multiphase microstructures offers the opportunity to further enhance and control properties. Designing such multiphase, multi-principal element alloys (MPEAs) requires the ability to efficiently survey compositional space for phases and microstructures of interest using integrated experimental and computational methods. Here, we build on prior studies of the Nb-V-Zr system, which forms a BCC solid solution phase and two Laves phases. Applying a convex hull analysis, we predict the effect of Ti, Ta, and Mo additions on the stability of the BCC phase as a function of temperature and composition. The predicted structures are compared with the microstructures observed in compositional libraries prepared using a high-throughput, laser deposition-based synthesis method. This work provides guidelines for predicting compositional effects on microstructure and properties, which will accelerate the design of MPEAs for high-temperature applications.

1:30 PM *SF01.06.02
A Machine Learning-Driven Framework for Predicting Strength and High Temperature Oxidation Properties in Refractory Complex, Concentrated Alloys Michael Titus; Purdue University, United States

Refractory complex, concentrated alloys (RCCAs) offer new avenues for designing high strength and oxidation resistant materials at elevated temperature. However, RCCAs often exhibit multiple oxidation mechanisms including oxide volatilization, internal oxidation, external scale formation, and pesting. In this talk, we will present a new machine learning for accelerated materials discovery (ML-AMD) framework that utilizes multi-fidelity and multi-cost experiments with physics-based modeling. New semi-high-throughput methods for characterizing hardness and oxidation resistance will be presented, and methods for implementing high-throughput simulations into the ML-AMD framework will be expounded. Our recent efforts utilizing this framework have resulted in the discovery of ultra-high hardness single phase body-centered cubic RCCAs with up to 35at.% Al content. We have additionally created an open-source, automated framework housed in NanoHub for experimental data ingestion and storage of high temperature oxidation experimental data. Predictions of mass gain behavior of RCCAs utilizing machine learning with physics-based descriptors will be presented, and recent efforts to design new RCCAs with superior oxidation resistance will be shown.

2:00 PM SF01.06.03
Accurate Determination of Two-Dimensional Energy Landscape of Dislocation Motion in bcc High-Entropy Alloy Yifan Wang[1], Nicolas Bertin[2], Vasily Bulatov[2] and Wei Cai[1]; [1]Stanford University, United States; [2]Lawrence Livermore National Laboratory, United States

The unusual low-temperature plasticity behaviors of bcc metals and alloys are known to be attributed to the complex core structure of screw dislocations, whose motion is governed by thermally activated kink-pair nucleation mechanisms on the two-dimensional Peierls potential. However, this 2D energy surface is usually estimated by simplified elasticity theory in pure bcc metals, with limited applicability to complex bcc systems such as bcc high-entropy alloys (HEA). Here we present an efficient minimum energy mesh (MEM) method foraccurately determining the 2D Peierls potential surface defined by the three ‘easy core’ configurations, to provide a complete picture of the smooth energy landscape of the core structure. The method proceeds by evolving triangulated meshes, i.e., the smooth surfaces with intrinsic parametrization whose dynamicsautomatically converges to the minimum energy surface in the configurational space. This MEM method accurately determines arbitrary 2D energy landscape, enabling the stress, composition, and short-range order dependence of thermally activated dislocation motion in bcc HEA.

2:15 PM SF01.06.06
On the Molten State Processing of Refractory Complex Concentrated Alloys Calvin H. Belcher, Sakshi Bajpai, Benjamin E. MacDonald, Diran Apelian and Enrique Lavernia; University of California, Irvine, United States

The field has witnessed significant growth in the experimental exploration and understanding of RCCAs. Molten state processing of RCCAs through vacuum arc melting has been the main processing path to produce components. However, there are still challenges in controlling impurity elements in RCCAs. Moreover, the behavior of the impurity elements in the RCCAs is not well understood. In this work, the chemistry of the chamber environment during arc melting was studied using a mass spectrometer. Process methodologies were studied to control impurity gas elements such as oxygen and nitrogen in arc melted RCCAs. Furthermore, by arc melting NbMoTaW and TiNbZr RCCAs in various environments, relationships between RCCA constituents and impurity element absorption were explored. Through mechanical testing, X-Ray diffraction, and electron microscopy, the behavior of impurity elements in various RCCA compositions will be reviewed and discussed.

SESSION SF01.07: Theoretical Modeling and Computational Simulations
Session Chairs: Hyunseok Oh and Michael Titus
Wednesday Afternoon, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate C2

3:30 PM *SF01.07.01
Simulations and Modelling of the High Temperature Yield Behavior of Compositionally Complex Concentrated BCC Alloys Satish Rao[1,2], B. Akdim[1,3], O. Senkov[1,2], Glenn Balbus[1] and E. Payton[1]; [1]Wright Patterson Air Force Laboratories, United States; [2]MRL Materials Resources LLC, United States; [3]UES Inc., United States

Atomistic simulations, using Johnson-Zhou and/or Snap potentials, of the core structure and mobility of ½[111] screw, edge and mixed dislocations in complex concentrated BCC alloys are presented. The core structure and its variations obtained for screw dislocations in NbTiZr using atomistic simulations are compared with first-principles calculation results and good agreement is found. Molecular Dynamics results show that a moving screw dislocation leaves behind interstitial and vacancy dipoles in these alloys. Average solute-dislocation core interaction energies are used to determine the critical stress for the motion of screw dislocations as a function of temperature using Rao- Suzuki model of kink migration / kink-kink collisions controlled mobility, developed for concentrated BCC random alloys. In addition, diffusional effects at very high temperatures on the predicted yield behavior are modelled. Simple expressions for yield stress based on the Rao-Suzuki model is presented. Edge dislocation mobilities in these alloys are modelled using the Maresca-Curtin model. The model results on yield behavior are shown to be in good agreement with experimental data in selected BCC complex concentrated alloys.

4:00 PM SF01.07.02
A Phenomenological Discrete Lattice Model for Simulating the Response of High-Entropy Alloys Vinod K. Tewary and Edward J. Garboczi; National Institute of Standards and Technology, United States

High-entropy alloys (HEAs) are a class of materials with revolutionary applications as structural and functional materials. They are very strong and have high melting points. Moreover, they can retain their strength at high temperatures, even fairly close to melting points. This makes them particularly suitable for use in extreme environments such as in turbines and power stations.
HEAs are essentially random alloys, typically containing five or more elements in approximately equal concentrations. The formulation of predictive theories for the strength of random alloys has been a topic of active research that has resulted into useful theories such as the effective medium theory. However, these theories are, in general, limited to low concentrations of the solutes and are not applicable to HEAs, in which the relative concentration of solutes is high.
We propose a new, phenomenological discrete lattice model for the analysis and representation of measurements of HEA characteristics. Our model is essentially an atomistic version of the theory given by Varvenne, Luque, and Curtin [Acta Materialia **118** (2016) 164]. Instead of the usual continuum approximation, we assume a discrete Born von Karman model for the underlying lattice of the alloy. We define an effective monoatomic lattice, which has the same Bravais lattice structure and bulk elastic and thermal characteristics as the original alloy. In our model, each lattice site is assumed to be occupied by a hypothetical, effective atom, which is an 'average' of all the constituent solutes. Thus, instead of averaging over the field, we average over the solute atoms and replace each real solute by an effective atom.
The next step is to locally replace one single effective atom by a real solute atom. This atom now becomes a defect, which distorts the host lattice. We calculate the lattice distortion by using the multiscale Green's function (GF) method, developed in our group for general solids. The key point of the model (Varvenne et. al.), is that the dislocations in the solid interact with the local distortion field of each defect. This interaction is responsible for the characteristic hardness of the alloy.
As an example, we apply our theory to a Ni-Co-Fe-Cr-Mn alloy. This alloy has been a popular choice in the literature and has an fcc Bravais lattice. The mass of each effective atom is the weighted average of all the solutes. For the interatomic interaction, we choose a two-exponential, four-parameter function, which extends up to second neighbors of each atom. The four parameters are determined using the literature values of the three elastic constants of the alloy, and its average binding energy, which also gives the effective lattice constant. Using this potential, we calculate the interatomic force constants, the phonon dispersion, and the phonon density of states by the method of the phonon GF. The interaction between the local distortion and dislocations is calculated by using the multiscale GF.
The primary advantages of our GF method, compared to the previous methods, are the following:
1. High computational efficiency. It can simulate a large crystallite (million atoms or more) in a few seconds even on an ordinary desktop. The computational expense of ordinary molecular dynamics generally limits the number of atoms that can be included in the model.
2. Multiscale. It is valid at close range as well as at asymptotic distances from the defect. The GF accounts for the discrete lattice effects and nonlinear contributions in the near field. The GF reduces seamlessly to the macroscopic continuum values in the far field limit. This is crucial for modeling the interaction between the dislocations and the defects, which is absolutely essential for HEAs.
3. Flexible model: It can be extended to include more distant neighbors, and more general potentials.
4. The phonon GF can be used to calculate the relevant thermodynamic functions, such as the specific heat and the vibrational entropy.

4:15 PM SF01.07.03
Short-Range Ordering in Unaged High-Entropy Materials Flynn Walsh[1,2], Mingwei Zhang[1,2], Wenqing Wang[1,2], Andrew M. Minor[1,2], Robert O. Ritchie[1,2] and Mark Asta[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

The prospect of local chemical ordering in high-entropy materials has received significant attention, but there remains little consensus on the issue. Fundamental questions, such as the role of compositional complexity and the quantitative degree of order expected in quenched or slow-cooled samples, appear largely unanswered. These topics are addressed from a theoretical perspective while drawing on a range of experimental studies. Transferable thermodynamic principles are extracted from lattice models for several types of systems with an emphasis on face-centered cubic alloys. In particular, phenomenological Landau theory is used to determine the forms of order that can arise above a critical temperature in many-component systems; these structures may differ from those obtained from long-term annealing below the critical temperature. The ability of various experimental techniques, such as electron microscopy and resistivity measurements, to directly or indirectly detect this form of order is also discussed.

SESSION SF01.08: Poster Session
Session Chair: Eun Soo Park
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SF01.08.01
Transmission Electron Microscopy of Temperature Dependent Deformation Mechanisms in High-Entropy Alloys Madelyn I. Payne[1,2], Mingwei Zhang[1], Punit Kumar[1], Mark Asta[1,2], Robert O. Ritchie[1,2] and Andrew M. Minor[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

High-entropy alloys (HEAs) have attracted attention from the metallurgy community due to their exceptional properties, often at both high and low temperatures. Transmission electron microscopy (TEM) provides a means to investigate various deformation mechanisms producing exceptional properties in both face-centered cubic (fcc) and body-centered cubic (bcc) HEA systems. High-resolution TEM and four-dimensional scanning electron microscopy (4D-STEM) analysis reveal an extended sequence of deformation mechanisms that produce exceptional fracture toughness. Spatially-resolved structural information from 4D-STEM datasets uncover how stacking faults, hcp laths, and nanotwins operate synergistically to prolong strain-hardening. Furthermore, TEM imaging of in-situ tensile straining of HEAs demonstrates dislocation mobility mechanisms at both room temperature and elevated temperatures, providing insight to differences of deformation properties at various temperatures. Here we report both ex situ and in situ TEM observations of deformation mechanisms in both fcc HEA and bcc refractory HEAs across a wide range of temperatures.

5:00 PM SF01.08.02
Formability optimization of complex concentrated alloys by utilization of elemental information Jeongwon Yeh[1], Chanyang Kim[2], Myoung-Gyu Lee[1] and Eun Soo Park[1]; [1]Seoul National University, Korea (the Republic of); [2]Korea Institute of Materials Science, Korea (the Republic of)

CCAs have been widely considered to be promising structural materials for extreme environment due to their unique mechanical properties at room temperature as well as cryogenic condition and elevated temperatures. Because the selected alloying elements and their composition decide the reactive phase formation and the resulting mechanical properties, many researchers in metallic material fields have focused on the effect of composition on the evolution of microstructures and mechanical behaviors of CCAs. In order to commercialize the CCAs, the formability should be researched in advance. However, there is very little attention up to date to evaluate formability in these materials.
Therefore, in this study aims to propose a compositional range with excellent formability depending on deformation mechanism in the Cr-Mn-Fe-Co-Ni CCA system. Firstly, we tried to equilibriate the $\Delta\chi$, which is known to be proportional to yield strength (σy), to eliminate the effect of strength difference. Afterward, to confirm the effect of deformation mechanism on the formability of CCAs. we evaluate the formability of CCAs by both numerical simulations (Fracture Forming Limit Diagram: FFLD) and experiments (Limit Dome Height test: LDH). To understand numerical and experimental results, microstructures were compared at the same equivalent strain values under plane strain condition and uniaxial strain condition, representing the forming strain condition and tensile strain condition respectively. Through these results, it was possible to proposed a deformation mechanism with excellent formability in Cr-Mn-Fe-Co-Ni CCAs system.

5:00 PM SF01.08.03
Enhancement of low-T impact resistance by activation of multi-deformation mechanisms in HEA with manipulated SFE Kooknoh Yoon[1], Hyunseok Oh[2], Je In Lee[3] and Eun Soo Park[1]; [1]Seoul National University, Korea (the Republic of); [2]Massachusetts Institute of Technology, United States; [3]Pusan national university, Korea (the Republic of)

Low-temperature structural materials have been used in various fields, including LNG pipes, tanks, etc. FCC alloys, such as austenitic stainless steel, invar, etc., are used for applications. Although the FCC alloys do not exhibit DBTT at low temperatures, the capability for elongation is still restricted under dynamic stress conditions due to the high tendency of dislocation entanglement at low temperatures. Therefore, it is necessary to consider the (impact) toughness as well as the mechanical properties for targetting low-temperature applications. Meanwhile, it has been reported that the FCC HEAs exhibit excellent toughness at low temperatures since they can have a large number of nano-twins during deformation at low temperatures. From this idea, we tried to suggest a design methodology to manipulate the deformation behavior at low temperatures of the CrMnFeCoNi alloy by controlling the SFE, as well as to increase the strength by alloying Al to this alloy simultaneously. Finally, the developed the HEA-2 ($Cr_{20}Mn_6Fe_{34}Co_{34}Ni_6$ + Al 2.5at%) shows 20% increased impact toughness than the Cantor alloy at -100ºC since the HEA-2 has a relatively large elongation due to the activation of multi-deformation mechanisms, despite it has 2-times larger yield strength. The results will provide a solid guideline for developing a novel HEA for low-temperature applications.

5:00 PM SF01.08.06
nergy Landscape for Screw Dislocation in Body-Centered Cubic Binary and Ternary Subsystems of MoNbTaW Wenqing Wang[1], Flynn Walsh[1], Mark Asta[1] and Robert O. Ritchie[2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Refractory high-entropy alloys (RHEA) exhibit high strength and compressive ductility at elevated temperatures. However, their engineering application is limited by their brittle failure modes under tension. The plastic deformation behavior of RHEAs may be closely linked to the energetics of screw dislocation cores, which depend on local chemical environments. Recent work has shown that, in contrast to pure metals, chemically disordered MoNbTaW exhibits a rough landscape of screw dislocation core energies, but the energy fluctuations are decreased by the formation of local chemical order. It is unclear, however, the extent to which these effects are related to the "high-entropy" nature of the system. We thus compare the dislocation core energetics of MoNbTaW and its binary and ternary subsystems. Using a machine learning interatomic potential, we calculate the dislocation energy landscapes in random and equivalently short-range ordered alloys. Results suggest that the specifics of the ordering phase transition are more important than the number of components.

5:00 PM SF01.08.07
Corrosion Behavior of AZ31 Magnesium Alloy with Different Grain Sizes Wenli Zhao and Qizhen Li; Washington State University, United States

AZ31 magnesium alloy is attractive as a candidate for biodegradable implanting devices. Depending on the actual applications, it is often necessary to modify the microstructure of materials to achieve different properties. It is critical to understand the relationship between microstructure and corrosion property of AZ31 magnesium alloy. This work focused on the effect of grain size on corrosion behavior of AZ31 magnesium alloy. Heat treatment was employed to obtain the samples with different grain sizes. Bio-corrosion test was conducted for the samples through being immersed in simulated body fluid for various time intervals. Scanning electron microscope was employed for observing morphology changes due to corrosion testing. The results show that the corrosion rates increased with the immersion duration for the samples, the samples with larger grain size exhibited better corrosion resistance, and the corrosion mechanisms for the sample was uniformly pitting corrosion.

5:00 PM SF01.08.08
A Study on the Characteristics of Ideal Glass State via Denary High Entropy Metallic Glasses Ji Young Kim[1], Geun Hee Yoo[1], Jung Soo Lee[1,2], Hyejung Chang[3], Jinwoo Hwang[4] and Eun Soo Park[1]; [1]Seoul National University, Korea (the Republic of); [2]Inha University, Korea (the Republic of); [3]Korea Institute of Science and Technology, Korea (the Republic of); [4]The Ohio State University, United States

In the field of metallic glasses, the ideal glass state has attracted special attention because it is expected to have exceptional characteristics of high mechanical strength based on its unique atomic structure. The unique structure is characterized by high diversity in local structure, which means that it is not dominated by particular motifs. Even though it is suggested that mixing a large number of elements with different atomic sizes is a way to fabricate ideal metallic glass, there is a lack of research on proving the ideal glass state experimentally. In this study, we designed high entropy metallic glasses (HE-MGs) with 10 different elements to make the atomic structure close to the ideal glass state. Using these HE-MGs, we studied the various characteristics of ideal glasses, such as medium range ordering (MRO) structure, mechanical and thermal response, and crystallization behavior. We expect that the results enhance the insight into the ideal glass state in terms of atomic structural characteristics, unique mechanical properties, and abnormal crystallization behaviors.

5:00 PM SF01.08.09
Porous High Entropy Alloy as Efficient Electrocatalysts for Water Splitting Taehyun Kwon, Suyeon Kim, Minsol Kwon and Dongju Lee; Chungbuk National University, Korea (the Republic of)

High Entropy Alloy (HEA) has attracted attention for its excellent corrosion resistance and adjustable properties due to four core effects. When a non-noble-metal such as Fe, Co, and Ni is used to form the HEA composition, better catalyst properties are exhibited than using each element. In addition, HEAs have good corrosion resistance and stability due to the lattice distortion effect and the slow diffusion effect. Therefore, HEAs are expected to be a key to solving the high price of catalysts for hydrogen production.
In this study, The HEA composition was designed by predicting the composition of the single phase through the CALPHAD program by referring to the Volcano plot. HEA powders were fabricated via a powder metallurgy process. The prepared porous HEAs exhibited remarkable performance in the oxygen evolution reaction and the hydrogen evolution reaction due to the adequate adsorption energy of hydrogen or oxygen atoms being adjusted by the cocktail effect. Based on these results, it is expected that HEAs electrocatalysts are possible to use large-scale alkaline water electrolysis electrode.

Acknowledgement
This work was supported by the National Research Foundation of Korean (NRF) grant funded by the Korea government (Ministry of Science and ICT) (2021R1F1A1058854) and the Development of 100 nm sized tungsten based material out of scrap and tool manufacturing technology using scrap for precision machining (20011520) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

5:00 PM SF01.08.10
Characteristic Change of High Entropy Garnet Structure $(Y_{0.2}Yb_{0.2}Lu_{0.2}Eu_{0.2}Er_{0.2})_3Al_5O_{12}$ by Fe^{3+} Substitution Hyeryang Choi, Janghyeok Pyeon, Bong-Gu Kim, Junseong Kim, Dong Gyeong Kim, Haeun Seo, Jung-Hun Son, Byungil Yang, Yeon-Gil Jung and SeungCheol Yang; Changwon National University, Korea (the Republic of)

YSZ (Yttria-Stabilized Zirconia) have been widely used as thermal barrier coating (TBC) materials for gas turbine. However, use of YSZ was limited at high temperature of over 1200 celsius due to phase transformation of YSZ accompanied with volume expansion and its low sintering resistance. In present work, we synthesized Fe-doped HEYAG (High Entropy Yttrium Aluminum Garnet) powder via a solid-state reaction. And then pellet, made with the powder, was sintered at 1450 celsius. The sintered Fe-doped HEYAG samples were characterized by using X-ray diffraction, scanning electron microscopy, Vickers hardness, thermal conductivity and thermal expansion coefficient. The Fe-doped HEYAG samples showed higher uniform element distribution compared to HEYAG samples. As Fe was more doped, XRD peaks of HEYAG shift to lower angle due to increment of average bonding length. Thermal conductivity of Fe-doped HEYAG is lower as Fe was more doped. When compared with YSZ, Fe-doped HEYAG with optimized Fe content shows lower thermal conductivity.

5:00 PM SF01.08.13
Effects of Mixing on High Entropy Spinel Oxides for Oxygen Evolution Reaction Jihyun Baek[1], Delowar Hossain[1,2], Michal Bajdich[2] and Xiaolin Zheng[1]; [1]Stanford University, United States; [2]SLAC National Accelerator Laboratory, United States

High entropy oxides (HEOs) consist of five or more metal cations, offering ample opportunities to tune their catalytic properties toward high oxygen evolution reaction (OER) efficiency. We combine theoretical and experimental studies to scrutinize the OER activity and stability for spinel-type HEOs. First, we employ density functional theory (DFT) calculations to predict mixing enthalpies and OER activity descriptors for various metal active sites using a spinel-type HEO impurity model under the equimolar mixing conditions. Our DFT results show that the randomly mixed metal sites exhibit negative Gibbs free energy of mixing and are hence thermodynamically stable. Later, we utilize the rapid sol-flame method to synthesize various spinel oxides with up to five metal cations (Co, Fe, Ni, Cr, and Mn). The HEO shows the highest OER activity compared to the lower entropy oxides under alkaline conditions and excellent durability with the slight formation of surface oxyhydroxide with Fe and Ni. Finally, the calculated HEO activity predicts the lowest overpotential for Co active site compared to other active sites and lower entropy oxides, which is in good agreement with experimental activity trends for different spinel oxides. Interestingly, the OER activity of HEOs with the same composition exhibits a distribution of overpotential varies due to the broadening of intermediates adsorption energies, which originates from the equatorial strain (contraction/expansion) of the active metal-oxygen bonding configurations, leading to weaker/stronger surface thermodynamics.

SESSION SF01.09: Functional Properties and Innovative Applications I
Session Chairs: Cecilia Cao and Mitra Taheri
Thursday Morning, April 13, 2023
Marriott Marquis, B2 Level, Golden Gate C2

8:30 AM *SF01.09.01
Tailoring High Entropy Alloys—From Nearest Neighbor to Bulk Processing Mitra L. Taheri; Johns Hopkins University, United States

High entropy alloys are promising for candidates for a wide variety of applications, from aerospace to medicine. One tuning knob that HEAs possess is the short range order. Designing alloys for short range order can be done but measuring order is time consuming and difficult. Here we describe a data-driven, high throughput approach to alloy synthesis, characterization, and scale up with short range order as a design element. We reveal that order can be tracked in hundreds of alloys in real time, on the fly, using ML tools for semi-autonomous experimentation. Notably, the presence of short range has been connected to metastable phase evolution and non-equilibrium structures. These findings provide a pathway for tailoring high entropy alloys through these novel microstructural evolution pathways. To that end, highlights from scaling these alloys via bulk processing will be discussed.

9:00 AM *SF01.09.02
High-Entropy Materials for Energy Applications Ben Breitung[1], Simon Schweidler[1], Anurag D. Khandelwal[1], Yanjiao Ma[1], Qingsong Wang[2], Abhishek Sarkar[1] and Jasmin Aghassi-Hagmann[1]; [1]Karlsruhe Institute of Technology, Germany; [2]Universität Bayreuth, Germany

Recently, the concept of high entropy has found its way into many different application areas. One example is applications whose operation is based on the properties of crystalline materials, which is a promising field for this type of materials.
High-entropy materials are materials that contain many different elements in a single-phase crystal structure and therefore exhibit high configurational entropy. Due to the complex interactions between the contained elements and other structural features such as lattice distortion by ions of different sizes, high-entropy materials can exhibit diverse and unexpected properties compared to binary materials. High entropy ceramics have only been known since 2015[1], so this field of research is still relatively unexplored, leaving room for further work.
In this talk, the advantages of different high entropy ceramics in the field of energy and electrical applications will be highlighted.[2] In particular, various high entropy ceramics for energy storage and materials for electronic applications will be discussed. It has been shown that certain high entropy ceramics can stabilize Li- and Na-battery cycling, increase capacity, or suppress structural changes that might otherwise lead to structural degradation of the active material.[3–5] In addition, their implications for some electronic applications are discussed, e.g., for catalytic applications or as functional materials for printed electronics.

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9:30 AM SF01.09.03
Tuning Morphology and Cation Selection for OER and ORR Bifunctional Catalytic Activity in Nano (nA1/n)Co2O4 Xin Wang[1], Harish Singh[2], Manashi Nath[2] and Katharine Page[1]; [1]The University of Tennessee, Knoxville, United States; [2]Missouri University of Science and Technology, United States

Reducing carbon emissions to meet the carbon neutrality goal while providing global energy demand on the terawatt level promotes the pursuit of clean energy technologies such as photovoltaics, wind turbines, and the production of hydrogen from water in a sustainable manner. Water splitting to produce hydrogen via the electrolysis pathway is considered a promising direction toward carbon-free energy production, especially considering the potential utilization of renewable (wind, solar, geothermal) and nuclear energy for the electricity source. A key research challenge lies in improving the energy efficiency for converting electricity to hydrogen over various operating conditions. With this regard, designing and developing economically feasible, earth-abundant, inexpensive, efficient electrocatalysts for the oxygen evolution reaction (OER) is a critical research factor. Even further, searching for electrocatalysts that can boost both the OER and the oxygen reduction reaction (ORR) simultaneously is crucial for deploying hydrogen production in a usable form, e.g., fuel cells. Conventional research focuses on noble metal (Pt, Ir, Ru, etc.) based electrocatalysts, which cannot meet the future goal of large-scale deployment due to their low abundance and high cost. Therefore, there have been intense efforts in exploring low-cost transition metal-based electrocatalysts, among which cobalt oxides are promising for both OER and ORR. Early this year, A. H. Li, et al. reported in Nat. Catal. a significant enhancement of the stability of Co3O4 spinel oxide by inserting Mn into the lattice. According to their report, the catalyst lifetime in solid acid (pH=1) environment was extended by two orders of magnitude. In fact, the exploration space can be enormously expanded by introducing compositional complexity in the cobalt spinel oxide system. In such scenarios, the rich variety of local geometry and coordination environment as induced by the compositional complexity enriches the type and/or strength of orbital hybridization. Consequently, the electronic structure could be tuned to control the reactivity of those active elements. Understanding how various local environments (geometry, distortion, coordination) are linked to electrocatalytic performance is therefore crucial, which then further necessitates a clear picture of the nature and tunability of the family's structure across length scales.

9:45 AM SF01.09.04
Understanding the Mixing and Properties of High Entropy Perovskites Ali Nasrallah[1], Colin L. Freeman[1], Ge Wang[2] and Derek Sinclair[1]; [1]University of Sheffield, United Kingdom; [2]The University of Manchester, United Kingdom

High-Entropy Oxides (HEOs) have gathered a lot of attention over the past few years particularly around their formation and properties[1–4]. The perovskite lattice (ABO_3) is a particularly exciting opportunity as mixing can be carried out on both the A or B site presenting a wealth of enthalpic and entropic possibilities to achieve a single-phase solid solution with a favourable Gibbs free energy[4].
Using a combination of computational modelling and experimental studies, we have examined several 3-, 4-, and 5-B element oxides with combinations of (Ga, Y, In), Nb, (Ti, Zr, Sn). We have studied the influence of a range of factors including the ionic size of the sites, the tolerance factor and the ionic size variation which we can then link to the formation of single-phase materials.

Our experiments on Ba-based perovskites demonstrate that single phases can be formed in a range of 4 and 5-B element perovskites with mixed valence charges (e.g. 3+, 4+ and 5+) but mixing was far more challenging with only 3-B element systems. By adjusting the A-site using Sr and Ca we were able to reduce the ionic size penalties and form further 3-B site single phase systems indicating that the size of the A cation also has an effect on the mixing process.

We have coupled the experimental work with a mixture of classical and ab initio simulation work examining the enthalpy of mixing and comparing to the phase formation from experiment. Our DFT simulations have identified the different mixing and hybridisation characteristics of the ions which affects their ability to mix and can run counter to expected ion size behaviour. Our classical simulations have optimised and examined hundreds of different structures which allows us to comment on the ideality of the solid solutions formed and the competition between entropy and enthalpy in the stability of a phase. We are also able to examine different secondary structures and how their enthalpic stability compares. Moreover, using computational and experimental Raman spectroscopy we are able to comment on the polymorphs obtained experimentally for the various perovskites.

From our results, we offer thoughts on the differing rules governing the mixing processes in these perovskite phases.

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10:00 AM BREAK

10:30 AM SF01.09.07

Nanoscale High-Entropy Oxides (HEO) from Spray-Flame Synthesis for Oxygen Evolution Reaction (OER) in Water Splitting and Catalytic Cyclohexene Oxidation Steven Angel[1], Vimanshu Chanda[1], Ignacio Sanjuán Moltó[1], Julia Büker[2], Corina Andronescu[1,1], Martin Muhler[2], Christof Schulz[1,1] and Hartmut Wiggers[1,1]; [1]University of Duisburg-Essen, Germany; [2]Ruhr-University Bochum, Germany

Alternative solutions for energy conversion and storage are continuously developed and envisioned to become ubiquitous and ever more efficient, affordable, and sustainable. This challenging endeavor is enabled by the sustained development and discovery of new functional materials. In this regard, high-entropy oxides (HEO) have recently gained much attention as novel, e.g., anode/cathode materials for Li-ion batteries or fuel cells, and catalysts for low-temperature CO oxidation [1, 2]. HEOs are compounds counting with a configurational entropy higher than 1.609 R (R: gas constant) – requiring to have at least five different cations with similar atomic concentration – which are stabilized above a critical temperature (e.g., >850 °C) [3]. Thus, the synthesis techniques of these compounds typically require high temperatures, which can be achieved using a calcination step after, e.g., a co-precipitation step of the required precursors as in conventional methods [4]. Alternatively, the spray-flame synthesis method – in which temperatures higher than 1300 °C are typically obtained [5, 6] – offers the option to continuously synthesize HEOs in a single step.

In this work, the spray-flame synthesis of three HEOs, HEO1: $(Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2})O$, HEO2: $(Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2})_3O_4$, and HEO3: $(Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.1}Mg_{0.05}Al_{0.05}Cu_{0.2})_3O_4$ – is explored. While the spray-flame synthesized HEO1 – according to XRD and SAED measurements – crystallizes as a single phase in the rock-salt (NaCl type) structure, the HEO2 and HEO3 samples were stabilized in the single-phase spinel Fd-3m structure. Based on TEM/EDX measurements, particles from the HEO1 were found to have a predominantly cubic morphology (d_p = 7–10 nm) and a homogeneous element distribution on the atomic scale with local fluctuations of Mg and Zn. In contrast, the HEO2 and HEO3 samples presented particles with polyhedral (e.g., rhombicuboctahedron) morphologies and spherical particles (d_p = 5–12 nm) with uniform elemental distributions. The samples were further characterized by temperature-dependent XRD/TEM, TGA/DSC, FTIR, and XPS.

All spray-flame-synthesized HEOs were tested as oxygen evolution reaction (OER) catalysts in the electrochemical water splitting. HEO1 presented a promising activity, reaching a current density of ~70 mA/cm^2 at a potential of ~1.65 V vs. RHE. Additionally, the HEO1 was also tested as a catalyst for cyclohexene oxidation, showing an unexpected selectivity towards 7-Oxabicyclo[4.1.0]heptan-2-one, which has not yet been found for other catalysts in this form.

References

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10:45 AM SF01.09.08

Corrosion Properties of Medium Entropy Alloys under Oxygen Evolution Reaction Conditions in Aqueous Electrolytes Annica Wetzel, Ozlem Ozcan, Julia Witt and Daniel Morell; Bundesanstalt für Materialforschung, Germany

Due to their favorable mechanical and anti-corrosion properties, medium entropy alloys (MEA) are of high academic and industrial interest as novel materials for engineering and catalytic applications. Previous studies indicate high transpassive currents without indication of pitting for MEAs, which makes them promising materials for oxygen evolution catalysts [1].

To understand the stability of MEAs CrCoNi and FeCrNi at high anodic potentials, we have investigated the mechanisms of transpassive dissolution and the oxygen evolution reaction (OER). Scanning electrochemical microscopy (SECM) was applied in the interrogative mode for the detection of evolving metal species and oxygen during controlled polarization. SECM operated with oxygen reduction at the probe precisely determined the onset of the OER. Inductively coupled plasma – mass spectroscopy (ICP-MS) analysis was performed to quantify dissolved metal species. Potentiodynamic, potentiostatic and chronoamperometric techniques as well as different electrolytes were used to induce precisely controlled corrosion loads during the SECM experiments and for the ICP-MS analysis. Macroscopic corrosion properties of the alloys, electrical and chemical properties of the passive films were studied by means of potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and X-Ray Photoelectron Spectroscopy (XPS), respectively.

Finally, the analysis of the corrosion morphology and the potential of the surface before, during and after passivity breakdown was carried out by means of in-situ atomic force microscopy (AFM) and scanning Kelvin probe force microscopy (SKPFM). Our results indicate that even though the OER accounts for the majority of the observed transpassive currents, for alloys showing excellent passivation behavior like CrCoNi, the localization of the corrosion at grain boundaries may still present a challenge for material durability. The presentation will summarize the detailed electrochemical characterization of the corrosion processes of the studied MEAs with a specific focus on the transpassive behavior under OER conditions.

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11:00 AM SF01.09.09
Modeling High-Entropy Intercalation Cathodes with Sparse Lattice Models Peichen Zhong[1,2], Fengyu Xie[1,2] and Gerbrand Ceder[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Disordered rocksalt materials are the most promising earth-abundant cathode materials for Li-ion batteries, and as such can enable scaling of Li-ion energy storage to many TWh/year production. Such modern battery materials can contain a large number of elements with substantial site disorder, and their state of short-range ordering has been shown to be critical for their performance. Ab-initio modeling of the configurational degrees of freedom increases exponentially with the number of species included. The problems to apply cluster expansion techniques include: (1) how to generate lattice models without over-fitting; (2) how to properly sample the configurational space in ionic systems with charge-neutrality.

To address these, we will demonstrate two novel methods to approach the multi-component space of DRX: (1) applying L0L2-norm regularized regression with structural hierarchy to construct a robust cluster expansion Hamiltonian. (2) implementing grand-canonical Monte Carlo to sample charge-balanced ionic configurations. We apply these approaches to compute the voltage profile of $Li_{1.3-x}Mn_{0.4}Nb_{0.3}O_{1.6}F_{0.4}$, and demonstrate how Mn and oxygen contributes to the redox potential as Li is intercalated.

SESSION SF01.10: Functional Properties and Innovative Applications II
Session Chairs: Ben Breitung and Hyunseok Oh
Thursday Afternoon, April 13, 2023
Marriott Marquis, B2 Level, Golden Gate C2

1:00 PM *SF01.10.01
Crystallography of High Entropy Metal Carbides—A New Class of Ultrahigh Temperature and Irradiation Resistant Ceramics Olivia A. Graeve, Ved Vakharia and Luyao Zhang; University of California, San Diego, United States

We will describe the unique crystallography and microstructure of high-entropy Mo-Nb-Ta-V-W carbides prepared using a novel solvothermal synthesis process. The compounds were produced by mixing metal chlorides and carbon powder in the presence of molten lithium. Solvothermal synthesis occurs at a high temperature (upwards of 2000°C), which allows the carbides to undergo reaction-driven alloying and form single-phase solid solutions of nanopowders without the need for further thermal treatment. We have produced binary, ternary, quaternary, quinary, and senary metal carbides through systematic manipulation of elemental composition, particularly counteracting the tendency of WC and MoC to form. Solid solutions have been confirmed by a combination of X-ray diffraction and energy dispersive spectroscopy. Subsequently, spark plasma sintering (SPS) was used to obtain dense specimens. Carbon was added to the carbide powders to facilitate densification of the targeted compositions at a low sintering temperature (1600°C), compared to typical temperatures required for carbides. Low temperature sintering avoids heat-driven grain growth and allows for a finer grain size distribution.

1:30 PM SF01.10.02
Ablation Threshold and Temperature Dependent Thermal Conductivity of High Entropy Carbide Thin Films Milena Milich[1], Kathleen F. Quiambao-Tomko[1], John Tomko[1], Jon-Paul Maria[2] and Patrick E. Hopkins[1]; [1]University of Virginia, United States; [2]The Pennsylvania State University, United States

High entropy carbides (HECs) are a promising new class of ultra-high temperature ceramics that could provide novel material solutions for leading edges of hypersonic vehicles, which can reach temperatures > 3,500 °C and experience extreme thermal gradients. Although the mechanical and thermal properties of HECs have been studied extensively at room temperature, few works have examined HEC properties at high temperatures or considered these materials' responses to thermal shock. In this work, we measure the thermal conductivity of a variety of five-cation HECs up to 1200 °C. We find that thermal conductivity increases with temperature, consistent with trends demonstrated in single-metal carbides. We also measure thermal conductivity of an HEC deposited with varying CH_4 flow rate, and find that although thermal conductivity is reduced when carbon content surpasses stoichiometric concentrations, the films all exhibited the same temperature dependent trends regardless of carbon content. To compare the thermal shock resistance of HECs with a refractory carbide, we conduct pulsed laser ablation measurements to determine the fluence threshold the HECs can withstand before damaging. We find that this metric for the average bond strength trends with the theoretical hardness of the HECs as expected.

1:45 PM SF01.10.03
Friction Behavior and Terminal Group Effect of High Entropy MXene at Nanoscale Jiaoli Li[1], Yuwei Zhang[1], Yanxiao Li[2], Yuxiang Gan[1], Risheng Wang[1] and Chenglin Wu[1]; [1]MST, United States; [2]NYU, United States

High entropy MXene (HE MXene) is a new frontier MXene that has great potential for solid lubricants due to its diverse composition, volatile physical and chemical features. Here we experimentally investigated the friction of two HE MXene ($TiVNbMoC_3T_x$ and $TiVCrMoC_3T_x$) and compared their friction properties with $Ti_3C_2T_x$ MXene, Ti_2CT_x MXene, graphene, and $MoSe_2$ at the nanoscale via atomic force microscopy (AFM). Different scan distances (15nm and 1μm) and layers (1, 2, 3, 4, 5, 6, and more than 6 layers) were applied to obtain the corresponding friction properties of each of these 2D materials. Moreover, effect of the terminal groups on the friction behaviors at the nanoscale was also investigated by removing the -OH functional groups on HE, $Ti_3C_2T_x$ and Ti_2CT_x MXene surfaces using annealing treatment. Our preliminary result has shown that the friction properties of HE MXene are similar to $Ti_3C_2T_x$ and Ti_2CT_x MXene, and superior to graphene and $MoSe_2$. Furthermore, decreasing the number of -OH groups could greatly improve the friction performance of all types of MXene. This study provides experimental basis for the application of modified MXene into solid lubrication.

2:00 PM SF01.10.04
Nanoscale Friction of High Entropy Alloy Sulfide Thin Films in Comparison with Molybdenum Disulfide Gokay Adabasi[1], Aditya Deshpande[2], Koichi Tanaka[2], Joshua Ancheta[1], Emmanuel Maldonado[1], Mehmet Ozdogan[1], Mehmet Baykara[1] and Suneel Kodambaka[2,3]; [1]University of California, Merced, United States; [2]University of California, Los Angeles, United States; [3]Virginia Tech, United States

Recent years saw accelerating interest from the scientific community in high entropy alloys (HEA), mainly due to their favorable mechanical properties and resistance to environmental stressors. In principle, their outstanding wear and corrosion resistance make them great candidates for coatings in mechanical systems. On the other hand, the question of whether HEA thin films will also act as solid lubricants, i.e. reduce friction at the interface of mechanical components in relative motion, remains open.

In order to find answers to this critical question, we performed nanoscale friction measurements on sputter-deposited HEA-sulfide ($(VNbTaMoW)S_2$) thin films via atomic force microscopy (AFM). Results reveal (i) the influence of deposition time on film morphology and (ii) the presence of isolated areas of low friction on film surfaces. Taking one step further, we compared the nanoscale friction results obtained on the HEA-sulfide thin films with those on sputter-deposited molybdenum disulfide (MoS_2), a widely-used material for solid lubrication. Friction values obtained on both types of films are on the same order. Finally, variable temperature X-ray diffraction (XRD), performed up to 800 °C, reveals that $(VNbTaMoW)S_2$ films exhibit improved oxidation resistance when compared with MoS_2 films. Combined, the results presented here demonstrate that HEA-sulfide thin films exhibit remarkable potential as environmentally-resistant solid lubricant coatings.

3:15 PM SF01.10.06
Mechanical and Magnetic Properties of an Additively Manufactured Soft-Magnetic High-Entropy $Al_{0.5}$CrFeCoNi Alloy Xipeng Tan; National University of Singapore, Singapore

The demand for new classes of high-performance soft magnetic materials (SMMs) has been rapidly rising in the context of sustainable and electrified world. However, there exists a dilemma between low hysteresis loss and high mechanical performance, thereby motivating the further exploration of advanced materials and manufacturing for the magnetically soft yet mechanically tough electrical machine components. Additive manufacturing (AM), popularly known as a layer-by-layer three-dimensional (3D) printing technology, offers new opportunities of processing SMMs in near-net-shape with superior soft magnetic and mechanical properties. Here, a promising soft-magnetic $Al_{0.5}$CrFeCoNi high-entropy alloy is additively manufactured by laser powder-bed fusion method. The mechanical properties and hysteresis loop of the 3D-printed soft-magnetic high-entropy alloy are examined and compared with state-of-the-art SMMs. Moreover, its as-cast counterpart is fabricated to better understand effects of AM processing on both mechanical and soft magnetic properties.

2:30 PM BREAK

3:30 PM SF01.10.07
Examining High Entropy Alloy Nanoparticles of Small Size and Tunable Composition Prepared via Colloidal Syntheses Evan Gardner and Matteo Cargnello; Stanford University, United States

High entropy alloy nanoparticles (HEA-NPs) – those containing at least five, homogeneously alloyed metals – have rapidly emerged as versatile nanomaterials suited for both thermo- and electrocatalysis. Their unique “high entropy mixing” lends to significantly hybridized electronic structures, which confers noble metal reactivity to base metals and provides improved thermal stability. Base metal containing HEA-NP catalysts provide the opportunity to dilute or eliminate precious metals in legacy catalysts. A preponderance of specialized, high temperature, thermal syntheses of HEA-NPs, however, limits respective catalyst design to carbon supports. Therefore, we have pioneered tunable and scalable colloidal syntheses of HEA-NPs, which are tailored to exploit a variety of active support materials such as alumina, ceria, and titania. Characterization via TEM and STEM-EDS mapping in conjunction with single area electron diffraction methods reveal spherical, 6-7 nm NPs with uniform alloy structures. These HEA-NPs also demonstrate intriguing thermocatalytic behavior and excite future studies designed to systematically probe the impact on HEA-NP composition on reactivity and structural evolution under reaction conditions.

3:45 PM SF01.10.08
Facile Synthesis of High-Entropy Alloy Nanoparticle Decorated Germanane Chuyi Ni and Jonathan Veinot; University of Alberta, Canada

High-entropy alloy nanoparticles have attracted substantial research interest because of their multi-elemental compositions, intriguing solid-solution structure, as well as applications (e.g., multifunctional catalysis). Various methods for the synthesis of these materials have been reported. Even so, the vast compositional space and complex structure result in great challenges related to comprehensive investigations and fundamental understanding. Herein, we will outline a new method for preparing high-entropy alloy nanoparticles comprising Au, Ag, Cu, Pd, Pt that are supported on germanane via comparatively mild solution reduction and in-situ growth. The resulting materials were characterized using X-ray diffraction, X-ray photoelectron spectroscopy, and transmission electron microscopy.

4:00 PM SF01.10.09
Retrosynthetic Design of Core@Shell Nanoparticles for Their Thermal Conversion to High Entropy Alloy Nanoparticles Nabojit Kar, Maximilian McCoy, Joshua Wolfe and Sara Skrabalak; Indiana University Bloomington, United States

In recent years, high-entropy alloy (HEA) nanoparticles (NPs) have attracted a lot of attention as a new class of nanomaterials in the field of catalysis and energy applications due to their tunable compositions, high hardness and strength, high-temperature resistance, and remarkable ductility. The synthesis of HEAs as monodisperse NPs is of high interest to understand how their structure and composition contribute to their function. However, downsizing HEAs to the nanoscale has been synthetically challenging as most colloidal routes to metal NPs rely on the reduction of metal salts, which will occur at different rates depending on the metal precursor. Past work has shown that colloidally prepared monodisperse core@shell NPs can be converted to monodisperse HEA NPs by annealing them at high temperatures. This approach requires fewer metal precursors in each step compared to direct coreduction, facilitating the formation of monodisperse samples with much more control. The initial system considered core@shell PdCu@PtNiM NPs as precursor NPs to HEA NPs, where M = Co, Ir, Rh, Ru, or Fe. These core@shell NPs were prepared by seed-mediated co-reduction (SMCR), and while quite versatile, some metals (e.g., Au and Sn) could not be used in the SMCR process with PdCu seeds. The conversion chemistry not only bounded to PdCu but other bimetallic seeds (e.g. AuCu, PdAg, Pd_3Sn) can also be used. However, consideration must be taken as to which metals go in the core and which metals go in the shell. Herein we propose that the metal precursors for the core and shell of the core@shell NPs synthesis should be judicially chosen according to their relative redox potentials with all the participating metals or metal precursors. We also show that metal precursors with a fast reduction rate that can generate homogenous nucleation in the SMCR step should go in the core of the core@shell NPs. Retrosynthesis is the technique of employing chemical reactions to "deconstruct" a target molecule into easily accessible starting ingredients. Similarly, considering different variables, we may design a retrosynthetic reaction pathway that results in HEA NPs with the targeted metal compositions. More generally, obtaining control over monodisperse HEA NP composition can pave the way for long-lasting catalysts for a variety of processes.

SESSION SF01.11: High Entropy Oxides I
Session Chairs: Cecilia Cao and Katharine Page
Friday Morning, April 14, 2023
Marriott Marquis, B2 Level, Golden Gate C2

10:00 AM *SF01.11.01
Compositionally Complex Oxides—Synthesis, Characterization, Challenges and Opportunities Veerle Keppens; University of Tennessee, United States

High entropy oxides (HEOs), also referred to as multicomponent oxides or compositionally complex oxides (CCOs), have attracted attention due to the tunability of multiple cations on a single site. Since the introduction in 2015 of HEOs stabilized in the rocksalt phase, the high entropy oxide concept has been expanded to various structures, offering a path for the discovery of innovative compounds with unique structure-property relations. However, the intrinsic disorder and highly localized chemical environments of HEOs bring along new challenges. In order to shed light on the complexities associated with multi-cation oxides, we have initiated a systematic study of polycrystalline and single crystalline HEO samples across multiple crystal systems. This work expands the multi-component concept to new compositions and crystal systems and investigates properties of materials across multiple crystal systems, including spinel, perovskite, and Ruddlesden-Popper multi-component materials.

10:30 AM SF01.11.02
Real Space Observation of Reaction Pathway in the Formation of Entropy-Stabilized Oxide John Heron and Avery-Ryan E. Ansbro; University of Michigan, United States

Configurational entropy has enabled a new synthesis pathway to previously unrealized, multi-component, single-phase oxides [1]. Such high entropy and entropy-stabilized oxides are a novel class of materials that offer a wide range of utility as well as an opportunity to understand the role of entropy in the solubility, phase behavior, and stability for the design of disordered materials [2][3]. There has been a large disparity between high entropy compounds that have been predicted to exist as single-phase materials and those that have been generated experimentally, with some high entropy oxides (HEOs) only being realized through high kinetic energy processing such as pulsed laser deposition rather than solid state processing [4]. This suggests that complex reaction pathways may be hindering the ability to discover stable HEOs [5]. Here we show that varying precursor choices can affect the ability to dissolve metal cations into a high entropy structure and in some cases can result in differing phase states at identical conditions. Dissolution of spinel Fe3O4 and corundum Fe2O3 into known entropy stabilized oxide, (Mg0.22Ni0.2Cu0.2Co0.2Zn0.2)O, individually is found to produce different products: Single phase and spinel rocksalt mixture respectively. This can be done reversibly. Using Co3O4 instead of CoO in the synthesis of (Mg0.22Ni0.2Cu0.2Co0.2Zn0.2)O hinders the formation of a single-phase material with spinel as a secondary. Notably, the dissolution of Co3O4 as a sixth component to (Mg0.22Ni0.2Cu0.2Co0.2Zn0.2)O precursor leads to a single phase. Our results demonstrate that precursor choice affects reaction intermediates and final structure under a fixed set of conditions. Further, synthesis from pre-formed (Mg0.22Ni0.2Cu0.2Co0.2Zn0.2)O instead of binary constituents also appears to affect the ability to dissolve metals into a high entropy complex. Examining the synthetic pathways and thermodynamic processes that result in these variances is crucial to understanding solubility and the rational design of disordered systems.

10:45 AM SF01.11.03
Entropy Engineering in the Spinel High Entropy Oxide Mario Ulises Gonzalez Rivas[1,1], Graham Johnstone[1,1], Mohamed Oudah[1,1], George A. Sawatzky[1,1], Robert Green[2,1], Keith Taddei[3], Ronny Sutarto[4] and Alannah Hallas[1,1]; [1]The University of British Columbia, Canada; [2]University of Saskatchewan, Canada; [3]Oak Ridge National Laboratory, United States; [4]Canadian Light Source, Canada

The discovery and development of high entropy oxides (HEOs) has garnered significant attention, in no small part due to the enhancement of functional properties that they often present. As an atomistic explanation of HEOs is beyond current theoretical techniques, auxiliary “descriptors” that characterize them are invaluable. Configurational entropy, being a measure of disorder, is considered a key descriptor when addressing the properties of HEOs. Notably, it has been demonstrated that in systems with inequivalent sublattices, crystal field effects can overwhelm and suppress configurational entropy, introducing a degree of site selectivity in the cationic distribution [1,2]. However, most studies on the subject treat configurational entropy as a fixed, static quantity.

Here, we address this matter within the framework of the 3d transition metal-based AB_2O_4 spinel-type HEO $(Cr,Mn,Fe,Co,Ni)_{3-x}Ga_xO_4$ system, an ideal setting that provides octahedral and tetrahedral sublattices with strong crystal field effects. We harness x-ray absorption and magnetic circular dichroism to elucidate the spinel HEO’s site selectivity and quantify its configurational entropy. Our analysis shows that Ga substitution provides an avenue to seamlessly tune the octahedral sublattice from the medium entropy to the high entropy regime, with the tetrahedral sublattice going from low entropy to medium entropy. These results imply that through careful cation selection, the two sublattices of the spinel HEO can be precisely tuned across different entropy regimes, demonstrating the principle of entropy engineering in HEOs [2].

We then briefly explore the prospect of another avenue through entropy engineering in HEOs. It is well established that changes to the processing conditions involved in the growth of binary spinel oxides can have striking effects on their degree of inversion and the materials’ final properties [3,4]. This tunability hints at the possibility of extending the principles of entropy engineering to other. Our study then turns to the fully 3d $(Cr,Mn,Fe,Co,Ni)_3O_4$ spinel HEO, where several synthesis routes and their effect on the final materials’ site selectivity are discussed, hinting at the richness of the energy landscape in the spinel HEO.

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11:00 AM SF01.11.04
Controllable Phase Heterogeneity in High Entropy Oxides Alexander D. Dupuy and Julie Schoenung; University of California, Irvine, United States

High entropy oxides (HEOs) consist of five or more oxide components which form a single-phase solid-solution structure after processing. Despite their recent discovery, HEOs already show promise in a variety of applications, particularly in electronics and battery components. A unique characteristic of HEOs is their reversible entropy-driven phase transformation between the single-phase and multiphase states. The phase transformation manifests as the formation of secondary phases, whose volume fractions can be controlled through heat treatment. This feature presents an opportunity to produce oxide materials with highly controlled phase states, microstructures, and behavior.

Here, we explore the behavior and consequences of this phase transformation in (CoCuMgNiZn)O. First, we show that solid-state synthesis and sintering can be used to consolidate fully dense HEO ceramics with grain sizes spanning several orders of magnitude. After heat treatment, we observe that the phase transformation manifests as the formation of Cu-rich tenorite and Co-rich spinel secondary phases. We demonstrate that the phase heterogeneity can be controlled through heat treatment, while the as-consolidated grain size significantly influences the secondary phase evolution and morphology. Furthermore, we discuss our efforts to characterize the secondary phases using atom probe tomography (APT), X-ray diffraction (XRD), and electron microscopy. From these investigations, we find that the secondary phases exhibit several interesting behaviors, such as a complex nucleation sequence and a size induced morphological transition.

We then explore how the controllable phase heterogeneity can be leveraged to tailor the electrical and mechanical behavior. We observe that the electrical conductivity and dielectric constant increase significantly with increasing amount of secondary phase, due to the formation of a conductive percolative network. Conversely, the interplay between the various secondary phases and their morphological evolution results in complex changes to the mechanical behavior and failure mechanisms. Our results demonstrate that the entropic transformation is a powerful tool for engineering the microstructure and behavior of high entropy oxide ceramics.

11:15 AM SF01.11.05

Predicting Entropy-Enthalpy Compensation in Metal Hydrides Using Machine Learning Mark D. Allendorf, Vitalie Stavila, Pinwen Guan and Matthew Witman; Sandia National Laboratories, United States

Metal hydrides are among the most promising materials for hydrogen storage because of their high gravimetric and volumetric energy density. In some cases, the volumetric capacity is higher than even liquid hydrogen. This makes them attractive for transportation applications, where minimizing storage system volume is paramount. The primary challenge to implementing metal hydrides is a "Goldilocks" tradeoff between the thermodynamics of H_2 release and the reversible capacity.[1] One strategy to surmount this challenge is to reduce (i.e., make more negative) the free energy of dehydrogenation (ΔG°(dehyd)) by maximizing the dehydrogenation entropy (ΔS°(dehyd)) and minimizing the corresponding enthalpy change (ΔH°(dehyd)). However, entropy-enthalpy compensation,[2-3] in which a reduced ΔH°(dehyd) is counteracted by a smaller ΔS°(dehyd), could defeat this strategy. Therefore, understanding the extent to which ΔH° and ΔS° can be independently controlled is crucial to designing strategies for tailoring the thermodynamics of metal hydrides.

Here, we discuss our recent use of a machine learning model to identify features correlated with ΔS°(dehydr) and ΔH°(dehydr) for metal hydrides.[4] For intermetallic (interstitial) metal hydrides, our results indicate that the material features that best predict ΔH°(dehydr) can differ from those for ΔS°(dehydr). In particular, ΔS°(dehydr) is most strongly correlated with the corresponding volume change upon dehydrogenation, whereas ΔH°(dehydr) is strongly correlated with the mean ground-state atomic volume, which depends only on composition and not structure. For several other classes of metal hydrides, including high entropy alloys (HEA),[5] metal-substituted TiFe, and AB_2 (Laves-type) hydrides,[6] we find entropy-enthalpy compensation effects are present to varying degrees, but these correlations are rather weak, suggesting that independent ΔS° tuning may be possible.

Finally, we report a statistical analysis of entropy-enthalpy compensation effects in metal hydride nanoparticles. Uncoupling ΔS°(dehyd) of nano-MH from ΔH°(dehyd) may be possible using material formats that strongly immobilize nanoclusters, thereby reducing S°(nanocluster) and increasing ΔS°(dehyd). Data for hydride nanoparticles are much more limited than for the bulk counterparts, but our statistical analysis of the available nanohydride data suggests that ΔS°(dehyd) and ΔH°(dehyd) are correlated for MgH_2 and PdH_x and this is dependent on particle size. The results suggest a structure-property correlation indicating that uncoupling ΔS°(dehyd) from ΔH°(dehyd) may be possible for nanoscale hydrides using material formats that strongly immobilize nanoclusters, thereby lowering S°(nanocluster) and increasing ΔS°(dehyd).

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11:30 AM SF01.11.06

Mw-plasma Produced High Entropy Borides Synthesized Based on Entropy Forming Ability and Mechanical Properties Bria C. Storr, Luke Moore, Cheng-Chien Chen and Shane A. Catledge; University of Alabama at Birmingham, United States

High entropy borides have favorable mechanical properties making them great candidates for materials that can withstand extreme conditions. This research seeks to look at samples with the entropy-forming ability for high entropy borides produced utilizing microwave-induced plasma. Precursors containing metal oxides and borons were annealed for a borothermal reduction resulting in an AlB2-type hexagonal crystal structure. The computationally predicted mechanical properties and first principle are compared to the synthesized high entropy borides (HEBs). Results from ongoing research have shown that MW-plasma synthesized HEBs are consistent with the calculated hardness and the entropy-forming ability (EFA) prediction. From ongoing research, the highest EFA does not correlate to the highest hardness. Therefore, this research focuses on the HEBs candidate with the highest and lowest EFA values. The MW-plasma HEBs microstructure, hardness, and oxidation resistance will be presented.

SESSION SF01.12: High Entropy Oxides II
Session Chair: Veerle Keppens
Friday Afternoon, April 14, 2023
Marriott Marquis, B2 Level, Golden Gate C2

1:30 PM *SF01.12.01

Tuning Magnetic and Catalytic Properties in a Family of Compositionally Complex ACo_2O_4 Spinel Nanostructures Katharine Page; The University of Tennessee, Knoxville, United States

Nanostructured materials offer promising physicochemical properties across diverse applications in the fields of energy storage, sensors, catalysis, biomedicine, and more. Compositionally complex oxides (CCO) may offer increased structure-property tunability due to their unique structure diversity, tunable compositions, and possible property enhancements/modifications through increased entropic disorder. Here, an eco-friendly low temperature soft-templating reaction route is applied to form a large family of spinel nanostructures with formula $A\mathrm{Co}_2\mathrm{O}_4$, where A includes n different equiatomic combinations of one to seven transition metal cations. The phase selectivity and temperature stability windows for the series of nano-compositions are found to be dominated by the inclusion (or exclusion) of specific cations, with the temperature required for formation influenced by increasing n (increasing configurational entropy). We apply a wide array of characterization techniques, including high resolution transmission electron microscopy, neutron diffraction and pair distribution function analysis, and Special Quasi-Random Structures Density Functional Theory approaches, to probe the influence of cation selection and processing parameters on structural, catalytic, and magnetic properties. Specifically, we demonstrate water splitting catalyst activity can be tuned through A cation selection and post heat treatment. Certain metastable $A\mathrm{Co}_2\mathrm{O}_4$ compositions are found to be novel precursor phases for synthesis of bulk hard-soft exchange magnets: we demonstrate that tunable magnetic performance can be achieved through control of the nanoscale heterogeneity of annealed products. Links between specific lattice defects, chemical short-range order, nanoscale heterogeneity and magnetic/catalytic performance in this ACo_2O_4 spinel family demonstrates a wider approach to promoting design principles and strategies for nanostructured CCOs and related materials.

2:00 PM SF01.12.02

Hydrogen Substituted Graphdiyne Assisted Ultra-Fast Sparking Synthesis of Metastable Nanomaterials for Li-S Batteries Xueli Zheng and Yi Cui; Stanford University, United States

Metastable nanomaterials, such as single atom and high entropy systems, with exciting physical and chemical properties, are increasingly crucial for next-generation technologies. The origin of these properties results from electronic and bonding structures far from equilibrium although the synthesis of metastable nanomaterials remains challenging. For example, extreme heating and cooling rates are often required to prevent cluster formation of single atoms and phase separation of high entropy alloys. Here, we developed a hydrogen substituted graphdiyne-assisted ultra-fast sparking synthesis platform for the preparation of metastable nanomaterials. Controlling the composition and chemistry of the hydrogen substituted graphdiyne aerogel framework, the reaction temperature can be tuned from 1640 K to 3286 K within milliseconds. We demonstrate the versatility of the ultra-fast high-temperature platform with the successful synthesis of single atoms, high entropy alloys, and high entropy oxides. Electrochemical measurements and density functional theories show that single atoms synthesized by the platform enhance the lithium-sulfur redox reaction kinetics, enabling high-performance all-solid-state lithium-sulfur batteries. Our design of the ultra-fast high-temperature platform offers a new powerful way to synthesize a variety of metastable nanomaterials.

2:15 PM SF01.12.03

High-Throughput Synthesis and Characterization of High-Entropy Oxides for Photosensitive Applications Mukesh Kumbhakar[1], Anurag D. Khandelwal[2], Ben Breitung[2], Shikhar K. Jha[1], Horst Hahn[2], Leonardo Velasco[3] and Simon Schweidler[2]; [1]Indian Institute of Technology Kanpur, India; [2]Karlsruhe Institute of Technology (KIT), Germany; [3]Universidad Nacional de Colombia, Colombia

High entropy materials have been widely investigated in recent years for their possibility to tailor functional properties. Unique interactions due to the presence of multiple elements in a single-phase structure give way to properties not generally seen in their binary counterparts.

Due to the inordinately large combinations available, the “trial and error” method becomes arduous while synthesising systems with four or more elements. A high-throughput approach to synthesising such systems can help fast-track this process by reducing the time and energy involved. This can be combined with characterisation techniques like XRD, SEM, UV-Vis spectroscopy etc., to help shortlist potential candidates for further investigation.

This talk focuses on the study of fluorite-type rare earth oxides with varying compositions of Ce, La, Pr, Sm, Y, Zr and Tb using the high-throughput approach to identify the impact of individual elements on the physical properties. The reversible tuning of their band gaps by changing the atmosphere and temperature of calcination was also examined. Further electrical and optical studies were conducted on a few chosen samples to compare their performance for potential photosensitive applications.

2:30 PM SF01.12.06

Development of TRIP-Maraging Steel with Excellent Fracture Toughness Through Complexion Precipitation Control Based on Segregation Engineering Jeongwon Yeh, Min Seok Kim and Eun Soo Park; Seoul National University, Korea (the Republic of)

Maraging steel is one kind of ultra-high strength steel, which is widely used in environments requiring high strength such as rocket engine, submarine hulls, aerospace and cryogenic missiles. However, it couldn’t overcome the strength-ductility trade-off issue and has brittle characteristics. Therefore, in this study, we tried to improve the ductility of the material by precipitating FCC austenite phase, which is a relatively ductile phase, in the grain boundary region through segregation engineering. Segregation engineering is represented by the value of grain boundary segregation enthalpy, and grain boundary segregation enthalpy is defined as the energy of the entire system that can be decreased when 1mol of a solid solution element is segregated to the grain boundary. In order to find the segregation element at grain boundary, it is necessary to search an element having positive segregation enthalpy value with the base system elements Fe, Ni and solid solution elements Co and Mo. As a result, it was confirmed that Mn has positive segregation enthalpy for all elements. In addition, the Mn element is known to greatly increase the stability of the FCC phase when dissolved in Fe based alloy. Therefore, Mn was finally selected as an optimal element for segregation engineering. Through this alloy design strategy, it was possible to design the alloys in which FCC austenite phase was locally precipitated. However, as the ductile FCC austenite phase was precipitated, the ductility increased but the strength decreased. To overcome strength-ductility trade-off, careful thermodynamic calculations were conducted to reduce the stability of the precipitated FCC austenite phase, resulting in martensitic transformation during deformation. This study provides a new pathway to design TRIP Maraging steel using relatively simply factors such as thermodynamic calculations, segregation enthalpy calculation, and comparing interphase relative stability. In addition, to obtain fracture toughness for the TRIP Maraging steels designed by the above strategy and to understand contribution of elastic and plastic in the process of crack growth, J-based crack-resistance curves, nonlinear-elastic fracture mechanics analysis method was conducted.

SESSION SF01.13: Virtual Session: High Entropy Materials

Session Chairs: Ivano Eligio Castelli and Koichi Tsuchiya

Tuesday Morning, April 25, 2023
SF01-virtual

9:00 AM *SF01.13.01
Autonomous Accelerated Workflow for the Discovery of High-Entropy Oxide Electrodes for Protonic Ceramic Fuel Cells Benjamin H. Sjølin and Ivano Eligio Castelli; Technical University of Denmark, Denmark

We develop and implement an autonomous multi-fidelity computational workflow to explore the chemical space of high-entropy perovskite oxide materials with general formula ABO_3, screening for stable, high-performance cathodes for low-temperature protonic ceramic fuel cells. The workflow, implemented in the framework of Density Functional Theory (DFT), is based on the calculation of thermodynamic, electric and kinetic properties, which include phase and electrochemical stability, electronic conductivity, and ionic diffusivity. To accelerate the calculation of the kinetic properties, we employ accelerated methods that leverage recent advances in machine learning for materials science to predict transition barriers for ionic diffusion. The computational cost of the workflow is additionally decreased, while retaining the quality of results, through a thorough examination of the required level of theory for all descriptive properties. Moreover, the aim is a general and chemistry-neutral approach that can be applied to other crystal prototypes and materials screenings.

9:30 AM SF01.13.02
Predicting Local Environments of Entropy Stabilized Oxides Using DFT and Machine Learning Lily J. Joyce, Kristen E. Johnson, Christina M. Rost and Kendra Letchworth-Weaver; James Madison University, United States

Entropy Stabilized Oxides (ESOs) are a novel class of materials which are enthalpically unfavorable, but entropically favorable due to high configurational disorder. The unique properties of these materials make them potentially useful as battery cathodes and in thermoelectric devices. Though not able to directly predict formation energies of ESOs, enthalpy based methods such as Density Functional Theory (DFT) remain useful for gathering bond length data, oxidation states, electronic band structure, and other statistics from the microstates representing the local environments of these materials. These statistics are useful for comparison to experimental methods such as XAS, provided that the microstates are representative of the real material. For representative systems, DFT can be quite computationally expensive, so instead we utilize Machine Learning (ML) algorithms to identify structural and energetic descriptors based on DFT. We aim to use these ML algorithms to scan through potential ESO candidates and predict which ones are the most promising for in-depth electronic structure calculations using the more accurate but computationally expensive DFT.

9:45 AM SF01.13.03
High-Entropy Materials Design: $A_6B_2O_{17}$-form Oxides Robert J. Spurling, Chloe Skidmore and Jon-Paul Maria; Pennsylvania State University, United States

High-entropy materials offer expanded opportunities for accessing unique and tunable property spaces via substantial structural disorder and compositional diversity. Exploring high-entropy single-phase stabilization in novel structural systems is essential for understanding structure-property relationships in these complex systems and promoting future materials design. Here, we probe the structure and thermodynamic stability of disordered $A_6B_2O_{17}$-form (A = Zr, Hf; B = Nb, Ta) oxides. Specifically, we report the synthesis of the novel multicomponent oxide $(Zr_3Hf_3)(NbTa)O_{17}$, which is structurally isomorphous with ternary and quaternary $A_6B_2O_{17}$ end members. This is accomplished through a bulk ceramic processing and sintering approach. Additionally, we employ high-temperature X-ray diffraction to study the single-phase transition *in situ*. We also report on bulk dielectric permittivity measurements on these $A_6B_2O_{17}$ species.

10:00 AM *SF01.13.05
Ultrafine Grain Formation, Grain Boundary Segregation and Phase Decomposition in CoCuNi Medium Entropy Alloy Koichi Tsuchiya; National Institute for Materials Science, Japan

FCC medium entropy alloys (MEAs), *e.g.*, CoCrNi, have been attracting much attention due to their excellent strength-ductility balance. The present talk will report the fabrication of an equiatomic CuCoNi MEA and its improvement of strength and ductility after high-pressure torsion (HPT).
An equiatomic CoCuNi MEA was produced by high-frequency melting and was hot-rolled and swaged into a cylindrical shape with a 10 mm in diameter. The samples were homogenized at 1150 °C for 1 hour and quenched into room temperature water. Severe plastic deformation by high-pressure torsion (HPT) was applied on the disk samples with a thickness of 0.85 mm at room temperature with a pressure of 5 GPa and a rotation speed of 1 rpm to 10 rotations. After the HPT, the sample was annealed at 400 °C, 600 °C for 100 h, and at 800 °C for 1, 10, and 100 h. XRD, SEM-EBSD, EDS, TEM, APT, Vickers hardness, and tensile tests were conducted to investigate the microstructures and mechanical properties.
The grain size of the sample before HPT was ~100 mm and was refined to ~90 nm after HPT. Tensile strength and elongation before HPT were 400 MPa and less than 10 %, respectively. HPT deformation improved both strength and elongation to over 1400 MPa and 16 %. The fracture surface observations revealed the intergranular fractured feature for the sample before HPT and ductile fracture for the one after HPT. APT analysis confirmed the segregation of a substantial amount of Cu along the grain boundaries in the sample before HPT. Severe deformation by HPT removed the grain boundary segregation, which may be the reason for the improved ductility.
We also investigated the effect of post-deformation annealing on microstructures and mechanical properties. XRD revealed that the sample after HPT, and then annealed at 400 °C showed the single FCC peaks while the sample annealed at 600 and 800 °C showed the splitting of the FCC peaks, indicating the phase separation. EBSD-EDS of CuCoNi annealed at 800 °C for 100 h showed typical recrystallized microstructure containing twin boundaries in equiaxed grain boundaries. EDS analysis visually and quantitatively identified the phase separation into Cu-rich (~80 at%Cu-20 at%Ni) and Cu-depleted (~55at%Co-40at%Ni) phases with the volume fractions of 0.34 and 0.66, respectively. The boundaries between the Cu-rich phase and Cu-depleted phase often coincide with the grain boundaries or twin boundaries. But the phase boundaries also exist within a single grain[ST1] , suggesting the simultaneous progress of phase separation and recrystallization. The tensile tests indicated that prolonged annealing at high temperatures leads to improved ductility at the expense of strength, compared to those after HPT.

10:30 AM *SF01.13.06
Tensile Creep Behavior of HfNbTaTiZr Refractory High Entropy Alloy at Elevated Temperatures An-Chou Yeh; National Tsing Hua University, Taiwan

This talk will present the tensile creep deformation of equiatomic HfNbTaTiZrr, we used the optical floating zone technique to fabricate sample with grain size larger than 1 mm on average; tensile creep tests under vacuum at 1100~1250^{o}C and stepwise loading of 5-30 MPa were performed. Creep of HfNbTaTiZr was dominated by solute drag creep behavior, and deformation was governed by a/2<111> type dislocations. Analysis suggests that creep rate of HfNbTaTiZr was controlled by Ta, which possesses the lowest intrinsic diffusivity in the system and contributes the most to drag dislocations. Findings in this work can provide a guideline to develop future high entropy alloys with creep resistance.

SYMPOSIUM

April 11 - April 25, 2023

Symposium Organizers
Kim de Groh, NASA Glenn Research Ctr
Yugo Kimoto, Japan Aerospace Exploration Agency
Ryan Reeves, International Space Station National Laboratory
Mark Shumbera, Aegis Aerospace Inc.

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* Invited Paper
\+ Distinguished Invited

SESSION SF02.01: Spacecraft Materials
Session Chairs: Jacob Kleiman and Masahito Tagawa
Tuesday Morning, April 11, 2023
Marriott Marquis, B2 Level, Golden Gate C1

10:30 AM *SF02.01.01
Additive Manufacturing (3D Printing) Materials for Space Applications Eitan Grossman[1,2], Irina Gouzman[1], Yuval Vidavsky[1] and Nurit Atar[1]; [1]SOREQ and Noga 3D Innovations, Israel; [2]Noga 3D Innovations, Israel

Additive Manufacturing (AM) has recently adopted a wide variety of materials ranging from plastics, metals, composites, alloys, and ceramics to food, fabric, concrete, and cement. The growing consensus of adopting the AM system over traditional techniques is attributed to several advantages including fabrication of complex geometry with high precision, maximum material savings, flexibility in design, and unique geometries that are lighter and cheaper. Started as a technology used for demonstrators and prototypes, AM has evolved to produce functional engineering structures and parts as more and more printable materials were introduced to the AM market. Common printing techniques are stereolithography (SLA), Digital Light Process (DLP), Fused Deposition Modeling (FDM) or Inkjet used for printing polymers and ceramics, and powder bed fusion (SLS, SLM) and direct energy deposition (DED) used mostly for metals and alloys in the form of powder and ceramics. The use of AM for space applications can be categorized by (i) printing in orbit or on the moon or Mars, or (ii) printing on Earth, depending on the ability to apply specific printing technique in the space environment. Applying AM in-space has advantages, such as, printing tools and spare parts on-demand (thus reducing the need to fly spare parts from earth), building structures that would not survive the stresses of launch, or build habitats on planets suitable for potential colonization in the future using local materials (e.g., regolith). On Earth printing can use, on the other hand, a large variety of printing techniques that are not available for in-space usage thus allowing vast applications ranging from small parts to full satellites. Examples may include ceramic mirrors, turbine blades, space suits, nano satellites, and even thrusters, rocket engines, and fully functioning rockets. The presentation will describe various printing techniques, printed materials used in space and the development of materials to withstand the space environment as well as current and future space and planetary applications.

11:00 AM SF02.01.02
Polymer Aerogels for Lunar Applications and Beyond Stephanie Vivod, Haiquan Guo, Sadeq Malakooti and Ariel Tokarz; NASA Glenn Research Center, United States

As the Space Community endeavors to reach new heights of exploration, advanced materials for extreme environments are at the forefront of research. One such material would include polymer aerogels. Polyimides are often found in aeronautic and aerospace applications due to their ability to retain their physical and mechanical properties over a wide range of temperatures and in chemically demanding environments. Cross-linked polyimide aerogels retain these same characteristics with added attributes of very low thermal conductivities (~14 mW/m-K), high specific surface areas (~850 m^2/g), low dielectric constant (~ 1.1), low densities (0.005-0.15 g/cm^3), and high porosities (>85%). Due to these interesting properties, aerogels are ideal as thermal and vibro-acoustic mitigating systems but are by no means limited to these applications. The high porosity and surface area also make aerogels an ideal host system for particle incorporation for applications such as IR scattering filters, chemical sensors, and dust and radiation mitigating materials. Herein, current polymer aerogel research will be discussed as it pertains to Space exploration and applications.

11:15 AM SF02.01.03
Ceramic Aerogels for Space High Temperature Applications Haiquan Guo[1,2] and Jamesa L. Stokes[2]; [1]Universities Space Research Association, United States; [2]NASA Glenn Research Center, United States

Ceramic Aerogels for Space High Temperature Applications
Haiquan Guo[1], Jamesa L. Stokes[2]
1.Universities Space Research Association

2.NASA Glenn Research Center

Aerogels play an important role in thermal insulation systems for space application. They are light-weight materials with low thermal conductivity, effectively suppressing heat transfer by conduction, convection, and radiation.Silica aerogels sinter at 600°C and polymer aerogels generally decompose below 450°C, meaning they are not suitable for high temperature insulation needs.This presentation will detail aluminosilicate aerogels, YSZ aerogel, and YbSZ aerogels that we have designed and developed for space high temperature thermal insulation applications. Aluminosilicate aerogels can be used up to 1100°C without losing the mesoporous structure, whereas YSZ aerogels and YbSZ aerogels can be used up to 1000°C. With further modification using SiO_2 coatings, they also can be used at 1100°C by maintaining the mesoporous structure.Ceramic felts, mats, or papers were used to reinforce those aerogels in composites that do not flake and can be flexible.Hydrophobicity was also achieved by manipulation of the surface of those aerogels and their composites.

11:30 AM SF02.01.04
Tribological Behavior of Polyimide-Hexagonal Boron Nitride Nanocomposites at Elevated Temperature for Aerospace Applications Priscila Rodrigues De Oliveira, Abhijith K. Sukumaran, Luiza Benedetti, Denny John and Arvind Agarwal; Florida International University, United States

Polyimide (PI) has significantly been used in aerospace applications due to its high strength-to-weight ratio, thermal stability up to 330°C, and chemical resistance. However, confronting harsh environments in the presence of radiation, orbital debris, and Lunar and Martian regolith may result in critical failure. Given this scenario, (h-BN), a solid lubricating with radiation shielding effectiveness, was added to the PI matrix at different concentrations (PI-2wt.% hBN and PI-5wt.% hBN). The samples were prepared by direct forming using ball milling to facilitate the uniform distribution of hBN in the PI matrix. Densification and thermal stability results showed considerable improvement compared to pristine PI. Moreover, tribological characterization by the rotatory ball on a disk tester revealed a reduction in COF by adding h-BN to the neat PI structure. Furthermore, the improvement in wear rate at ambient temperature was 55.9% and 75.9% for PI-2wt.% hBN and PI-5wt.% hBN, respectively. The wear rate for the samples tested at high temperature (300°C) greatly improved by 55.8% for PI-2wt.% hBN and 70.3% for PI-5wt.% hBN, respectively. Adding h-BN nanoparticles has significantly enhanced the lubrication properties of the Polyimide matrix. This nanocomposite has the potential to be a great candidate for space applications and harsh environments.

11:45 AM SF02.01.05
Black Coatings for Space Instruments—A Comparison of Traditional Ebonol-C Processes, a Recipe for Repeatability in the Future and a Baseline for Comparison for New Ultra-Black Coatings Daniel E. Hooks, Bradley Carpenter, Courtney Clark, Michael McBride, Ilker Loza-Hernandez, Jamie Stull and Carlos Maldonado; Los Alamos National Laboratory, United States

Ultra-black coatings have served various roles in space instrumentation and hardware. The Ebonol C coating has been used for various missions requiring low reflectivity on aluminum. This coating is produced through the formation of a cupric oxide structure on an intermediate layer of copper applied to the aluminum. For many years, this commercial formulation has been used ubiquitously for space plasma instruments to minimize contaminating background counts due to forward scattering of photons. The coating relies upon details of the copper intermediate layer that have been trade secret at various finishing companies, and the availability of the Ebonol C formulated chemistry from the chemical supplier. In recent years, this product has been discontinued at various times, leaving vendors to either rely on expired stock or to formulate their own equivalents. Here, we detail the processing methods, chemistries, and resultant coating structures that produce reflectance performance equivalent to baseline historical reflectance data. This process detail will ensure equivalent performance for such coatings for future missions and link the performance to past and currently deployed instruments. Additionally, the results serve as a baseline for comparison to new coatings under development for reflectance optimization, two of which will be described.

SESSION SF02.02: Spaceflight Exposure Experiments I

Session Chairs: Irina Gouzman and Jonathan Volk
Tuesday Afternoon, April 11, 2023
Marriott Marquis, B2 Level, Golden Gate C1

1:30 PM *SF02.02.01
CNES Flight Experiments for Thermal Coatings Aging—THERME and SESAME Stéphanie Remaury, Sophie Perraud and Pascale Nabarra; CNES, France

The in-flight evolution of thermo-optical properties of thermal coatings is of great concern when defining the thermal control system (TCS) of spacecraft. Experience (in-flight measurements and aging tests in laboratory) demonstrates that the parameter really affected by the in-orbit aging is the solar absorptivity a_S, which often increases when coatings are under space environment conditions. To define spacecraft TCS, thermal engineers have to take into account, from beginning of life (BOL) to end of life (EOL), the thermo-optical properties evolutions of the external coatings they intend to use (a_S and e_{IR}). Radiative surfaces sizes cope with the hottest conditions of the mission, which generally depend on the EOL properties of external coatings. But the larger the surfaces, the higher the heating power needed for the coldest conditions of the mission, which generally depend on BOL properties. Improving the knowledge of the in-orbit evolutions of the solar absorptivity of thermal coatings is consequently of paramount importance to optimize the TCS designs, and then to better master the on-board heating power consumption.
In this context, CNES has developed since 1990 a very simple and low cost experiment, called “THERME”, to evaluate the degradation of space coatings in real orbital conditions[1, 2]. This experiment was previously carried on low Earth orbit (LEO) spacecraft such as SPOT 2 and 5, HELIOS 2A and 2B and Demeter, all removed from operational service. In the last few years, the THERME experiment design was extended for geostationary (GEO) mission typical constraints[2] and is now flying on ATHENA-FIDUS and KOREASAT from TAS and on a telecom mission from ADS.
Moreover, CNES and ESA recently collaborate to develop the Euro Material Ageing (EMA) experiment. This will offer recurrent testing opportunities for European institutes to perform materials sciences research and validate new materials technologies in the real space environment on the International Space Station. EMA is currently under development and includes two main experiments:
- SESAME for studying materials and coatings behavior in real space environment and recording in-orbit parameters such as atomic oxygen flux, contamination, radiation, for a better knowledge of the LEO space environment and its effects on materials.
- IR-Coaster for characterizing the stability or evolution of biological and organic compounds when exposed to UV solar radiation.

The intended duration of the EMA mission is between 12 and 18 months. For the first EMA flight opportunity, 141 passive materials samples and 8 active sensors are under the ISS ram direction, offering unrestricted view to space. Various European research groups samples have been selected following a competitive tender process managed by ESA. Exposed materials include novel types of innovative multilayer insulation (MLI), optical and thermal coatings, reinforced composites, 3D printed polymers and exotic metallic alloys... CNES and ESA are also providing samples from their own internal research programs and collaborations. Each material undergoes the measurements of their physical and chemical properties before and after flight. In particular, this allows the thermo-optical properties aging assessment of the new TCS coatings developed by CNES. The launch of the first EMA is planned by end of 2023.

In this paper, we present the overall concept and design of THERME and SESAME experiments. We discuss also in flight results of THERME and scientific objectives of SESAME for TCS coatings.

[1] S. Remaury, P. Nabarra, E. Bellouard and S. D'Escrivan. "In-Flight Aging of Thermal Coatings: THERME Experiment", Journal of spacecraft and rockets, vol. 48, No.1, pp. 27-33, (2011).
2 S. Remaury, S. d'Escrivan, and P. Nabarra, "New THERME Experiment Concept for Measuring Thermal Coating Aging in LEO an GEO", Journal of spacecraft and rockets, vol. 53, No. 6, pp. 1105-1113, (2016).

2:00 PM *SF02.02.02
Shear Thickening Fluid Treated Space Suit Layups—MISSE-9, -10, and -13 Low-Earth Orbit Studies Overview Maria Katzarova[1,2,3], Norman J. Wagner[2,3], Richard D. Dombrowski[3] and Erik Hobbs[3]; [1]Lubrizol, United States; [2]University of Delaware, United States; [3]STF Technologies LLC, United States

The durability in low-Earth orbit (LEO) of the soft-goods portion of extra-vehicular activity space suit layups treated with a specially formulated, low-volatility, shear thickening fluid is investigated on the exterior of the International Space Station (ISS) as part of the Materials on the International Space Station Experiment (MISSE), missions MISSE-9, -10, and -13. Performance of a control layup and a shear thickening fluid treated layup exposed to LEO for nearly one year in the Ram-orbiting direction of the ISS on MISSE-9, informed the next iteration of materials tested on MISSE-10, Nadir-oriented, which in turn led to a design of materials tested on MISSE-13, Ram-oriented. The effect from exposure to atomic oxygen, space radiation, large temperature variations, and potential threat from micrometeoroid and orbital debris impact was assessed post-flight using a suite of techniques including spectroscopy, puncture resistance, and optical properties. Ground controls are used to compare both mechanical and optical properties to the flown samples and discussed relative to monitoring data from the MISSE experiments, including photographs, temperature data, UV intensity, and particle contamination. The cumulative data obtained from this multi-mission study of these state-of-the-art soft composite materials can inform their further development and possibly future crewed exploration efforts, including the Artemis program, Lunar Orbital Platform-Gateway, and subsequent Lunar and Martian surface missions.

2:30 PM BREAK

3:00 PM SF02.02.03
Low Earth Orbit (LEO) Exposure Effects on Polyimide Aerogels During MISSE Missions Sadeq Malakooti, Ariel Tokarz, Jessica Cashman, Kim de Groh and Stephanie Vivod; NASA Glenn Research Center, United States

As part of 'Materials on the International Space Station Experiment' (MISSE) missions, polyimide aerogel samples at varying densities were part of a test series positioned on the exterior of the International Space Station (ISS) during MISSE-9 and MISSE-12 missions. At low Earth orbit (LEO), spacecrafts are subjected to extreme environmental conditions such as thermal cycling, cosmic ray, and solar wind charge particle radiations as well as atomic oxygen. Herein, the aerogel materials were characterized for changes in physical and mechanical properties as well as thermal and optical properties. Results were then compared with the corresponding data obtained from the baseline samples of similar batches stored under ambient conditions on Earth.

3:15 PM SF02.02.04
3D-Printed Polymers with High Resistance to Atomic Oxygen Erosion and Orbital Debris Impact Rishik Keshari, Kelly Chang, Debashish Das, Leon Dean, Lawrence Salvati, Dana Dlott, Nancy R. Sottos and Ioannis Chasiotis; University of Illinois at Urbana-Champaign, United States

There is increasing need to protect and repair structural material systems deployed to the adverse environment of Low Earth Orbit (LEO) from Atomic Oxygen (AO) erosion and damage due to orbital debris impact. Of special interest are polymer-based composites because of their lightweight properties and the new capabilities to directly 3D-print in Space. This presentation focuses on AO-erosion studies at the International Space Station (ISS) coupled with ground-based simulated debris impact experiments with tough polydicyclopentadiene (PDCPD) and its nanocomposites that were 3D printed via highly energy efficient frontal polymerization. The AO-erosion experiments were conducted through runs 13 and 15 of the Materials International Space Station Experiment (MISSE). Results from AO-erosion experiments with different PDCPD formulations and their nanocomposites at the ISS demonstrated a 10-fold reduction in erosion rate, setting a path for even further increases in AO erosion resistance. The same materials in both as-fabricated and AO-eroded form were subjected to ground-based impact experiments with sub-millimeter size aluminum projectiles propelled to hypervelocities approximating orbital space debris velocities. The experimental projectile velocity profiles and the residual impact crater geometries were utilized to calibrate a hydrodynamic computational model that provided damage predictions for different debris velocities. This combined experimental and modeling approach to debris damage opens new quantitative routes for predictive and efficient design of advanced lightweight materials for Space applications.

SESSION SF02.03: Poster Session
Session Chairs: Kim de Groh and Ryan Reeves
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SF02.03.01
Radioprotectant Ceria Nanoparticle (CNP) Drug Delivery System to Prevent Reactive Oxygen Species (ROS) and Mitigate Spaceflight Osteopenia Balaashwin Babu, Elayaraja Kolanthai, Craig J. Neal, Shreya Pawar, Agastya Mittal, Melanie J. Coathup and Sudipta Seal; University of Central Florida, United States

Space exploration is reaching new heights as we traverse beyond low earth orbit. In this extreme environment, radiation induced health issues will be a major concern. The ability to induce higher levels of free radicals and reactive oxidative species (ROS) are factors to be addressed. Ceria nanoparticles (CNPs) can provide a means to scavenge ROS; free radicals known to cause cell apoptosis and thus may serve as a radioprotectant. Further, conjugation of

CNP to the drugs used to treat osteoporosis such as bisphosphonates, may offer a possible solution to space-induced osteopenia, and provide a dual functionality that can protect the bone cells from ROS and slow down overall bone loss. Current results indicate high Ce^{3+} structural confirmation of ceria nanoparticles using a wet-chemical synthesis. The synthesized nanoparticles were then conjugated with risedronate, a third-generation bisphosphonate. Three experimental combinations including, 1,1'-carbonyldiimidazole (CDI) linker only, CDI + polyethyleneimine (PEI), and CDI + diamine were confirmed to be successfully conjugated through UV/Vis characterization. Superoxide inhibition results show that all three conjugated products displayed higher antioxidant properties as tested using a superoxide dismutase assay inhibition kit. Preliminary microwave radiation studies indicated that CNP was able to be used as a radioprotectant as it prevented changes in drug chemistry as detected by UV/Vis spectra after exposure to 60 seconds of microwave radiation. Finally, in vitro cell studies using human mesenchymal stem cells showed excellent viability when exposed to all combinations of drug and CNP at 50ug concentration as demonstrated using an MTT colorimetric assay. These results indicate ceria nanoparticles show promise as a radioprotectant material that may also work well as a drug encapsulant. Further studies are necessary to investigate this further.

5:00 PM SF02.03.02
Evaluation of Out-Gassing Test(CVCM, TML) for EEE Parts Material in Space Wooje Han, Min-Seok Jeon, Kyunghee Kim, Woki Bae and Minhyeong Gil; Korea Testing Laboratory, Korea (the Republic of)

EEE (electrical, electronic, and electromechanical) parts, which are components for space, are being developed mainly in the US and Europe, and are still in their minor interesting in South Korea. In particular, in the case of the United States, the use of space parts is restricted their applications in many nations based on the regulations of ITAR and EAR, and the European replacement parts market to solve this problem is very active. In particular, various component companies, centering on ESA, are producing space components that meet the European space standard, and many satellites and launch vehicles are being developed using them. A lot of new parts are being tried in micro(nano-) satellites, which have recently been spotlighted, and ground environmental testing is essential to confirm that these parts are suitable for space.
In this atmosphere, expectations for the development of space-grade parts are concentrated in South Korea. Korea is a very strong leader in the semiconductor component market such as memory. It is the hope of most world-class space researchers to make these parts suitable for the space applications. Recently, in South Korea, the space parts test center of the Space testing center (Korea Testing Laboratory) has established a facility for professionally testing space parts. It is a specialized testing institute that develops device-grade component tests and confirms suitability for space applications.
In particular, the space-grade materials are being tested very strictly. The CVCM (collected volatile condensable mass) and TML (total mass loss) machines to test the characteristics of outgassed in space vacuum, including substances prohibited for use in space, have been set-upped. Through these equipment, suitable materials are tested in a vacuum environment in space. Some parts (transformer, inductor) are being introduced using these materials that have passed the test in South Korea. By providing such analysis technology, we would like to introduce our contribution to the determination of suitability for the space applications in ground test.

5:00 PM SF02.03.03
Complex Radiation Shielding Properties of Polyethylene Nanocomposites with Tungsten Nanoparticle Attached Boron Nitride Nanosheets Seulgi Kim, Yunhee Ahn and Dongju Lee; Chungbuk National University, Korea (the Republic of)

There has recently been an increase in demand for complex radiation shielding (neutron and γ-ray shielding) in the atomic energy, aerospace, and medical fields. In contrast to neutron shielding, which uses neutron absorbing materials (B or Gd), γ-ray shielding mostly employs heavy metals such as Pb, Fe, and W. Heavy metals are difficult to disperse in the polymer matrix due to the density differential with the polymer. However, when these materials are present as nanoparticles attached on the surface of two-dimensional (2D) materials, nanoparticle aggregation is reduced due to the large surface area of 2D materials, which can assist in matrix dispersion.
Herein, we prepared polyethylene (PE) nanocomposites incorporated with tungsten nanoparticles (W NPs) decorated on boron nitride nanosheets (BNNS) hybrids. The cross-sectional area of the reaction of W NPs was increased by uniformly attaching to the BNNS surface with interfacial chemical bonding. Furthermore, non-covalent functionalization of the hybrids leads to increase the dispersibility of the hybrids in the matrix. The W-BNNS/PE nanocomposites demonstrated improved mechanical characteristics and thermal conductivity due to the interfacial bonding between W and BNNS and the interconnection of W NPs. The nanocomposites provided excellent radiation shielding properties for neutron (4.80 cm^2/g) and gamma (γ) ray (0.093 cm^2/g) radiation; this confirmed its potential as a complex radiation shielding material.

Acknowledgement
This work was supported by the Development of 100 nm sized tungsten based material out of scrap and tool manufacturing technology using scrap for precision machining (20011520) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) and the National Research Foundation of Korean (NRF) grant funded by the Korea government (Ministry of Science and ICT) (2021R1F1A1058854) and the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government (MOTIE, 20217510100020, Development of platform process using common core and materialization technology for rare metal recovery from industrial low-grade waste liquid).

5:00 PM SF02.03.04
Chemical and Morphological Evolution of Surface Conversion Coatings in Low-Earth Orbit Space Environment Ankita Mohanty[1], Cheng-Chu Chung[1], Xiaoyang Liu[1], Donald Vonk[2], Kim Kisslinger[3], Xiao Tong[3], Gary P. Halada[1], Bruce Ravel[4], Stanislas Petrash[2], Kate Foster[2] and Yu-chen K. Chen-Wiegart[1,5]; [1]Stony Brook University, United States; [2]Henkel Corporation, United States; [3]Center for Functional Nanomaterials, Brookhaven National Laboratory, United States; [4]National Institute of Standards and Technology, United States; [5]National Synchrotron Light Source II, Brookhaven National Laboratory, United States

Surface conversion coating is one of the most promising technologies for a wide range of industrial applications to protect the surface of alloy materials from corrosion, and to enhance the adhesion of decorative paints to treated metal components. Understanding the chemical stability and structural integrity of conversion coatings for their applications in an outer space environment for potential aerospace industry, is of great interest. Under extreme conditions of atomic oxygen, thermal cycling and ultra-high vacuum, the coating materials may undergo morphological and chemical changes. In this work, we utilized a multi-modal characterization method where synchrotron and laboratory X-ray techniques as well as electron microscopy, were combined to study the evolution of surface conversion coatings as a result of the exposure to the low-earth orbit environment in space. The samples were part of an MISSE mission, during which the samples were placed outside of the International Space Station and compared with the twin samples aged on Earth. We will discuss the influence of the space conditions on the surface conversion coatings.

5:00 PM SF02.03.05
UV-Initiated Healing of Punctures Due to Hypervelocity Impacts on Metal Composites for Space Applications Ashanti M. Sallee and Enrique Barrera; Rice University, United States

The space environment can have a severe impact on materials. In low Earth orbit (LEO) materials must withstand the effects of high vacuum, extreme temperature variations, micrometeoroid and orbital debris (MMOD), and exposure to atomic oxygen and UV radiation. Mechanical, chemical, and thermal degradation can occur due to exposure to a few or all these conditions. To help mitigate these damages, self-healing systems for the space environment are of interest. The objective of these systems is to autonomously repair damage without any external diagnosis, which can result in increased time/savings on repairs and the increased safety and reliability of materials. Our group is focused on designing metal composite self-healing pressure vessels for space that can heal hypervelocity impacts that occur due to MMOD. Many metallic self-healing systems require high temperatures for healing, which may not be effective in space due to the severe temperature variations. Our research group has designed a self-healing system that is more feasible for space. Instead of relying on heat, our system's healing is UV-initiated, exploiting the UV radiation in space and it can be done in ambient temperatures. We designed a metal composite that sandwiches a liquid solution between two aluminum plates. The liquid is a precursor solution for a poly(ethylene glycol) diacrylate (PEGDA) hydrogel that cures via UV irradiation for less than 5 minutes. Upon puncture of the composite using a hypervelocity light gas gun to simulate space impacts, the precursor solution will be released and exposed to UV light, forming a hydrogel that will serve as a solid plug and heal the damage. In my presentation, I will discuss the design and characterization of the composite, along with a comparison of the mechanical properties before and after healing. I will also examine further testing methods that can analyze the efficiency of the system in space.

5:00 PM SF02.03.06
The Influence of Oxygen and Temperature on Optical and Chemical Structure Changes by the UV Irradiation Kazuki Yukumatsu[1], Shogo Yamane[2], Yuki Horiuchi[2], Junji Mizukado[2], Hideaki Hagihara[2] and Yugo Kimoto[1]; [1]Japan Aerospace Exploration Agency, Japan; [2]National Institute of Advanced Industrial Science and Technology, Japan

Polymeric materials are often used as thermal control materials in spacecraft. Many polymeric materials discolored under ultraviolet (UV) irradiation, which changed their solar absorptance affecting the thermal design of spacecraft. For this reason, many ground experiments have been performed to evaluate the solar absorptances during the end of life (EOL) of the spacecraft mission. However, it takes a long time to irradiate the same amount of UV fluence as the actual mission period, and it is difficult to perfectly simulate the UV irradiation conditions such as thermal cycle. Therefore, it is important to study the prediction of the solar absorptance after UV irradiation.
This study aims to quantitatively understand the correlation between the changes in the chemical structures and solar absorptances to make a prediction technique. In this presentation, we report the results of UV irradiation experiments focusing on the presence of oxygen, which has a significant effect on the degradation mechanism of the polymeric materials. We primarily focused on the polyetherimide film which is a relatively transparent material having a good tolerance to the radiation. The surface analysis used by X-ray photoelectron spectroscopy (XPS) and Fourier Transfer Infrared Spectroscopy (FTIR) were performed. We also measured the solar absorptance by a UV-Vis-NIR spectrometer. As a result, the irradiated samples in the air were observed the structure after oxidative deterioration. On the other hand, the irradiated sample in vacuum were not observed such structures. The solar absorptances of the irradiated samples in air were larger than the samples in vacuum. In vacuum, the solar absorptances of samples were not saturated at a maximum of 600 ESD. Moreover, the dependency of the sample temperature in vacuum UV irradiation condition was evaluated, and same analysis was conducted.
Finally, we will discuss the degradation mechanisms based on the surface structure analysis of each of these materials, and the prediction method of solar absorptances.

SESSION SF02.04: Radiation Effects, Electronic Devices and Photovoltaics
Session Chairs: Sophie Duzellier and Adrian Tighe
Wednesday Morning, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate C1

8:30 AM *SF02.04.01
Introduction of the Radiation Hardening Activities on Semiconductor Devices for Space-Use Keita Sakamoto; Japan Aerospace Exploration Agency, Japan

The presentation will introduce the activities of enhancing semiconductor devices for space-use especially in digital devices against to the radiation effects. Although the categories of space-part has gradually been changing with the entry of new space players, a fundamental concept of the radiation hardening technology remains important, because the EEE component which is required high reliability like bus-system still needs high radiation torelance. In my presentation, the basic mechanisms and radiation hardening technology against to both Single Event Effects (SEE) and Total Ionization Dose (TID) effect will be introduced, together with our research activities.

9:00 AM SF02.04.03
Effects of 10-Month Low Earth Orbit Exposure on Hybrid Perovskite Thin Film Samuel Erickson[1], William; Delmas[1,2], Calista Lum[1,3], Jorge Arteaga[1], Kyle Crowley[4], Jennifer Williams[5,6], Lyndsey McMillon-Brown[4], Timothy Peshek[4] and Sayantani Ghosh[1]; [1]University of California, Merced, United States; [2]Sandia National Laboratories, United States; [3]University of California, Irvine, United States; [4]NASA Glenn Research Center, United States; [5]Wilberforce University, United States; [6]Ohio Aerospace Institute, United States

The high defect tolerance and potential for extremely high specific power in metal-halide perovskite (MHP) solar cells make them promising materials for space-based photovoltaics. Additionally, moisture, by far the most significant variable in MHP degradation, is negligible outside of the earth's atmosphere. In this work, we examine the effects of low earth orbit (LEO) on an MHP sample through high-resolution spectroscopic characterization. An encapsulated methylammonium lead iodide film was flown to the International Space Station as part of the 13th Materials International Space Station Experiment (MISSE-13) and exposed to the LEO environment for 10 months. Placed at zenith orientation, the sample underwent 45 minutes of AM0 illumination followed by 45 minutes of darkness a total of 4800 times, cycling between 100° C and -100° C each revolution. By comparing the spectral behavior, recombination lifetime, and phase transition temperature to a control sample, we quantified the changes in the flight sample.

Overall, the flight sample emitted a strong photoluminescence signal and showed little sign of degradation. The film was encapsulated with Dow Corning 93-500 silicone elastomer and a 1 mm borosilicate cover glass. Glass of this thickness blocked protons with energies up to 13 MeV in simulation, so galactic cosmic rays were unlikely to have affected the sample. The flight sample also showed no visual changes or significant lead iodide (PbI_2) formation under confocal microscopy, indicating that ultraviolet light transmitted through the cover glass was not damaging. Our analysis showed that the most significant and advantageous change in the film was a decreased tetragonal to orthorhombic phase transition temperature, likely caused by tensile strain from rapid temperature cycling. Calculations reveal in-plane tensile strain in the perovskite film at low temperatures due to the thermal expansion mismatch with its glass substrate. When this strain was relaxed through light soaking following 15 hours of AM1.5 illumination from a solar simulator, the flight sample's low phase transition temperature (56 K) increased to nearly match its control (130 K). The slightly larger bandgap of the MISSE-13 sample (1.612 eV) also red-shifted to match that of its control sample (1.594 eV). Likewise, confocal microscopy revealed a reduction in lead iodide regions of the flight film. Finally, the average charge recombination lifetime of the flight sample tripled after this illumination. These behaviors indicate a combination of photo-annealing and strain relaxation within the film, further improving its performance. Altogether, the excellent optical response and stability of the flight sample demonstrates that MHPs can be properly encapsulated to withstand space stressors.

*This work was supported by NASA grants no. NNX15AQ01 and NNH18ZHA008CMIROG6R

9:15 AM SF02.04.04
Ultra-Thin and Ultra-Light Si Solar Cells with Hyperuniform Disordered Light Trapping Alexander Lambertz[1], Nasim Tavakoli[2], Richard Spalding[3], Stefan Tabernig[2], Marian Florescu[3], Jorik Van de Groep[4] and Esther Alarcon-Llado[2]; [1]NWO-i AMOLF / UvA Amsterdam, Netherlands; [2]AMOLF, Netherlands; [3]University of Surrey, United Kingdom; [4]University of Amsterdam, Netherlands

Ultra-thin crystalline silicon solar cells could, in contrast to their thick counterparts, simultaneously reduce levelized cost of electricity by a large factor and be deployed on curved or non-static surfaces, windows, as well as facilitate building integrated photovoltaics. Moreover, their light weight, integrability into systems or tandem devices, and robustness to (cosmic) radiation also renders them excellent candidates for space applications. Silicon at micron-scale thickness, however, suffers from poor light absorption and conventional light trapping approaches such as random KOH texturing fails due to the feature sizes produced.

We present hyperuniform disordered (HUD) light-trapping structures applied to ultra-thin solar cells via substrate-conformal imprint lithography. This approach enables rapid patterning of large areas (m2) at the nanoscale and can be performed on virtually any substrate and for any type of functional layer, such as the absorber, back-reflector, anti-reflection coating or carrier transporting layers. Correlated-disorder structures were shown to outperform periodic as well as random light trapping approaches [1] and the hyperuniform platform in addition offers tailored scattering to engineer light coupling to guided modes of ultra-thin absorbing layers [2]. To this end, we developed a coupled-mode theory (CMT) approach for estimating absorption with HUD patterns of arbitrary power spectral density distributions, which affords optimizations at low computational effort. CMT predictions are validated by determining the in-coupling rates per guided mods for different HUD designs, which we achieve through FDTD simulations. Furthermore, we show experimentally measured absorption in ultra-thin, free-standing, hyperuniform-patterned silicon slabs of thicknesses ranging from 1-30µm and compare with simulations. Finally, we show the performance of ultra-thin Si solar cells before and after the application of HUD light trapping structures.

In conclusion, our work exploits stealthy hyperuniformity for exceptional light trapping and aims to further expand the success of earth-abundant silicon to ultra-thin, flexible, semi-transparent, airborne, and off-planet PV devices, which can be produced with kerfless bottom-up technologies at significantly reduced capex and accompanying CO2 emissions while maintaining high power conversion efficiencies – A type of device that could literally pave all roads, roofs, walls, windows, and spacecraft by 2050!

Publication
N. Tavakoli et al., "Over 65% Sunlight Absorption in a 1 µm Si Slab with Hyperuniform Texture", *ACS Photonics 2022, 9, 4, 1206–1217*, DOI: 10.1021/acsphotonics.1c01668

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9:30 AM BREAK

10:00 AM *SF02.04.05
Low Energy Ionizing Radiation and Plasma Contributions to Radiation Dose in Materials at Sun-Earth Lagrange Points Joseph I. Minow; NASA, United States

The relatively low energy (few MeV or less) component of the charged particle environments beyond the Earth's radiation belts represents a radiation source with potential impacts to materials used on the exterior surfaces of spacecraft for missions to the Sun—Earth Lagrange points. Sun-Earth L1 and L2 are of particular interest to mission designers since L1 provides opportunities for monitoring the Sun and incoming plasma and radiation events upstream of the Earth's magnetosphere and L2 is a low temperature thermal environment far from Earth and the Moon useful for astrophysics missions. The low energy radiation and plasma environments are generally considered relatively benign to materials with little or no threat to spacecraft operations even though the total ionizing dose generated by electrons, protons, and alpha particles to exterior surfaces and volumes of thin materials over a mission life can be in the megarad to gigarad range. Radiation damage of materials by the low energy charged particle environments may be a concern for current and future spacecraft designs using very thin materials or bulk materials where the surface properties are mission critical. Some examples where radiation dose from low energy particles should be evaluated include radiation degradation of solar sail propulsion systems, changes in thermo-optical properties of thermal control coatings, radiation damage to thin sunshield materials, and modification of surface charging properties for materials used on the exterior surfaces of spacecraft with requirements to be electrostatically clean. This presentation will first discuss the characteristics of ionizing radiation and plasma environments relevant to thin materials including solar wind and low energy contributions from solar particle events at Sun-Earth L1, L3, L4, and L5 and the additional contributions of magnetosheath and magnetotail plasmas at Sun-Earth L2. Next, low energy charged particle damage mechanisms for materials will be summarized including total ionizing dose, hydrogen blistering, changes in thermo-optical properties, and sputter erosion yields. Finally, examples of modeling techniques used to compute the charged particle fluence to material surfaces and volumes of thin materials will be described along with methodologies for estimating total ionizing dose as a function of depth for materials in the low energy environment.

10:30 AM SF02.04.06
Defect Pathways for Disordering of Oxide Electronics in High-Radiation Environments Bethany Matthews[1], Kayla H. Yano[1], Sarah Akers[1], Michel Sassi[1], Sandra Taylor[1], Le Wang[1], Rajendra Paudel[2], Ryan Comes[2], Yingge Du[1], Eric Lang[3,4], Khalid Hattar[4,5] and Steven R. Spurgeon[1,6]; [1]Pacific Northwest National Laboratory, United States; [2]Auburn University, United States; [3]University of New Mexico, United States; [4]Sandia National Laboratories, United States; [5]The University of Tennessee, Knoxville, United States; [6]University of Washington, United States

Due to lack of protection from the earth's magnetic field and atmosphere, space materials often experience high levels of irradiation from the sun's rays, cosmic rays, and solar winds. Because material properties are heavily tied to their microstructure, crystal structure, and atomic bonding, it is important to understand how materials progress in disorder and damage under irradiation and how defects and compositional changes may affect that progression. Oxide thin films make up crucial portions in many electronic components, therefore understanding disorder progression in them is of particular interest.

To begin to understand changes in a material, it is helpful to examine one that has been thoroughly studied, understanding viable defects, bonding, phase diagrams, etc. To that end, we chose to examine thin films of LaFeO3 (LFO) grown on SrTiO3 (001) (STO) substrates, both well-known perovskites. Films were grown by molecular beam epitaxy (MBE), known to allow for precise, and controlled film growth, to obtain the highest quality growth. To examine the effects of introducing defects and variation in microstructure, LFO films were grown by pulsed laser deposition (PLD) on STO. To probe effects of composition, alloyed films of $La_{1-x}Sr_x$FeO3 (LSFO) grown on STO (x = 0.25 and 0.5) were also grown by PLD. Prior to irradiation, cross-sections of the film were extracted by standard focused ion beam (FIB) preparatory procedures and examined by scanning transmission electron microscopy (STEM) imaging and STEM energy dispersive x-ray spectroscopy (EDS) to verify film quality.

To simulate the intensity of high energy particles in space and to induce different stages of disorder, films were irradiated *ex situ* at room temperature by Au^{2+} ions at 2.8 MeV at Sandia National Laboratories' Ion Beam Laboratory. A metal mask was used to selectively irradiate portions of the film to doses of 0.1 and 0.5 displacements per atom (dpa) (3.74E13 ions/cm^2 and 1.87E14 ions/cm^2 respectively). Post-irradiation, lamellae were extra by FIB and inspected by STEM imaging and STEM-EDS, then they were compared to pre-irradiation films.

Pre-irradiation, the LFO film grown by MBE and LSFO films were found to be uniform and smooth with a sharp interface at the substrate. The LFO film grown by PLD had small vertical domains that appeared Fe-poor in addition to occasional crystal defects. We found at 0.1 dpa, there was little difference in microstructure between the high-quality LFO film grown by MBE and the LSFO films. Films appeared less uniform near the surface of the film with some regions having fully amorphized; however, the LFO film with vertical defect domains was most amorphized in the top 2/3 of the film with small crystal domains embedded in the amorphous material, some of which had rotated. The regions that had amorphized most were similar in size to the Fe-poor domains in the unirradiated film, suggesting that the defective regions had broken apart first. After 0.5 dpa, the LFO film with vertical defect domains was fully amorphized, and the x=0.25 LSFO was nearly fully amorphous with only small portions at the substrate interface still crystalline. However, the MBE LFO was only roughly 2/3 amorphized, whereas the x=0.5 LSFO film was surprisingly not even ½ amorphized. This indicates that while composition can have a strong effect, compositional microstructural uniformity is more important for material robustness under ion irradiation.

10:45 AM SF02.04.07

Anisotropic Radiation Shielding and Thermal Properties of 2D Boron Nitride Nanoplatelet Foam via Freeze-Drying Kazue Orikasa[1], Cheol Park[2], Sang-Hyon Chu[2,3], Calista Lum[4], Tony Thomas[1] and Arvind Agarwal[1]; [1]Florida International Universtiy, United States; [2]NASA Langley Research Center, United States; [3]National Institute of Aerospace, United States; [4]University of California Merced, United States

Neutron radiation exposure and extreme thermal cycling are some of the main challenges faced during various aerospace missions. There is a critical need for advanced lightweight radiation shielding and thermally conductive materials. Polymer composites are commonly used in aerospace technology due to their low density, hydrogen richness, and ease of processing. However, polymers have limitations such as poor thermal conductivity, poor mechanical properties, and low neutron shielding properties. Two-dimensional (2D) Boron Nitride Nanoplatelets (BNNP) are excellent candidates for polymer matrix fillers due to their superior thermal neutron shielding and thermal properties. The 2D material anisotropic behavior unlocks the potential for composite property tailoring. However, the nanomaterial dispersion within polymer matrices is challenging due to their agglomeration tendency. In this study, a highly dispersed and lightweight BNNP foam (density 0.05 g/cm^3 and porosity 97.5%) was fabricated via Freeze-Drying processing. Freeze-Drying overcomes nanomaterial agglomeration challenges and enables the foam microstructure design through the control of the thermodynamic processing parameters such as mold geometry, mold material, and solid loading. The foam microstructure was designed to be lamellar, enhancing the anisotropic behavior of 2D BNNP. Subsequently, neutron radiation shielding and thermal conductivity tests were performed on the foams with different wall orientations with respect to the probing directions. The neutron radiation test results revealed excellent radiation shielding properties with an orientation-dependent shielding behavior. The neutron shielding effectiveness or mass absorption coefficient of the BNNP foams with walls perpendicular to the radiation source was significantly higher than those with a parallel configuration. Similarly, Flash Diffusivity studies revealed that the thermal conductivity of the foam with walls parallel to the heat source was much greater than those with a perpendicular configuration. The BNNP foam in this study has the potential to benefit advanced tailorable radiation shielding and thermal management for future aerospace missions.

SESSION SF02.05: Atomic Oxygen Exposure
Session Chairs: Eitan Grossman and Sharon Miller
Wednesday Afternoon, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate C1

1:30 PM *SF02.05.01

Real-Time Atomic Oxygen Measurements—From Lab to Space Irina Gouzman[1], Ronen Verker[1], Asaf Bolker[1], Moshe o. Tordjman[2], Nurit Atar[1], Eitan Grossman[1], Brian Riggs[3] and Timothy K. Minton[3]; [1]Soreq NRC, Israel; [2]Technion–Israel Institute of Technology, Israel; [3]University of Colorado Boulder, United States

The atomic oxygen (AO) presence in a low Earth orbit (LEO) environment is one of the primary factors responsible for the degradation of spacecraft external surface due to its ability to cause severe oxidation and surface erosion. As a result, thermal, mechanical, and optical properties of AO-exposed materials, especially polymers, are vulnerable. Therefore, information concerning the flux of AO is very important for spacecraft design and mission lifetime assessment. Moreover, AO monitoring can be used to detect real-time changes in solar activity, thus providing data of great importance to "space weather" forecasts.

Many spectrometric, optical, gravimetric, and semiconductor-based methods to measure AO flux have been developed over decades of space research. Advantages, as well as shortcomings of some of the most useful methods, will be reviewed. Furthermore, two new, elegant, and cost-effective methods for AO monitoring in space, developed in our laboratory, will be discussed.

The first method is based on material erosion measurements using the on-orbit material degradation detector (ORMADD). The ORMADD is comprised of solar cells coated with a semi-transparent AO-sensitive layer. Recently an ORMADD, coated with amorphous carbon and Kapton, was integrated on the TAUSAT-1 nanosatellite. TAUSAT-1 mission was to study the low Earth orbit space environment and its effect on electronic components and materials. It was ejected from the international space station into its orbit in March 2021. Using ORMADD we were able to follow the erosion of the coatings in real-time and to calculate the AO flux at the TAUSAT-1 orbit. The flux calculated using ORMADD data was on-par when compared to the AO flux calculated using the SPENVIS software.

The second method is based on the unique electrical properties of diamond substrate overcoated with a thin transition-metal oxide (TMO) layer. This device, abbreviated as DTMO sensor, was implemented using type IIa (001) single crystal diamond and atomic layer deposited (ALD) tungsten oxide (WO_3). The TMO serves as an electron acceptor, promoting hole conductivity on the diamond surface through a process of transfer doping. When exposed to AO, the TMO goes through a redox process, thereby changing its band structure and reducing the hole concentration in the diamond surface. This process results in an increase in the diamond surface resistivity that can be monitored in real-time. The results of AO flux and fluence measurements with the DTMO, obtained during ground-based exposure using 5 eV AO laser detonation source, are very promising. The change in the diamond resistance, while exposed, was measured *in-situ* and compared to the LEO equivalent AO fluence, calculated based on polyimide mass loss as a standard. The results showed a linear increase in the diamond resistance as a function of fluence up to 2×10^{20} O-atoms/cm^2 without reaching saturation. The sensitivity of the DTMO sensor with 10 nm WO_3 coating was ~6×10^{14} O-atoms/cm^2 Ω. Our work demonstrated the potential of the DTMO sensor to enable fast and reliable real-time on-orbit AO flux monitoring.

2:00 PM *SF02.05.02
Real-time Observation of Polyimide Erosion in Very Low Earth Orbit (VLEO) and Its Impact on Space Environmental Effect on Materials Masahito Tagawa[1], Kumiko Yokota[1], Atsushi Fujita[1], Wataru Ide[1], Towa Ushijima[1], Koki Yao[1], Sasuga Horimoto[1], Santa Nishioka[1], Kaichi Nakayama[1], Yuta Tsuchiya[2], Aki Goto[2], Kazuki Yukumatsu[2], Eiji Miyazaki[2] and Yugo Kimoto[2]; [1]Kobe Univ, Japan; [2]JAXA, Japan

Superlow altitude test satellite (SLATS) was launched on Dec. 23, 2017 and recorded the lowest altitude for Earth observing satellite (167.4 km, Guinness World Record). SLATS carried the world first material erosion mission, atomic oxygen fluence sensor (AOFS), to measure polyimide erosion in real time in very low Earth orbit (VLEO) environment. This presentation describes the results of AOFS. It includes the correction method of shielding/shadowing effect by the SLATS fuselage, and enhancement of polyimide erosion by the simultaneous N2 collision in VLEO environment. The erosion yield (Ey) of polyimide, which has been believed to be 3.0E-24 cm3/atom in all altitudes as a reference value of material erosion, will also be re-evaluated based on the recently updated atmospheric model (MSIS2.0) and experimental results by SLATS/AOFS.

2:30 PM SF02.05.03
Atomic-Oxygen-Induced Microstructures Formed on Hydrocarbon Polymer Films Aki Goto[1,2], Takashi Tanji[2], Masahito Tagawa[3], Koji Michishio[4], Toshitaka Oka[5] and Shinichi Yamashita[2]; [1]Japan Aerospace Exploration Agency, Japan; [2]The University of Tokyo, Japan; [3]Kobe University, Japan; [4]National Institute of Advanced Industrial Science and Technology, Japan; [5]Japan Atomic Energy Agency, Japan

Atomic oxygen (AO) is a dominant constituent of the residual atmosphere in low Earth orbit (LEO). Spacecraft collides with AO at the relative velocity of 8 km/s, which corresponds to the translational energy of 5 eV. Polymers used for thermal control are oxidized and eroded by such AO collisions, degrading their mechanical and thermo-optical properties. In the erosion processes, AO forms nanoscale protrusions on the polymer surface. If the surface morphologies and physical properties (e.g., wettability and optical property) can be controlled by AO irradiation, it would be useful in modifying the surfaces for various polymers.
This study aims to clarify the factors that determine the characteristics of AO-induced microstructures (protrusions' size and numerical density). Hydrocarbon polymers with a simple chemical structure were selected for the samples: polyethylene (PE), polypropylene (PP), and polystyrene (PS). The polymer films (23–30 μm in thick) were irradiated with AO by a laser-detonation source at Kobe University (5–7 km/s). The mass losses were measured by an electronic microbalance. The changes in chemical bonds were evaluated by Fourier transform infrared spectroscopy (FT-IR). The surface morphologies were observed by a field emission scanning electron microscope (FE-SEM) and an atomic force microscope (AFM). The changes in depth profiles for the chemical structures and free-volume holes' sizes were evaluated by positron annihilation lifetime spectroscopy (PALS) at AIST (1.3–10 keV).
The three polymers had similar changes in masses (or erosion yields) and chemical bonds but different surface morphologies. The protrusions formed on PE and PP were larger and fewer than those formed on PS, which was irradiated with comparable AO fluences [Goto, A., et al. Langmuir 2022, 38, 3339-3349.]. The polymers are known to have different higher-order structures, so it might affect the spatial scales where interactions occur with AO, leading to the different morphologies. Further, the formed protrusions became larger and fewer with rising temperature of the polymer irradiated with AO (25–75 °C, controlled by the sample holder with a heater). The PALS evaluations indicated that the polymers have different radii in free-volume holes (PS (0.29 nm) < PP (0.31 nm) < PE (0.32 nm)) and different thicknesses of an oxidized layer formed by AO (PS < PE ≈ PP). Based on these results, the regions where AO interacts with the polymer would depend on the thermal motions of polymer chains and/or sizes in free-volume holes.

2:45 PM BREAK

3:15 PM *SF02.05.04
Low-Drag, Atomic-Oxygen Resistant Materials for Satellites in Very Low Earth Orbit Timothy K. Minton[1], Chenbiao Xu[1] and Thomas E. Schwartzentruber[2]; [1]University of Colorado, United States; [2]University of Minnesota, United States

The environment encountered by satellites in very low Earth orbit (VLEO, 180 – 350 km altitude) contains mostly atomic oxygen (AO) and molecular nitrogen (N_2), which collide with ram surfaces at relative velocities of ~7.5 km s^{-1}. Structural, thermal-control, and coating materials containing organic polymers are particularly susceptible to AO attack at these high velocities, resulting in erosion, roughening, and degradation of function. Copolymerization or blending of a polymer with polyhedral oligomeric silsesquioxane (POSS) yields a material that can resist AO attack through the formation of a passivating silicon-oxide layer. Still, these hybrid organic/inorganic polymers become rough through AO reactions as the passivating layer is forming. Surface roughness may enhance satellite drag because it promotes energy transfer and scattering angle randomization during gas-surface collisions. As potential low-drag and AO-resistant materials, we have investigated POSS-containing films of clear and Kapton-like polyimides that have an atomically smooth AO-resistant coating of Al_2O_3 that is grown by atomic layer deposition (ALD). Coated and uncoated films were exposed to hyperthermal molecular beams containing atomic and molecular oxygen to investigate their AO resistance, and molecular beam-surface scattering studies were conducted to characterize the gas-surface scattering dynamics on pristine and AO-exposed surfaces to inform drag predictions. The AO erosion yield of Al_2O_3 ALD-coated films is essentially zero. Direct simulation Monte Carlo (DSMC) simulatios of drag on a representative satellite structure, which are based on the observed scattering dynamics, suggest that the use of the Al_2O_3 ALD-coated POSS-polyimides on external satellite surfaces have the potential to reduce drag to less than half that predicted for diffuse scattering surfaces. These smooth and AO-resistant polymer films thus show promise for use in the extreme oxidizing and high-drag environment in VLEO.

3:45 PM SF02.05.05
Evaluation of the Effect of Space Debris Impact on Atomic Oxygen Protectant Materials for MLI Yuko Kubo[1], Yugo Kimoto[1], Kaori Umeda[2] and Sunao Hasegawa[1]; [1]Japan Aerospace Exploration Agency, Japan; [2]Advanced Engineering Services Co., Ltd., Japan

Multi-layer insulation (MLI) generally covers the surfaces of spacecraft, and it contributes to thermal control of that. Because of the excellent heat and radiation resistance, polyimide is often used as the outermost layer of MLI. But polyimide is known to be eroded by atomic oxygen (AO) in low earth orbit. Coating a polyimide with an inorganic layer is one way to improve AO tolerance of MLI, and this method is widely used. However, inorganic layers sometimes tend to contain manufacturing defects and they also tend to be fragile, and AO erosion occurs from these areas. To solve the issue mentioned above, we have been developing AO protectant materials, polyimide itself, and coating agent for MLI with keywords of self-organization and self-healing. Self-organization is the property which generates AO-resistant layer on the surface by the material itself with AO irradiation. In addition, if the AO-resistant layer is damaged, the material re-generates AO-resistant layer by itself with AO irradiation again. We call this property as self-healing. Our materials have been studied in orbital exposure experiments and self-organization property of our materials have been demonstrated. In addition, we

demonstrated that our materials have self-healing property in ground test.
However, we haven't known that whether our materials maintain self-organization and self-healing properties after collision with space debris. It is known that collision with debris occurs high heat, high strain rate etc. and some materials break in different destruction mode compared with that on the ground. Therefore, it is necessary to evaluate whether our materials have the same self-organization and self-healing properties after collision with debris and we conducted a series of the ground test. In this presentation, we will report our plans and experimental results obtained to date.

4:00 PM SF02.05.06
Approaches to Technological Challenges of the Space Elevator Yasuhiro Fuchita[1], Yoji Ishikawa[1], Takashi Hitomi[1], Yoku Inoue[2] and Naoko Baba[3]; [1]Obayashi Corporation, Japan; [2]Shizuoka University, Japan; [3]Japan Manned Space Systems Corporation, Japan

The space elevator is a future space transportation system that connects Earth and space by a cable and climber (vehicle) back and forth. When completed, the system will have the following advantages: "the cost of going to space will be greatly reduced," "space travel will be less physically demanding," "it will serve as a starting point for other celestial bodies," and "solar power generation will be possible without loss." However, the elevator's mass was too large, and the materials were not strong enough to make it feasible as a structure.
Carbon nanotubes (CNTs), discovered in 1991, are composed of carbon atoms and are lightweight (specific gravity is about half that of aluminum), and have high mechanical strength (tensile strength is about 20 times that of steel). CNTs as a material for cables have increased the feasibility of space elevators. However, to make it viable as a transportation system, it is necessary to manage the same processes as on the ground, such as design, construction, and maintenance, and to deal with the special movement mechanism that moves vertically through the Earth's gravity zone and exposure to the unique space environment.
This paper reports on the current status of efforts to test space elevator cable materials for exposure to the space environment. The space environment resistance of twisted CNT yarns, which are assumed to be the cable material for space elevators, was investigated using the Exposed Facility of the Japanese Experiment Module "Kibo" on the International Space Station (ISS) at an altitude of about 400 km. At altitudes between 200 km and 600 km, atomic oxygen (AO) is a major component of the atmosphere, accounting for more than 80% of the atmospheric composition at an altitude of 400 km, where the ISS orbits.
The 1-year exposure test specimens were placed at the rear and front of the ISS, and the 2-year exposure test specimens were placed at the rear of the ISS. For the ground control tests, the first test was conducted from November 12, 2014, to March 2, 2015, and the second from June 8 to 30, 2016, at the JAXA-owned vacuum complex environment test facility. The test conditions were full-period irradiation, with the irradiation dose corresponding to approximately six months of space environment exposure. Strength tests were not conducted on thin-stranded CNTs due to their serious damage. For thick-stranded CNTs, the tensile strength was measured to be lower on the front than on the back. The results of the ground control test were reproducible. The tensile strength of the flown product was lower than the pre-flight product. For the specimen of the flown product, the portion covered by the cover for fixing the specimen and the portion exposed to the space environment were compared. The diameter of the exposed part was smaller than that of the part covered by the cover. It was also found that CNTs were gouged from the surface to a depth of several CNTs in the exposed area.

SESSION SF02.06: Space Material Ground Testing and Modeling
Session Chairs: Timothy Minton and Stéphanie Remaury
Thursday Morning, April 13, 2023
Marriott Marquis, B2 Level, Golden Gate C1

8:30 AM *SF02.06.01
Combined Radiation and Environmental Effects Testing for ESA's Space Projects Adrian T. Tighe and Nuno Dias; European Space Agency, Netherlands

The Environmental Testing Team in ESA's Materials Physics and Chemistry Section is tasked with supporting ESA's space projects to verify the performance of exposed items in simulated space environments. For this purpose, the group's experimental capabilities include a wide range of radiation and environmental test facilities and associated measurement techniques, ready to adapt for new missions. Combined testing is performed to assess the impact of different environmental factors, using both simultaneous and sequential irradiation. Flight experiments are also undertaken when the opportunities are available to compare the performance of items exposed to the ground and space environment.

This paper will present results of radiation and environmental effects testing recently performed in our laboratories for various space projects and early phase technology development studies. This includes UV exposure of white ceramic coatings for the Earth Return Orbiter, high intensity solar illumination testing of optical coatings, combined radiation and atomic oxygen testing of thermal control paints and combined UV and particle radiation testing of deposited contamination layers on optical coatings.

An update will be provided on an activity being performed with ESA's industrial partners to test optical coating samples in a simulated space radiation environment. The testing will be complemented by numerical modelling and simulations, in order to establish a set of practical lessons learnt and best practices for radiation testing. In the future, this shall be used to support the development of a new European test standard on radiation testing of optical coatings for space applications.

The paper will also describe some of the new facilities and testing techniques under development within our team for future missions. This includes a multipurpose radiation simulation facility for combined environmental testing of cube-sat class items and small payloads, and a combined dust contamination and radiation effects simulation facility for lunar surface studies. To conclude, a new "open lab" campaign on Radiation and Environmental Effects Testing will be described. This campaign is being planned to provide opportunities for academia and small enterprises to make use of the environmental test facilities within ESA, in support of early phase developments for future space projects. A short update will also be provided on the on-going preparations for the EuroMaterialAgeing flight experiment, which will be expose materials to combined radiation environments in the real space environment.

9:00 AM BREAK

9:30 AM SF02.06.02
Payload Carrying Capabilities of Ultralight Lightsail Spacecraft Michael Kelzenberg, Ramon Gao and Harry A. Atwater; California Institue of Technology, United States

Lightsails harvest the radiation pressure of incident light for the propulsion of spacecraft, eliminating the need to carry and expel reaction mass, and in principle allowing acceleration to relativistic velocities.[1] Recent efforts have sought to develop technologies for ultra-lightweight lightsail space probes that could be launched using an earth-based high-power-intensity laser, allowing execution of interstellar flyby missions on a time scale of a few decades.[2] This mission concept calls for a spacecraft comprising a ~1 g, ~10 m^2 lightsail, carrying a payload of similar mass, including all sensors, communications systems, and power sources.[3] Prior work has identified materials and technologies suitable for construction of lightsails and payload components within these extremely limited mass budgets.[4] However, the question remains as to whether such large-area ultrathin lightsail membranes could support the attachment of payloads without tearing or destabilizing during acceleration, owing to the changes in mass distribution and the concentration of inertial forces at the points of attachment.

Here, we study the effects of various payload integration schemes on the behavior of interstellar lightsail spacecraft during acceleration, to determine the limits on payload mass and distribution imposed by the strength and stability of the lightsail. Specifically, we look at lightsails made from silicon nitride (SiN_x), with either specific shape curvature or flat photonic metagrating patterned surfaces, which have been previously shown to achieve beam-riding stability in the absence of an attached payload.[5] We start with static structural analysis to determine the limits on localized mass loading for the membranes, concluding that for the nominal acceleration target of ~10^5 m/s^2, the membranes can support center-mass payloads on the order of 100 g. However, we show that localized reinforcement of the membrane, by increasing its thickness, can increase this limit several-fold with modest mass penalty to the sail. Furthermore, distributing the payload mass between multiple components spaced across the sail can further reduce the peak stress.

Then, a time-domain mesh-based simulation tool, specifically developed for lightsail modelling, is employed to study the behavior of unconstrained flexible membranes with integrated payload mass(es) during acceleration. This allows us to evaluate not only the mechanical integrity of the lightsail by observing the dynamic stress distribution, but also the effects of payload integration on the trajectory and ultimately the beam-riding stability of the integrated sailcraft. We have observed that modest (~100 g) center-located payloads can be carried by the previously reported self-stabilizing lightsail designs, with little reduction in stability or strength margins, and are working to further optimize designs to determine the limiting payload mass that can be carried in center-located and distributed-mass configurations. Results of the simulations will be presented, including acceleration trajectories, stress and temperature distributions, and animations of shape perturbations.

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9:45 AM SF02.06.04
Demisability and Structural Performance Assessment of Novel Composite Systems for Spacecraft External Panel Assembly Alexandre A. Looten[1], Véronique Michaud[1], Muriel Richard[1] and Antonio Caiazzo[2]; [1]EPFL, Switzerland; [2]European Space Agency, Netherlands

With the recent awareness of the space sector on the fragile near-Earth space region and the forecast of the booming number of satellited objects, various mitigation approaches are currently being evaluated and starting to be implemented to limit the impact of space activities, and achieve a safe and sustainable space environment. Unfortunately, knowledge uncertainties and technology gaps delay our capability to act immediately, especially to apply a design-for-demise (D4D) approach, which aims to modify a spacecraft design and conception process to achieve the safest destructive reentry possible by material substitution, specific geometries, or dedicated subsystems.
As part of a Network Partnering Initiative launched by the Swiss Federal Institute of Technology in Lausanne (EPFL) and the European Space Agency (ESA), this work focuses on the design and experimental evaluations of novel composite components to improve the overall spacecraft demisability. The new system is compared to baseline critical systems, targeting higher altitude break-up while maintaining equivalent mission-relevant properties. The project's main attention landed on a complementary dual strategy with the material substitution of a benchmark system composed of an external sandwich panel and its fasteners. First, a hybrid reinforcement made of carbon and demisable flax fibers is evaluated to replace aluminium panel skins or critical full carbon composite skins. The integration of a thermally conductive and reactive metallic matrix filler composed of aluminium-magnesium alloy micro-powder has also been investigated. Second, a novel short carbon fiber reinforced polyetheretherketone (CF/PEEK) bolted joint design is evaluated to replace critical titanium or steel alloys currently used.
The demisability assessment is performed at material and lab scale component levels. This involves the measurement of material's mechanical properties under static loading at room temperature, and dynamic loading over a temperature range to detect their softening point. Static and dynamic reentry simulation tests were carried out using a laboratory-scale high-temperature creep test and a plasma wind tunnel test to evaluate on one-hand, the thermo-mechanico-physical property change over typical uncontrolled reentry conditions, in particular the material break-up point, and on the other hand, the composite degradation. Results to date led to the selection of a promising reinforcement architecture. An optimal ply-by-ply carbon-flax hybrid/epoxy shows the best trade-off in terms of demisability and specific mechanical properties for the skin, with respectively a 180% ablation rate improvement starting at a lower temperature as compared to CFRP, while having an equivalent specific bending modulus to CFRP or 40% higher as compared to aluminium. The addition of the AlMg filler improved the matrix degradation rate by more than 10% while reducing its onset by 40°K. The study of the joints demonstrated that stainless-steel bolts present no sign of effective demise under testing up to 1070°K, whereas the novel CF/PEEK bolts start to demise before reaching 670°K, while having a superior specific tensile, σ/ρ, and shear strength, τ/ρ, within a typical space mission temperature range (120-400°K).
The project's next phases will focus on the demisability sequence of a bolt-insert fastening system on a sandwich panel assembly to improve the technology readiness level of the concept.
This multi-collaborative project aims to reduce current uncertainties regarding composite materials' demise and implement these technologies on a typical spacecraft platform to move a step forward toward casualty risk mitigation.

SESSION SF02.07: Lunar and Martian Regolith and Environments
Session Chairs: Sara Rengifo and Debbie Senesky
Thursday Afternoon, April 13, 2023
Marriott Marquis, B2 Level, Golden Gate C1

1:30 PM *SF02.07.01

Lunar Dust and Dust Mitigation Testing Sharon K. Miller; NASA Glenn Research Ctr, United States

Lunar dust was one of the most persistent problems for the Apollo astronauts due to its' abrasiveness and strong adherence to surfaces. With the Artemis program, NASA is planning longer stays on the lunar surface, with more activities that have the potential to put the astronauts and equipment in contact with greater quantities of lunar dust. The success of these missions will depend on our understanding of material interactions with lunar dust and the development of ways to mitigate dust effects. This is particularly true in cases where exposure to dust will lead to failure of components, unacceptable loss of power or thermal control, unacceptable loss of visibility, or health issues. Lunar dust, issues with lunar dust, and ground testing with lunar simulant will be discussed as well as the development of and planned flight testing of optically transparent work function matching coatings to reduce adhesion of dust on the lunar surface.

2:00 PM *SF02.07.02
Evaluation of Lunar Dust Mitigation Technologies on the Moon and in Ground Simulators Jacob I. Kleiman and Zelina Iskanderova; Integrity Testing Laboratory Inc, Canada

The interaction of lunar dust and other environmental factors, like vacuum, temperatures, solar radiation, ultraviolet irradiation, and electron (e-) and proton (p+) irradiation with structures on the Moon and the outside of the future Gateway Lunar station may lead to permanent change or complete loss of the thermal, optical, and other functionalities that could potentially lead to catastrophic failures. Among the other factors, lunar regolith dust is the most aggressive, causing the main problems.
To evaluate the efficiency of passive dust mitigation techniques, a materials experiment that was funded by NASA and developed and built by Alpha Space Test and Research Alliance, named Regolith Adherence Characterization (RAC) Payload, will be launched to the Moon in 2023-2024 timeframe. The goals of the RAC Payload mission are to evaluate several materials and coatings with dust mitigation properties for their ability to repel or shed lunar regolith/dust, (e. g. solar cells, optical systems, coatings, sensors) and to determine regolith accumulation rates: 1) caused by landing, and 2) during routine lander operations.
ITL is taking part in this experiment with four samples. Through a series of experiments in the ITL-developed Lunar Simulator, ITL demonstrated that it is possible to mitigate accumulation of lunar dust simulant, and enhance surface durability of some important sensitive external structural materials using a special ITL dust mitigation technology.
To complement the information from the RAC samples on the Moon, ITL recently initiated a program to evaluate, further develop, and enhance its unique cornerstone lunar Dust Mitigation Technology (DMT) for sensitive materials on external space structures that ITL used for the RAC samples. In the framework of this program, ITL is preparing a set of DMT-treated samples as well as samples closely resembling the ones on the RAC Payload cassette. To understand the results of the RAC lunar exposure experiment, we will conduct an extensive set of experiments on interaction of lunar dust simulants with sample surfaces, similar to the RAC Payload experiments on the Moon, in our Lunar Environment Simulator that will be upgraded for this project.

2:30 PM BREAK

3:30 PM SF02.07.03
Additive Manufacturing of Regolith Composites Through UV-Assisted Direct-Ink-write in Simulated Space Environments Alexandra Marnot, Lena Konzelman and Blair K. Brettmann; Georgia Institute of Technology, United States

Direct-ink-write (DIW) of Lunar and Martian regolith simulants is of particular interest to promote in-situ resource utilization (ISRU) in the upcoming Artemis missions. The span of formulation design parameters for DIW of high solid suspensions of regolith is wide and offers a lot of freedom for additive manufacturing in space environments. Regolith simulants, incorporated in a polymeric binder and used in conjunction with UV-curing solidification after extrusion, enable reduced energy demands for construction of parts, but require precise formulation characterization to successfully cure these dense inks. In this work we investigate several regolith simulants, including LHS-1, LMS-1, and MGS-1, in acrylate-based binders. We utilize photo-DSC in conjunction with the ISO 4049 method to assess cure degree and cure depth respectively, while rheological assessments give us insights into the flowability of these inks. The results from these preliminary tests allow us to produce dense and opaque suspensions which can be printed both at ambient and in a simulated space environment at -30°C. The adhesion at the regolith-binder interface is evaluated through tensile testing on as-printed parts and parts subjected to thermal cycling imitating the typical Lunar or Martian weather conditions. These efforts aim to help guide the future of additive manufacturing through formulation design for both processing and end-use on the Moon and Mars.

3:45 PM SF02.07.04
***In Situ* 3D Lunar Manufacturing Using Digital Light Processing** Brandon A. Aguiar, Ambreen Nisar, Tony Thomas, Cheng Zhang and Arvind Agarwal; Florida International University, United States

As the thirst for space exploration has creeped back into the public zeitgeist, the aerospace industry is gearing up to become residents of our closest celestial neighbor. A lunar expedition to the south pole offers a multitude of challenges. The logistics and cost of getting resources from Earth to the moon clearly enables the need for predominantly in-situ part and structure additive manufacturing (AM) using locally available materials. In this regard, Greenland Anorthosite lunar regolith was three-dimensionally (3D) printed using Digital Light Processing (DLP). Complex and intricate geometries with high dimensional accuracy were printed and sintered with no signs of delamination. The solid loading of Greenland regolith was 60 wt% with a shrinkage post sintering of less than 6% in all three directions. The mechanical integrity and thermal stability of the printed part has also been studied. The compressive failure of the sintered sample was validated using Finite Element Analysis (FEA). This research is a step towards validating the use of lunar regolith for part and colonist habitat manufacturing.

4:00 PM SF02.07.05
Tribological and Radiation Shielding Response of Novel Titanium-Boron Nitride Coatings for Lunar Structural Components Abhijith K. Sukumaran[1], Cheng Zhang[1], Sara Rengifo[2], Sang-Hyon Chu[3], Cheol Park[4], Michael Renfro[5], Calista Lum[6], Katie Stephens[7] and Arvind Agarwal[1]; [1]Florida International University, United States; [2]NASA Marshall Space Flight Centre, United States; [3]National Institute of Aerospace, United States; [4]Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, VA, United States; [5]Plasma Process, United States; [6]University of California, Irvine, United States; [7]University of California Merced, United States

Lightweight alloys of Aluminum (Al) and Titanium (Ti) are significant components of space systems because of their high strength-to-weight ratio. However, their poor tribological response in the presence of lunar regolith and lack of space radiation shielding ability can result in premature failures. Hexagonal Boron Nitride (hBN) reinforced titanium coatings were produced by atmospheric and vacuum plasma spray methods at low and high-volume concentrations of hBN to counter these undesirable results after powder preparation by cryo-milling. The microhardness results showed that coating hardness was 3.0 times that of conventional Ti6Al4V (335 HV) substrate in the case of low vol.% hBN (900 HV) concentration and 1.5 times in the case of high vol.% hBN coating (516 HV). Furthermore, tribological characterization by ball-on-disk tests in the presence of JSC-1A lunar regolith simulant revealed a 70% reduction of wear volume on the Ti/low vol.% hBN coatings compared to conventional material. The science of boron nitride retention and secondary phase effect in the coatings were examined using characterization techniques such as SEM, XRD, and Raman spectroscopy. Developed coatings were subjected to the simulated extreme lunar condition of neutron radiation. The coatings exhibited effective radiation shielding ability up to 31.8 % with an increase in % hBN content. Computational studies indicate that the presence of boron-based inclusions can effectively suppress generation of undesirable secondary radiations through the metal alloys against galactic cosmic rays (GCR) and solar particle events (SPE) as well. The coatings will be subjected to harsh erosive conditions on a custom-made high-velocity dust impact setup to evaluate erosion performance.

4:15 PM SF02.07.06
Investigating the Adhesion Force of Lunar Regolith Particulates on Air Plasma Sprayed Alumina Coatings Perla C. Latorre-Suarez[1], Quentin Fouliard[1], Christopher J. Wohl[2], Valerie Wiesner[2] and Seetha Raghavan[1]; [1]University of Central Florida, United States; [2]NASA Langley Research Center, United States

Ceramic materials, often used to protect components due to their high strength, and wear resistance, have combined benefits of being lightweight and providing multifunctional properties. They are, therefore, significant to provide durability and support during long-duration missions to the moon's surface for rovers, landers, robotic systems, habitats, and many other components. Materials such as aluminum oxide with high mechanical strength and hardness can help to improve the durability of structures used in space exploration. Devices used for space exploration require the use of materials with the ability to withstand exposure to extreme environments. Lunar regolith is a constituent with the ability to adhere electrostatically and damage the components used to perform these missions due to adhesion of lunar dust projectiles that can cause delamination on surfaces, which may not be physically visible. The particulates of lunar dust are classified as corrosive material, leading to the degradation of structures. Aluminum oxide presents excellent resistance to different types of wear due to its high strength and hardness. Air plasma sprayed (APS) aluminum oxide coatings have demonstrated the potential to protect the surface to which they are applied. However, the parameters of roughness and porosity of the coatings need to be considered to establish if they can protect the components from extreme environments. Considering the electrostatic forces that the components are exposed to, the adhesion between the lunar regolith and the surface of the components needs to be investigated. In this work, the adhesion forces of lunar dust simulants with an average size of 30 µm are investigated considering the roughness of the surface of the APS aluminum oxide. The centrifugal technique utilized here offers the advantage of establishing the adhesion force between particles with different shapes on smooth or rough surfaces. The simulants were deposited on the surface of APS aluminum oxide using an aerosolization technique to achieve a monolayer coating in three different locations across the specimen to determine the increments in adhesion force at the centrifuge. Using a profilometer, the roughness of the APS aluminum oxide was determined to be around 2.25 µm. The specimen was tested under an incremental centrifugal speed from 100 rpm to 3000 rpm for 20 seconds. Low magnification microscopy images were collected to cover a larger surface area of the tested coating. The adhesion force was measured considering the distance from the centrifugal axis and the rotational speed. Due to the coating roughness, and the distance from the centrifugal axis, the results demonstrated a larger adhesion force in locations closer to the centrifugal axis. Smaller particles were entrapped within the roughness of the coating, and a stronger adhesion force was measured. In order to continue designing wear-resistant coating for structural protection in space missions, press-on experiments using a centrifuge will be performed. Future experiments will allow us to determine the design parameters for APS aluminum oxide coating to protect the structures from harsh space environments.

SESSION SF02.08: Spaceflight Exposure Experiments II
Session Chairs: Patrick Flowers and Rose Hernandez
Tuesday Morning, April 25, 2023
SF02-virtual

10:30 AM SF02.08.01
Exposure of Polyphenylsulfone and Polyphenylsulfone-Hexagonal Boron Nitride Composite Films in the LEO Wake Environment Tiffany Williams[1], Witold Fuchs[1], Baochau Nguyen[2,1], Kim de Groh[1] and Diana Santiago[1]; [1]NASA John H. Glenn Research Center, United States; [2]Universities Space Research Association, United States

Polyphenylsulfone (PPSU) is a high-performance thermoplastic with one of the highest glass-transition temperatures (T_g) in its class that is currently being evaluated for potential use as an electrical insulation material in high power dense motors in electrified aircraft. Polymeric electrical insulators can experience degradation caused by UV radiation induced by corona discharge, which is exacerbated at altitude, and would further contribute to aging in the polymer. In addition, although PPSU is reported to be resistant to gamma radiation and unstable in UV radiation according to literature, not much information exists related to its exposure in space environments, which are difficult conditions to replicate on Earth. As of now, UV exposure reported for this family of polymers has only been limited to short-term exposure. This study describes a post-flight assessment of PPSU after 0.44 years of exposure to the low Earth orbit (LEO) wake environment. The PPSU sample was flown as part of the Polymers and Composites Experiment-4 (PCE-4) on the Materials International Space Station Experiment-13 (MISSE-13) mission [1]. In addition, a sample of PPSU extruded with 10 wt% hexagonal boron nitride (h-BN) was also flown to determine whether or not any improvement to its resistance to UV radiation occurred when exposed to the wake environment. A post-flight visual inspection of both samples of virgin PPSU and PPSU- 10 wt% hBN showed film discoloration from colorless to amber, which is likely attributed to light absorption in the wavelength of the chromophoric structures from aromaticity in PPSU [2, 3] and is not believed to cause changes to Young's modulus and tensile strength [4]. A series of tests were used to characterize the samples pre-flight and post-flight, such as attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to identify changes in molecular structure, microscopy to observe changes in morphology, as well as thermogravimetric analysis and differential scanning calorimetry to identify changes in thermal stability and T_g, respectively, which could have occurred due to changes in chain length, branching, or chain rearrangement in the matrix.

References
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10:45 AM SF02.08.02
Chemcial and Physical Characterisation of Aerogel-Phosphor and PDMS-Phospor Composites after Exposure to Low Earth Orbit Conditions Atul Regmi[1,2], Sagar Ghimire[1], Steve Allison[1] and Firouzeh Sabri[1]; [1]University of Memphis, United States; [2]University of Florida, United States

Aerogel-phosphor and PDMS-phosphor composites containing La_2O_2S: Eu and $Mg_3F_2GeO_4$: Mn thermographic phosphors were flown on the MISSE-14 mission and completed 5,408 orbits. Phosphor thermometry is a versatile, accurate, noncontact, and rapid method of thermometry that uses the luminescent properties of phosphors to measure temperature. This precise, remote, and instantaneous method of thermometry covers temperatures ranging from cryogenic to 1700 C and potentially beyond. Thermographic phosphors were embedded superficially in either a polyurea crosslinked silica aerogel host, or a RTV 655 siloxane host. The spectral, mechanical, and luminescing behavior of these composites were thoroughly characterised pre and post flight and results will be presented. The study presented here focuses on evaluating the effect of atomic oxygen and UV radiation on these composites. Post exposure tests ranged from -50 to 250 C for luminescence excited by 365 and 405 nm. It is expected that decay time should be a sensitive indicator of radiation damage. Examination and comparison of results of decay time versus temperature for both exposed and unexposed samples appears to indicate no discernible change for these characteristics within measurement uncertainty. This suggests little or no damage to the thermographic phosphors. The spectral and mechanical tests performed on the composites however indicate radiation damage and will be thoroughly discussed.

11:00 AM SF02.08.04
Effect of Defects on the Mechanical Properties of Boron Nitride Nanotubes (BNNT) Nachiket Makh[1] and Ajit D. Kelkar[2]; [1]North Carolina A&T State University, United States; [2]North Carolina A & T State University, United States

High-energy radiation hazards is the major concerns for flights involving long term durations in space, as exposure to high energy radiation particles can cause serious biological damages and also can result damages to the structural materials and electronic components of the spacecraft. Typical radiation shielding materials are heavy, bulky and not able to block the emission of secondary neutrons. As such considerable efforts are being made to develop efficient, lightweight, cost effective multifunctional radiation shielding materials, which can provide structural integrity and damage tolerance. One of the leading materials that being explored is the use of Boron Nitride Nanotubes (BNNT) in conjunction with fiber reinforced material that can not only provide radiation shielding but also help to improve mechanical strength of the aerospace structures. BNNTs are polymorphs of boron nitride arranged in a hexagonal atomic structure in a tubular form. Their structure is very much like carbon nanotube (CNT) having the carbon atoms replaced by boron and nitrogen atoms. These nanotubes are classified as arm-chair nanotubes and zig-zag nanotubes. The type of nanotube can be defined by the chiral vector of the original hexagonal lattice. The nanotube is chiral if it is represented as (n,m) where $m>0$ and $m\neq n$. Since its discovery in 1995, BNNTs have come a long way, and due to the advancements in their synthesis, their properties have been improved leading them to be used for promising applications. Radiation shielding is one of the important applications of BNNT owing to its good mechanical properties. These properties get compromised if the BNNTs are having defects. Point defects are very common in boron nitride nanotubes. This study presents the effect of defects on the mechanical properties of BNNTs with different chirality using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) and Visual Molecular Dynamics (VMD) software. The study would help to understand effects of defects in BNNTs when dispersed in polymer matrix composites for radiation shielding applications.

11:15 AM SF02.06.03
Acrylic Adhesive Contamination Testing and Mitigations for James Webb Space Telescope (JWST) and Roman Space Telescope (RST) Elaine Stewart[1], Eve Wooldridge[1], Alan Abeel[1] and Kelly Henderson-Nelson[2]; [1]NASA Goddard Space Flight Center, United States; [2]KBR, United States

Acrylic adhesive has been used as an alternative to silicone adhesives due to molecular contamination concerns causing degradation in infrared and UV wavelength ranges. Tape with Y966 adhesive is used to attach thermal blanketing to structures, wrap electrical cabling, and secure thermocouples and diodes. The James Webb Space Telescope (JWST) operates at Lagrange Point 2 (L2) at temperatures between -223. 15 to -243.15 °C for near and mid-infrared observations. Through initial thermal vacuum (TVAC) testing of ground support equipment at cryogenic temperatures for JWST, acrylic adhesive was found to become brittle, facture, and generate acrylic foreign object debris (FOD) and particles. Since the glass transition temperature is -40°C, missions operating at cold temperatures are at risk of adhesive contamination generated during cryogenic TVAC testing and on-orbit operations. Tests were conducted at Goddard Space Flight Center studying exposed adhesive in vacuum chambers. Black Kapton tape was found to be a more significant particle generator than regular Kapton tape. Mitigation techniques included cleaning and removing exposed or excess adhesive, proper cleaning of surfaces prior to application of tape, burnishing the tape to the surface, and securing it with tie wraps around beams and circular structures. Additionally, inspections and cleanings were conducted to ensure there was no adhesive in or near deployment mechanisms. The Roman Space Telescope (RST) will launch in late 2020 and operate also at L2. RST observes in the visible and infrared wavelengths but not cryogenic temperatures. Testing was conducted for RST at -60°C and no adhesive contamination was identified. Mission wavelengths and temperatures must be carefully considered when choosing acrylic over silicone tape adhesive to reduce the risk of contamination from this material during TVAC testing and on-orbit operations.

SYMPOSIUM

April 10 - April 25, 2023

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* Invited Paper
\+ Distinguished Invited

SESSION SF03.01: Thermal Materials—From Fundamentals to Applications
Session Chairs: Yee Kan Koh and Lucas Lindsay
Monday Morning, April 10, 2023
Moscone West, Level 3, Room 3009

8:00 AM SF03.01.01
Thermal Transport Across Dry and Wet Interfaces with Voids Husam Walwil and Yee Kan Koh; National University of Singapore, Singapore

Due to challenges to quantify nanometer-sized voids at the interfaces, the effects of voids to interfacial thermal transport is yet to be experimentally determined. In this talk, we present our recent experimental results of how nano-voids impact the thermal transport across wet and dry transferred interfaces. We first employ a picosecond acoustic technique to experimentally quantify void density at the interfaces. To verify our approach, we transfer Pd films unto a series of holey SiO_2 substrates, and compare the void densities derived from our approach to those derived from scanning electron microscope (SEM); a good agreement is achieved. We then prepare a series of interfaces of Pd films transferred unto Al_2O_3, Si and GaN substrates, by wet and dry transfers. We systematically reduce the void densities of the interfaces, from 90% to 40%, by annealing the samples at different temperatures and durations. We then measure thermal conductance of the interfaces by time-domain thermoreflectance (TDTR). We found that the measured thermal conductance is void-density-weighted average of the thermal conductance of the solid/solid contacts and thermal conductance through the voids. We found that for the wet transferred films, the voids are mostly filled with water and thus relatively large thermal conductance is achieved. Our results provide fundamental understanding on heat transport across imperfect interfaces with voids.

8:15 AM SF03.01.02
Observation of the Chiral Phonon Activated Spin Seebeck Effect Kyunghoon Kim[1], Eric Vetter[1], Liang Yan[2], Cong Yang[1], Ziqi Wang[1], Rui Sun[1], Andrew Comstock[1], Yu Yang[3], Xiao Li[3], Lifa Zhang[3], Jun Zhou[3], Wei You[2], Dali Sun[1] and Jun Liu[1]; [1]North Carolina State University, United States; [2]University of North Carolina at Chapel Hill, United States; [3]Nanjing Normal University, China

Utilization of the interaction between spin and heat currents is the central focus of the field of spin caloritronics. The recent emergence of chiral phonons possessing angular momentum arising from the broken symmetry of the lattice creates the potential for generating spin currents at room temperature in a non-magnetic material in response to a thermal gradient, precluding the need for a ferromagnetic contact. In this talk, we will show the observation of spin currents generated by chiral phonons in a two-dimensional layered hybrid organic-inorganic perovskite implanted with chiral cations when subjected to a thermal gradient. Identified by transient magneto-optical Kerr effect measurements, the generated spin current shows a strong dependence on the chirality of the film and external magnetic fields, of which the coefficient is orders of magnitude larger than that produced by the reported spin Seebeck effect. Our findings indicate the potential of chiral phonons for spin caloritronic applications and offer a new route toward spin generation in the absence of magnetic materials.

8:30 AM SF03.01.03
Oscillating Gadolinium Thermal Diode Using Temperature-Dependent Magnetic Forces Qing Zhu, Kaitlyn Zdrojewski, Lorenzo Castelli and Geoffrey Wehmeyer; Rice University, United States

High-performance thermal diodes would enable improved waste heat scavenging, thermal energy storage, and thermal management systems. Although prior work indicated that the temperature (T)-dependent magnetic response of ferromagnetic materials near the Curie temperature provides a potential mechanism for thermal rectification via thermally-induced mechanical oscillations, this mechanism has not been investigated in a macroscopic thermal device.
Here, we construct a centimeter-scale oscillating gadolinium thermal diode and measure steady-state thermal rectification ratios as large as 23 in air and 16 in vacuum. In the forward mode when the top surface is warmer than 26°C and the bottom surface is colder than 20°C, an unstable balance between gravitational forces and T-dependent magnetic forces causes a shuttle containing gadolinium to oscillate and transfer thermal energy. In the reverse mode, the shuttle does not oscillate and energy is transferred via parasitic conduction and radiation.
Our measurements show that the diode is durable over $>10^3$ oscillation cycles and can be used in thermal circuits to achieve rapid and asymmetric thermal regulation. In addition, thermal circuit modeling shows that the device can achieve half-wave thermal rectification with up to 50% of the ideal-diode performance. Thus, our experiments and models show that oscillating gadolinium thermal diodes can achieve large rectification ratios in a convenient geometry and tempearture range for applications in thermal management and control.

Reference: Q. Zhu, K. Zdrojewski, L. Castelli, G. Wehmeyer. Oscillating gadolinium thermal diode leveraging temperature-dependent magnetic forces. *Advanced Functional Materials,* 2206733 (2022).

8:45 AM SF03.01.04
GPU-Accelerated Simulations of Thermal Transport Using Machine Learning Force Fields Anders Johansson, Jennifer Coulter, Andrea Cepellotti and Boris Kozinsky; Harvard University, United States

Controlling thermal conductivities of materials is important for a wide range of applications, from thermoelectrics for clean energy generation to electronic devices and thermal barrier coatings. The thermal conductivity is commonly estimated using molecular dynamics simulations within the Green-Kubo formulation. This requires a force field that is both 1) an accurate estimate of the interatomic interactions and 2) fast enough to allow simulations with sufficiently large length and time scales. An accurate force field can also be used to accelerate the calculation of force constants for transport simulations via the Boltzmann transport equation.

In this work, we employ the Gaussian Process-based FLARE force field, which automatically learns the interactions of more complex materials than empirical force fields. The resulting model can then be mapped to a low-dimensional, computationally efficient model. Through GPU-acceleration with LAMMPS and the Kokkos library, we achieve excellent performance and obtain well-converged estimates for the thermal conductivity with Green-Kubo molecular dynamics. Our newly developed transport code, Phoebe, computes the thermal conductivity with force constants calculated by FLARE. The data efficiency of FLARE reduces the total number of DFT calculations required, and Phoebe has been highly optimized to solve the Boltzmann transport equation efficiently on GPUs using the Kokkos and cuSOLVER libraries.

9:00 AM SF03.01.05
Probing Coupled Electron-Phonon Transport at 2D Atomic Junctions Using Femtosecond Diffraction Thermometry Aditya Sood; Princeton University, United States

Van der Waals (vdW) layered 2D materials offer unique opportunities to create designer 3D solids with tailormade properties. To predict the emergent behaviors arising from heterostructure formation, it is necessary to understand how different degrees of freedom interact at individual atomic junctions. In particular, what is the role of lattice degrees of freedom (phonons) on electron transfer at vdw interfaces? Or more generally, how does electron-phonon coupling influence thermal transport across a heterojunction? Here, using a combination of femtosecond electron diffraction and ab initio theory, we uncover a new regime of coupled electron-phonon transport at vdW interfaces [1]. Our system of interest is a type-II heterojunction comprising vdW monolayers of WSe_2 and WS_2. Following selective photo-excitation of WSe_2, and using ultrafast electron diffraction as a probe, we measure surprisingly concurrent heating of both WSe_2 and WS_2 on a picosecond timescale. This corresponds to an *apparent* thermal boundary conductance that is >100x larger than that due to phonons alone. Using DFPT, we identify a fast channel, involving an electronic state hybridized across the heterostructure, enabling phonon-assisted interlayer transfer of photoexcited electrons. Phonons are emitted in both layers on femtosecond timescales via this channel, consistent with the simultaneous lattice heating observed experimentally. Taken together, our work indicates strong electron-phonon coupling via layer-hybridized electronic states – a novel route to control thermal transport across interfaces.

[1] A. Sood*, J. Haber*, J. Carlstrom, E. Peterson, E. Barre, J. Georgaras, A. Reid, X. Shen, M. Zajac, E. Regan, J. Yang, T. Taniguchi, K. Watanabe, F. Wang, X. Wang, J. B. Neaton, T. F. Heinz, A. M. Lindenberg, F. H. Jornada, A. Raja, "Bidirectional Phonon Emission in Two-Dimensional Heterostructures Triggered by Ultrafast Charge Transfer", *Nature Nanotechnology* (in press)

9:15 AM SF03.01.06
Liquid Heat Capacity From Instantaneous Normal Modes Ethan Meitz, Gerald J. Wang and Alan McGaughey; Carnegie Mellon University, United States

Liquid heat capacities fall below the Dulong-Petit limit, with a deviation that increases with increasing temperature. Existing nanoscale models for a liquid's heat capacity require fitting parameters and cannot explain how energy is partitioned across the liquid's degrees of freedom. Liquids pose a unique challenge because their molecules are not bound to lattice sites (like in a solid) and do not weakly interact (like in a gas). We hypothesize that deviations from the Dulong-Petit limit in liquids originate from anharmonicity in molecular interactions and present an approach for calculating a liquid's heat capacity that is based on its instantaneous normal modes (INMs) and explicitly includes anharmonicity.

Starting with a single anharmonic oscillator, we calculate its expected potential energy and its heat capacity. The results provide insight into how anharmonicity can either increase or decrease heat capacity compared to the Dulong-Petit limit. We then consider a simple monatomic liquid, whose dynamics can be decomposed into a set of coupled anharmonic oscillators. We propose an approach using INMs that decouples the system of anharmonic oscillators and allows us to treat them as single oscillators. The coefficients of the anharmonic terms in the potential energy for each oscillator can be calculated from atomic trajectories acquired in a molecular dynamics simulation. The contribution to heat capacity from each INM is then calculated independently. The modal contributions are summed to give the total heat capacity, which is compared to the heat capacity calculated from system-level energy fluctuations. This approach can be extended to molecular liquids and applied to predict the properties of novel liquid compositions and accelerate materials discovery.

9:30 AM SF03.01.07
A Cavity Optomechanical Platform for GHz Phonon Amplification via Anderson-Localized Optical Modes Pedro D. García Fernández; Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), Spain

We explore [1] Anderson-localized cavity optomechanics in a two-dimensional optomechanical platform: a waveguide etched in a suspended silicon membrane that incorporates a slotted line air defect. Inherent and unavoidable fabrication imperfections are adequate to induce sufficient backscattering to realize Anderson-localization of optical modes. The introduction of an air slot allows for a strong confinement of the electromagnetic field that is guided along the slot, and enhances the ability for light to couple to in-plane mechanical motion. The resulting tightly confined Anderson-localized modes can be driven to enable mechanical amplification and self-sustained phonon lasing via optomechanical back-action. We design the photonic and phononic band structures [2,3] to realize mechanical lasing up to 6.8 GHz that results from confinement of the mechanical mode. We confirm the existence of this mode through a combination of cavity optomechanical techniques and Brillouin light scattering spectroscopy. The role of disorder in cavity optomechanics has thus far been largely overlooked but our results show that disorder plays a crucial role, which in part can have a decisive impact on device functionality and in part opens perspectives for studies of multiple scattering and Anderson localization of bosonic excitations with parametric coupling to mechanical degrees of freedom.

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Omar Florez, Guillermo Arregui, Marcus Albrechtsen, Ryan C. Ng, Jordi Gomis-Bresco, Søren Stobbe, Clivia. M. Sotomayor-Torres, Pedro David García. Engineering nanoscale hypersonic phonon transport. Nature Nanotechnology 17, 947 (2022)
Guilhem Madiot, Ryan C Ng, Guillermo Arregui, Omar Florez, Marcus Albrechtsen, Søren Stobbe, Pedro D Garcia, Clivia M Sotomayor-Torres. Optomechanical generation of coherent GHz vibrations in a phononic waveguide. Preprint at https://arxiv.org/abs/2206.06913

9:45 AM SF03.01.08
Coupling Between Conduction and Near-Field Radiative Heat Transfer in Tip-Plane Geometry Chams Gharib Ali Barura, Philippe Ben-Abdallah and Riccardo Messina; Laboratoire Charles Fabry, CNRS, France

Two bodies at different temperature separated by a vacuum gap exchange an energy flux mediated by photons. This radiative heat flux is limited at large distance by the well-known Stefan-Boltzmann's law. Nevertheless, the development of fluctuational electrodynamics (thanks to the pioneering works of Rytov, Polder and van Hove) allowed to show that in the near field, i.e. at distances smaller than the thermal wavelength (some microns at ambient temperature), the flux can dramatically increase because of photon tunneling. Although this prediction has been confirmed in many experiments, some of them have observed deviations from theoretical results, both in near field and in extreme near field (nanometer and sub-nanometer range of distances). In this sense, one possibly relevant aspect could be the coupling between exchanged radiative flux and conduction. We have shown that in the configuration of two parallel slabs this coupling can induce a temperature profile in each body (neglected in most previous works) and induce, in turn, a saturation of the exchanged flux. This result was later generalized to the configuration of two nanorods, for which the different spectral behavior and the participation of volume modes of the field increases the exchanged flux and induces a non-linear temperature profile even in the diffusive regime. Finally, we present a recent work in which we addressed the coupling between two concentric cylinders of different radii, allowing us to simulate the configuration of a sharp tip in front of a planar substrate. We obtained analytical expressions for both the temperature profiles and the exchanged flux, showing that also in this scenario the conduction-radiation coupling can induce a significant temperature change in the smaller cylinder (the tip), up to tens of degrees in the case of polar materials, along with a strong reduction of the flux (of more than two orders of magnitude) with respect to the scenario of absence of coupling. Our results show that, with an appropriate choice of the materials and geometrical configuration, the effect of conduction-radiation coupling could be within experimental observability.

SESSION SF03.02: Nanoengineering for Energy and Electronics

Session Chairs: Yongjie Hu and Dimos Poulikakos
Monday Morning, April 10, 2023
Moscone West, Level 3, Room 3009

10:15 AM *SF03.02.01
Leveraging the Physics of Sunlight-Surface Interactions to Architecture Transparent Materials Preventing Fogging Dimos Poulikakos; ETH Zurich, Switzerland

Interfaces separating different kinds of matter, or different phases of the same matter, abandon in nature and technology. What is more, they invariably play a critical role in all systems where they occur, from regulating transport of energy and species, to dictating system shape and form. Interfaces differ in their structure and properties from the bulk matter they surround and can be engineered to effect remarkable outcomes in a broad palette of applications. Here, I will primarily focus on liquid/gas and liquid/solid interfaces and their interaction with sunlight, employed in the rational design of photothermal materials, to control atmospheric water condensation, according to our will (1-3). I will discuss the design and architecture of energy neutral photothermal metasurface coatings, which, when material transparency is required, prohibit condensation and resulting “fogging” of surfaces. These coatings function with selective sunlight absorption, which enables them to maintain surface transparency to visible light. The photothermal coatings are unprecedented in their thinness (less than 10 nm) and performance, absorbing about one third of the solar energy selectively, mostly in the near infrared range (3), where half of the energy of sunlight resides. They can be easily deposited also on deformable and soft materials and are fabricated with common industrial processes. These combined capabilities render them a perfect candidate for a host of applications such as eyewear, car windows and windshields, mirrors and building windows. Finally, I will discuss the surface architecting of transparent materials able to maintain transparency alone, in the case of most severe condensation conditions and vapor influx, such as in the direct neighborhood of boiling liquids (4). Again, such architectures can be readily fabricated and up-scaled via simple molding or roll-to-roll processes.

(1) Mitridis E., et al., ACS Nano, 2018, 12 (7), pp 7009–7017.
(2) Walker C., et al., Nano Lett., 2019, 19 (3), pp 1595–1604.
(3) Haehler at al,. Nature Nanotechnology, 2023, in press.
(4) Park. H. et al., in review.

10:45 AM SF03.02.03
Integration of Boron Arsenide with Gallium Nitride Devices for High-Performance Thermal Management Man Li, Joonsang Kang, Huan Wu, Huuduy Nguyen and Yongjie Hu; University of California, Los Angeles, United States

Thermal management is critical in modern electronic systems. Efforts to improve heat dissipation have led to the exploration of novel semiconductor materials with high thermal conductivity, including boron arsenide (BAs) and boron phosphide (BP). However, the integration of such materials into devices and the measurement of their interface energy transport remain unexplored. Here, we show that BAs and BP cooling substrates can be heterogeneously integrated with metals, a wide-bandgap semiconductor (gallium nitride, GaN) and high-electron-mobility transistor devices. GaN-on-BAs structures exhibit a high thermal boundary conductance of 250 MW/m^{2}K, and comparison of device-level hot-spot temperatures with length-dependent scaling (from 100 micrometer to 100 nanometer) shows that the power cooling performance of BAs exceeds that of reported diamond devices. Furthermore, operating AlGaN/GaN high-electron-mobility transistors with BAs cooling substrates exhibit substantially lower hot-spot temperatures than diamond and silicon carbide at the same transistor power density, illustrating their potential for use in the thermal management of radiofrequency electronics. We attribute the high thermal management performance of BAs and BP to their unique phonon band structures and interface matching.

11:00 AM SF03.02.04
Superdiffusive Thermal Transport in $Si_{0.4}Ge_{0.6}$ Thin Films Fengju Yao[1], Deyu Li[2], Hong Lu[3] and Dongyan Xu[1]; [1]The Chinese University of Hong Kong, Hong Kong; [2]Vanderbilt University, United States; [3]Nanjing University, China

Superdiffusive thermal transport represents a unique phenomenon in heat conduction, which is characterized by a size (L) dependence of thermal conductivity (κ) in the form of $\kappa \sim L^{\beta}$ with a constant β between 0 and 1. Although superdiffusive thermal transport has been theoretically predicted for SiGe alloys, direct experimental evidence is still lacking. Recently, we conducted a systematic experimental study of the thickness-dependent thermal conductivity of $Si_{0.4}Ge_{0.6}$ thin films grown by molecular beam epitaxy (MBE). The cross-plane thermal conductivity of $Si_{0.4}Ge_{0.6}$ thin films spanning a thickness range from 20 to 1120 nm was measured in the temperature range of 120-320 K *via* a differential three-omega method. Results show that the thermal conductivity follows a consistent $\kappa \sim t^{0.26}$ power law with the film thickness (t) at different temperatures, providing direct experimental evidence that alloy-scattering dominated thermal transport in SiGe is superdiffusive.

11:15 AM SF03.02.05
Nanoscale Laser Flash Measurements of Ballistic Heat Currents in AlN Heterostructures Samreen Khan[1], Wanyue Peng[1], John Wright[2], Yongjin Cho[2], Debdeep Jena[2], Huili G. Xing[2] and Richard Wilson[1]; [1]University of California, Riverside, United States; [2]Cornell University, United States

This study aims to understand the interplay of ballistic heat currents, interfacial phonon scattering, and mean-free-path distributions on heat conduction in AlN heterostructures. On submicron length-scales, theory predicts that heat transfer will be carried across an AlN heterostructure by a combination of ballistic and diffusive heat-currents [1,2]. The fraction of ballistic vs. diffusive heat currents is expected to depend the mean-free-path distribution of AlN and the frequency dependence of interfacial phonon scattering rates. Experimental metrologies like time-domain thermoreflectance and frequency-domain thermoreflectance cannot test such theoretical predictions because they struggle to differentiate ballistic vs. diffusive heat-currents. In this talk, we describe a new experimental approach that overcomes this challenge. Our approach relies on integrating an epitaxial buried heater layer into an AlN heterostructure during sample growth. We used MBE to grow an epitaxial 60nm-TiN/650nm-AlN/60nm-NbN tri-layer on sapphire. We then performed nanoscale laser flash measurements of heat conduction [3,4] across the AlN between 80 and 600 K. We monitor the time-evolution of the surface TiN layer’s temperature after ultrafast heating of the buried NbN layer. Energy carried ballistically traverses the AlN layer at the speed of sound, while energy transported diffusively arrives more slowly. By comparing our experimental data to theoretical simulations, we were able to quantify the importance of sub-continuum ballistic transport effects. At room temperature, we observe that approx. one quarter of the heat-current across the 650nm AlN layer is ballistic. Our experimental study improves fundamental understanding of how heat evolves as a function of time and space in sub-continuum heat transfer problems, and improves understanding of the frequency-dependence of interfacial phonon scattering.

Acknowledgement: This work was supported as part of ULTRA, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0021230.

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11:30 AM SF03.02.06

Interfacial Bonding and Thermal Conductivity in Polymer-Glass Nanocomposites with Ultra-High Interfacial Density David W. Collinson[1], Yang Wang[1], Heungdong Kwon[1], Robert D. Miller[1], Krystelle Lionti[2], Kenneth E. Goodson[1] and Reinhold H. Dauskardt[1]; [1]Stanford University, United States; [2]IBM Almaden Research Center, United States

Manipulating and controlling heat flow across the interface between two materials is a significant issue for modern devices and materials where the small length scales result in a high density of interfaces that dominate the effective thermal conductivity (*k*). To control nanoscale heat transport between dissimilar materials, a deeper understanding of how the underlying chemistry and interfacial structure manipulates the thermal boundary conductance (TBC) of the interface is required. While many experimental techniques have been described for studying thermal transport in thin films, and specifically polymer nanocomposites, there is a lack of experimental investigations that can directly link the interfacial bonding to the resulting TBC between amorphous materials. The dearth of experimental data is caused by poor TBC measurement sensitivity in the case of the single interface in a substrate-supported polymer thin film structure due to the low polymer intrinsic thermal conductivity and due to the complexity of the analysis in the case of particle-polymer nanocomposites with high interfacial density. Separately, particle-based nanocomposites tend to have an unstable structure as the relative strength of particle-particle and particle-polymer interactions determines the dispersion of particles throughout the nanocomposite. As a result, changes in the TBC of the particle-polymer interfaces in the nanocomposite becomes highly convoluted with changes to the particle dispersion and particle-particle contact.

In this study, we show that the thermal conductivity of a polymer-glass nanocomposite with polymer molecules under nanometer scale confinement in an organosilicate matrix can be characterized using time-domain thermoreflectance spectroscopy. The thermal conductivity characterization is made possible by the ultra-high internal interfacial density and can be further quantitatively linked to the nature of the organosilicate matrix surface chemistry. The TBC at the polymer-organosilicate interface is extracted by comparing the measured thermal conductivity with effective medium and numerical model calculations. Fourier transform infra-red spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to characterize the hydrogen bonding between the polymer molecules and organosilicate matrix. Thin-film fracture measurements were used to quantify the molecular polymer bridging contribution to the cohesive fracture resistance and its dependance on interfacial bonding. This new experimental metrology provides a direct experimental link between thermal and mechanical properties and the nature of interfacial bonding between polymer molecules and surfaces.

SESSION SF03.03: Theory I: Coupled and Correlated Thermal Transport
Session Chairs: Ming Hu and Yongjie Hu
Tuesday Morning, April 11, 2023
Marriott Marquis, B2 Level, Golden Gate A

10:30 AM *SF03.03.01

***Ab Initio* Studies of Coupled Electron-Phonon Transport and Drag Enhanced Thermopower** David Broido[1], Chunhua Li[1], Nakib H. Protik[2], Pablo Ordejón[3] and Miguel Pruneda[3]; [1]Boston College, United States; [2]Humboldt-Universität zu Berlin, Germany; [3]Catalan Institute of Nanoscience and Nanotechnology, Spain

In doped semiconductors and metals under an applied electric field or temperature gradient, momentum transfer between charge carriers and phonons through electron-phonon interactions boosts the thermoelectric power, a phenomenon known as electron-phonon drag [1, 2]. Using a recently-developed first principles approach to solve the coupled electron and phonon Boltzmann transport equations [3], we have examined the thermoelectric transport coefficients (electrical conductivity, Seebeck and Peltier thermopowers, and electronic and phonon thermal conductivities) in doped semiconductors. Excellent agreement is obtained with the measured thermopower of Si across a wide range of charge carrier densities and extending to the strong drag regime at low temperatures. Enormous enhancements to the thermopower, *S*, and thermoelectric power factor, *PF*, of lightly doped diamond are revealed [4]: Around 100 K, *S* and *PF* values of around 100,000 $\mu V\ K^{-1}$ and 7000 $\mu W\ K^{-2}\ cm^{-1}$, respectively, are achieved. These values are much larger than the corresponding previously reported record measured values in the correlated metal, $FeSb_2$, and they also occur at significantly higher temperatures. The remarkable behavior stems from exceptionally weak anharmonic phonon decay at low *T* that minimizes dissipation of the phonon current, a feature that also gives large thermal conductivity thereby preventing diamond from being a useful thermoelectric material, and even when accounting for phonon frequency filtering [5].

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11:00 AM *SF03.03.02

Novel Vistas in Thermal Transport: Relaxons, Viscosities and Coherences Nicola Marzari[1,2]; [1]EPFL, Switzerland; [2]Paul Scherrer Institute, Switzerland

First, we examine the emergence of correlated transport phenomena in systems described by the linearized Boltzmann transport equation (LBTE), with examples centered around heat transport. We show how phonons are only a high-temperature approximation to the exact carriers, that we term relaxons, and that the thermal conductivity can be mapped exactly into a kinetic theory of the relaxon gas. We also calculate the viscosity of this gas, and coarse-grain the LBTE into coupled viscous equations that describe the hydrodynamic regime of heat propagation. Then, we discuss thermal transport in materials with low conductivity (thermoelectrics, thermal barrier coatings, glasses), highlighting the importance of a broader formulation - in the form of a Wigner transport equation - that includes also the tunnelling of phonon wavepackets.

11:30 AM SF03.03.03
Anomalous Thermoelectric Transport Phenomena from Interband Electron-Phonon Scattering Boris Kozinsky[1,2], Natalya Fedorova[1], Andrea Cepellotti[1], Jackson Weaver[1] and Jennifer Coulter[1]; [1]Harvard University, United States; [2]Bosch Research, United States

The Seebeck coefficient and electrical conductivity are two central quantities to be optimized simultaneously in designing thermoelectric materials, and they are determined by the dynamics of carrier scattering [1]. We uncover a new regime where the presence of multiple electron bands with different effective masses, crossing near the Fermi level, leads to strongly energy-dependent carrier lifetimes due to intrinsic electron-phonon scattering. In this anomalous regime, electrical conductivity decreases with carrier concentration, Seebeck coefficient reverses sign even at high doping, and power factor exhibits an unusual second peak [2]. We explain the origin and magnitude of this effect using a general simplified model as well as first-principles Boltzmann transport calculations in recently discovered half-Heusler alloys. We identify general design rules for using this paradigm to engineer enhanced performance in thermoelectric materials. We performed detailed first-principles electron-phonon transport calculations for several candidate materials to investigate the potential for increased thermoelectric performance based on this light-heavy band mechanism.
[1] B. Kozinsky, D. J. Singh, *"Thermoelectrics by Computational Design: Progress and Opportunities"*, Annual Reviews of Materials Research, 51, 565 (2021)
[2] N. Fedorova, A. Cepellotti, B. Kozinsky, *"Anomalous thermoelectric transport phenomena from interband electron-phonon scattering"*, Adv. Func. Mater., 32, 2111354 (2022)

11:45 AM SF03.03.04
Million-Scale Atomic Data Integrated Deep Learning for Predicting Thermal Transport Properties of 100,000 Structures Ming Hu; University of South Carolina, United States

Existing machine learning potentials for predicting phonon properties of crystals are limited to either small amount of training data or a material-to-material basis, primarily due to the exponential scaling of model parameters with the number of atomic species or elements. This renders high-throughput infeasible when facing large-scale new materials. Unlike previous machine learning models with inherently limited training on small data and global properties, we develop Elemental Spatial Density Neural Network Force Field (Elemental-SDNNFF) with abundant atomic level environments as training data. Benefiting from this innovation, we integrate ~30 million atomic data to train a single deep neural network without increased expensive ab initio simulations. The effectiveness and precision of the Elemental-SDNNFF approach is demonstrated on a set of ~100,000 inorganic crystals spanning 63 elements in the periodic table by prediction of complete phonon properties. Our algorithm achieved a competitive force root mean square error of less than 10 meV/Å and a speed-up of 3 – 4 orders of magnitude in comparison to first principles. Self-improvement schemes such as active learning and data augmentation techniques are also incorporated allowing human-free refinement of the force accuracy on arbitrary combinations of chemistries. As case studies of our predicted phonon properties, deep insight into the ultralow lattice thermal conductivity (<1 W/mK) of predicted structures are gained by p-d orbital hybridization analysis and charting the thermal conductivity data in the bonding-antibonding map, which offers a quick approach for future screening of crystals with strong intrinsic phonon anharmonicity. Our algorithm is promising for accelerating discovery of novel phononic crystals for emerging applications, such as heat dissipation in electronics, thermoelectrics, and coherent phonons for quantum information technology.

12:00 PM SF03.03.05
Efficient Calculation of Nanoscale Thermal Conductivity Using Equilibrium Monte Carlo Simulations That Bridge the Boltzmann Transport Equation and the Green-Kubo Formalism S Aria Hosseini[1], Alathea E. Davies[2], Laura de Sousa Oliveira[2], Jackson R. Harter[3], Giuseppe Romano[1] and Alex Greaney[4]; [1]Massachusetts Institute of Technology, United States; [2]University of Wyoming, United States; [3]Idaho National Laboratory, United States; [4]University of California, Riverside, United States

We present a novel approach for computing phonon mediated thermal conductivity in nanoscale systems using Monte Carlo simulations of the system at equilibrium. In this approach the thermal conductivity is computed from the autocorrelation function of the equilibrium heat current fluctuations using the Green-Kubo (GK) method. We show that the heat current autocorrelation function can be constructed from the average of the autocorrelation function of individual phonons, making convergence of its calculation very efficient. The approach has the advantage that, being at equilibrium, it does not require convergence of the temperature at every point in the simulation domain and thus the equilibrium approach can be significantly less computationally intensive than traditional non-equilibrium Monte Carlo simulations. We further show that the theoretical framework underpinning this work can be used to derive the analytic expressions for the thermal conductivity in a thin slab that comes from solving the Boltzmann transport equation (BTE), providing a bridge between the BTE and the GK approaches. However, our stochastic model can also be used to obtain analytic predictions for the thermal conductivity in other geometries, and helps us to understand transport through systems with two different and orthogonal characteristic length scales.

12:15 PM SF03.03.06
Heat Transfer Modelling in the Crossover Regime Between Conduction and Radiation Mauricio Gómez Viloria, Philippe Ben-Abdallah and Riccardo Messina; Laboratoire Charles Fabry, France

Fluctuational electrodynamics (FED) theory describes the near field radiative heat transfer for separation distances below the thermal wavelength (some microns at ambient temperature), where the heat flow between two solids at different temperatures can exceed the far field limit by several orders of magnitude, in particular when the bodies exchanging heat support surface resonant modes, such as surface phonon-polaritons or surface plasmons.
At even smaller distances, in the so-called extreme near field (distances in the nanometer range and below) the physics is expected to change radically. Interestingly, two recent scanning thermal microscopy (SThM) experiments, approaching gold tips to gold substrates, reach apparently opposite conclusions. While one of them shows large deviations from FED for separation distances of few nanometers, another experiment shows no deviations from FED even at sub-nanometer gaps, where acoustic phonons and electrons are expected to contribute as further channels to the heat exchange.

Here we introduce a theoretical framework to investigate the heat transfer mediated by photons, phonons and electrons between two metallic bodies. We quantify the role of electron tunnelling currents by paying attention to the role played by the shape of the electronic barrier in the presence of electron-electron screening interactions. Using an approach based on the elastic theory, we address the role of acoustic phonons coupled through the Van der Waals and the electrostatic forces. Finally, we employ FED to study the role played by photons, by taking into account the contribution of non-local effects. This theoretical work allows us to outline the relative weight of the different carriers with respect to the separation distance, and to highlight the crucial role played by the external bias voltage on the heat flux carried by the three types of carriers.

SESSION SF03.04: Thermal Properties of Materials

Session Chairs: Jeffrey Grossman and Vinod Tewary
Tuesday Afternoon, April 11, 2023
Marriott Marquis, B2 Level, Golden Gate A

1:30 PM *SF03.04.01
Passive Sub-Ambient Cooling with an Evaporation-Insulation Bilayer Jeffrey C. Grossman; MIT, United States

Passive evaporative cooling, which does not rely on electricity, shows promise to alleviate the ever-increasing global cooling needs but has been largely limited by environmental heating. Once sub-ambient temperatures are reached, the environmental heat gain accelerates the dry-out of evaporative materials, which is also detrimental to the cooling performance. Here, we address this critical challenge with an evaporation-insulation cooling design based on hydrogels and aerogels, inspired by the fur layer on the sweating skins of desert animals. Our transparent bilayer structure relies on water evaporation from hydrogels through highly porous aerogels for heat removal. At the same time, the low thermal conductivity of aerogels minimizes the parasitic heat gain. We establish a comprehensive model for heat and mass transfer in the system, which shows good agreement with our experimental data. We demonstrate that the addition of the porous insulation layer allows for optimization between the temperature drop from the ambient and the effective cooling time. Our bilayer structure can extend the lifetime of the cooling package by 400% compared to the conventional single-layer design. We further identify the relationship between the performance metrics and material properties of the insulation layer and provide design guidelines for various cooling applications including thermal regulation of food, pharmaceuticals, and buildings.

2:00 PM SF03.04.02
***Ab Initio* Determination of New Ultrahigh Thermal Conductivity Materials** Huan Wu, Hang Fan, Man Li and Yongjie Hu; University of California, Los Angeles, United States

Discovering new materials with ultrahigh thermal conductivity has been a critical research frontier and driven by many important technological applications ranging from thermal management to energy science. Conventional materials with ultrahigh thermal conductivity are prototyped by single-element materials, i.e., diamond. Binary compounds such as boron arsenide has been predicted to have ultrahigh thermal conductivity based on first-principles calculations, and later on experimentally verified to show thermal conductivity at 1300 W/mK, as a record high beyond common semiconductors. Now the question is whether such an HTC can exist in even complicated crystal structure, perhaps ternary compounds, which has not yet been explored. Here we have rigorously investigated the fundamental lattice vibrational spectra in ternary compounds and determined groups is systematically quantified with different crystal structures and high order anharmonicity involving the thermal conductivity using a predictive *ab initio* approach. Phonon transport in B-X-C (X = N, P, As) four-phonon process. Our calculation found an ultrahigh room-temperature thermal conductivity through strong carbon-carbon bonding up to 2100 W/mK beyond most common materials and the recently discovered boron arsenide. This study provides fundamental insight into the atomistic design of thermal conductivity and opens opportunities in new materials searching towards complicated compound structures.
References:
[1] Huan Wu, Hang Fan, and Yongjie Hu. *Ab initio* determination of ultrahigh thermal conductivity in ternary compounds. *Physical Review B* **103**, L041203 (2021).
[2] Hang Fan, Huan Wu, Lucas Lindsay and Yongjie Hu. *Ab initio* investigation of single-layer high thermal conductivity boron compounds. *Physical Review B* **100**, 085420 (2019).

2:15 PM SF03.04.03
Finding Locons is a CINCH: Classifying and Identifying Normal Modes using Convex Hulls Daniel Xiao, Ethan Meitz, Gerald J. Wang and Alan McGaughey; Carnegie Mellon University, United States

We propose a new methodology for quantifying the spatial localization of the collective atomic vibrations (i.e., normal modes) in a disordered material. The normal modes can be classified into three categories: propagons (non-localized, propagating), diffusons (non-localized, non-propagating), and locons (localized, non-propagating). It is important to classify the normal modes because each type makes a different contribution to thermal conductivity. A failure to account for non-propagating modes is why the phonon gas model cannot describe thermal transport in amorphous solids.
Reliably identifying propagons, diffusons, and locons remains an open challenge. Here, we focus on the distinction between localized and non-localized modes. The standard method for quantifying localization is through the mode participation ratio (PR), which reflects how many atoms participate in a given mode. The PR ranges between 1/N (fully localized) and 1 (fully delocalized), where N is the number of atoms in the system. Localization is specified by placing an arbitrary cutoff on the PR and any modes with PRs below this cutoff are considered localized. This methodology, however, has a significant shortcoming: the PR contains no spatial information. For example, the PR for a mode with only two participating atoms does not depend on the relative positions of the two atoms. Such a mode may be *constrained* to two atoms, but is not necessarily *localized*.
Our new method works as follows. We construct a set of convex hulls for each normal mode, starting with the four atoms with the largest participation. Atoms are then added in the order of highest to lowest participation. At each step, the volume of the convex hull and the PR of the contained atoms are calculated. By considering the entire convex hull expansion process, we can describe how much volume is needed to reach a given PR. The algorithm is applied to amorphous silicon and silica systems of various sizes. Strongly localized modes have a steep initial slope of PR versus number of atoms before saturating, indicating that they approach their total PR at small volume. Non-localized modes approach the total PR linearly with volume. This method is easy to apply to a set of normal modes obtained from a lattice dynamics calculation and provides a quantitative parameter that accurately classifies their localization.

2:30 PM SF03.04.04
Causal Green's Function Method for Simulating Nanoscale Heat Transport Vinod K. Tewary and Edward J. Garboczi; National Institute of Standards and Technology, United States

Heat management in semiconductor devices at nanoscale is a subject of strong topical interest. It requires materials of high as well low thermal

conductivities and involves phonons of a wide frequency range. Robust mathematical tools are needed for simulation at the nano length scales, that are comparable to or even less than the phonon mean free path. At these scales, the continuum theory is not valid, and a fully discrete lattice or multiscale simulation must be carried out.
In addition to the length scales, simulation at multiple time scales is also a challenging problem. The conventional molecular dynamics (MD) is usually limited to a very small temporal range for reasonable convergence. In practice, the integration of the temporal part of the MD equations needs the integration interval to be less than a few femto seconds, whereas the physical processes of interest require simulation up to nanoseconds or even microseconds. This requires at least a few million temporal iterations, may be closer to 100 million iterations. That is computationally too expensive. Various schemes for accelerating the MD are available in the literature but much more is needed for the proper simulation of nanoscale heat transport.
We show that the use of causal Green's function (GF) in MD can accelerate its temporal convergence by several orders of magnitude. To see this, we recall that in MD, at every time step, we expand the potential energy of the system to first order in atomic displacements and then use the linear Newtonian solution to calculate the atomic displacements at the end of that time interval. The process is continued iteratively until the displacements converge. The process of iteration effectively accounts for the nonlinear terms in the potential. Attempts to improve upon the temporal convergence consist of better solution of the temporal part of the MD.
We approach the problem by a totally different technique. We expand the potential energy up to quadratic terms in displacements and not just linear terms as in MD. It would appear at first sight that the quadratic terms would make the solution of the temporal problem more difficult. We show that the temporal equations can still be solved exactly by using the GF. To ensure causality, we use the retarded GF, for which we use the Laplace transform. We show that the Laplace as well as inverse Laplace transforms are obtained analytically.
Cubic and higher order terms in the potential are accounted through MD type iterations, but the advantage is that much fewer iterations are needed and the time interval can be much larger. We show in certain idealized test cases that the temporal convergence can be improved by 7-8 orders of magnitude. Physically, the improvement is significant for phonons and elastic properties materials because the phonons' characteristics of a material are determined by the quandratic terms in the potential. Our GF technique includes the phonon terms exactly, whereas the MD accounts for these term only through computaionally expensive iterations.
We will illustrate our causal GF technique by applying it to real 2D solids of contemporary interest such as graphene or silicene. This will bring out the important characteristics of the nanoscale heat transport such as the size effect, non-Fourier heat conduction and show the power of the causal GF technique for simulating nanoscale heat transport.

2:45 PM *SF03.04.05
Thermal Properties of Complex Semiconductors G. J. Snyder; Northwestern University, United States

Thermal transport in complex semiconductors is often analyzed using the phonon gas model including several scattering terms [1]. Experimentally it is hard to uniquely determine which scattering mechanisms are truly dominating. Combining experiment and theory can elucidate the contributing effects that can help engineer thermal conductivity in complex materials. For example, dislocation scattering now appears to be an important mechanism in thermoelectric materials and may even have been overlooked as the primary mechanism for scattering of grain boundaries as evidenced by the temperature dependence of thermal conductivity at low temperature being closer to *T2* experimentally rather than the *T3* traditionally expected for boundary scattering. In addition to scattering, phonon soften can also be important to achieve very low thermal conductivity. Ultra-low thermal conductivity in solids appears to be dominated by diffusions rather than wave like phonons which suggests a better understanding of diffusion heat transport is needed to further engineer low thermal conductivity materials. A reexamination of the traditional phonon gas model with the rigid distinction between harmonic and anharmonic contributions may also be needed as there appears to be a harmonic contribution to thermal expansion which is often assumed to only arise from anharmonic terms that appears to be connected to gas-like phonon pressure. Strategies to find materials with low phonon speed and high scattering rates can be used to engineer good thermoelectrics but also thermal barrier coatings and high power electronics.

[1] Hanus et al, Applied Physics Reviews 8, 031311 (2021); https://doi.org/10.1063/5.0055593

SESSION SF03.05: Nanoscale and Non-Equilibrium Thermal Transport
Session Chairs: Thomas Beechem and Sebastian Volz
Tuesday Afternoon, April 11, 2023
Marriott Marquis, B2 Level, Golden Gate A

3:30 PM *SF03.05.01
Spatial and Frequency-Domain Multiplexing Approaches to Thermal Property Mapping in 2D and 3D Chris Dames[1,2]; [1]Univ of California-Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Thermal property mapping in 2D and 3D has diverse applications, from identifying buried voids to property screening for combinatorial materials development. Here I will describe two efforts in this regard, which are respectively based on the superposition of multiple heat forcings in space (i.e., multiple heating pixels in x,y) and in frequency (multiple heating frequencies, omega). First, we are developing the next generation of an all-optical "structured illumination, thermal imaging" (SITI) method [Q. Zheng et al., Appl. Phys. Rev. 9, 021411 (2022)] for spatially-multiplexed thermal measurements, here with simpler hardware, a larger field of view, and new algorithms for extracting the property map. Second, the thermal property variation as a function of depth into a sample (z direction) can be probed by varying the frequency of a periodic surface heat source and thus its thermal penetration depth. While this can be done by sequentially sweeping the frequency of a pure sinusoidal excitation, a more information-dense approach is to simultaneously apply multiple sinusoids of several different frequencies and study the superposed system response. To demonstrate the latter scheme we developed an electrothermal "3-omega" apparatus using a fine wire suspended horizontally in a shallow oil bath, which measured the depth of the oil with accuracy around ±18 microns [W. Hodges et al., Rev. Sci. Instrum. 90, 094903 (2019)]. A common theme across both studies is the need to condition the property fitting by thoughtfully incorporating prior knowledge about the allowed variabilities of the unknown thermal property field.

4:00 PM *SF03.05.02
SuperPlanckian Far-Field Phonon-Polaritons Sebastian Volz; CNRS, France

S. Volz
Laboratory for Integrated Micro Mechatronic Systems, CNRS-IIS,
The University of Tokyo, Tokyo 153-8505, Japan

Recent studies showed that surface phonon-polaritons, i.e. evanescent electromagnetic waves propagating along the surface of polar dielectric materials [1] [2], may potentially serve as novel heat carriers to enhance the thermal performance in micro- and nanoscale devices.
We will expose the significant contribution of these carriers to thermal conductivity in ultra-thin (<100nm) films [3], but also to radiation, yielding SuperPlanckian emission and absorption between surfaces of larger scales (10mm).

References

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[2]J. Ordonez-Miranda, L. Tranchant, T. Tokunaga, B. Kim, B Palpant, Y. Chalopin, T. Antoni, and S. Volz, J. Appl. Phys. **113**, 084311 (2013).
[3] Y. Wu, J. Ordonez-Miranda, S. Gluchko, R. Anufriev, D. De Sousa Meneses, L. Del Campo, S. Volz, and M. Nomura, Science Advances 6(40):eabb4461, (2020).

4:30 PM *SF03.05.03
Thermal Transport in Amorphous Materials with *Ab Initio* Machine Learning Potentials Davide Donadio[1], Zekun Chen[1], Giuseppe Barbalinardo[1], Alfredo Fiorentino[2] and Stefano Baroni[2]; [1]Univ of California-Davis, United States; [2]Scuola Internazionale Superiore Studi Avanzati, Italy

Glassy materials are found ubiquitously in nature and are essential components in technological applications. Their thermal conductivity controls heat flows from planetary-level macroscales down to the microscale of electronic components. While lattice thermal conduction in crystals has been extensively studied, much less is known about the relation between structural properties and heat transport in glasses.
Here we exploit the recently developed quasi-harmonic Green-Kubo approach based on lattice dynamics to investigate heat conduction in two systems of broad interest at both the fundamental and the applicational level: diamond-like carbon and amorphous ice. Both systems exhibit structural transitions as a function of the vitrification conditions. In the case of amorphous ice, there are at least two forms separated by a first-order phase transition. Using machine learning potentials trained on ab initio density functional theory datasets enables accuracy and transferability over the broad range of local structures encountered in these materials and allows us to probe vitrification at various thermodynamic conditions.
Through our lattice dynamics approach, we sort out the structural features that lead to vibrational modes diffusion and localization, which modulate the nature and the magnitude of heat conduction in the different forms of glassy carbon and amorphous ice.

5:00 PM SF03.05.04
Identifying Materials for Ultrathin Conduction via Polaritonic Thermal Transport Jacob Minyard and Thomas Beechem; Purdue University, United States

Microelectronics no longer gain efficiency as they are made smaller. Dennard scaling is dead. With every uptick in clock speed or node size reduction, heat load increases. Balancing the thermal budget necessitates dissipating these continually increasing heat loads. It hasn't happened. As a result, heating now limits performance, shortens lifetimes and requires that up to ≈ 50% of an integrated circuit is turned off, or dark, at any given time. Improving computing requires not just smaller, more capable, devices but more capable methods of moving heat at extremely small scales.

The most obvious solution points to merely utilizing higher thermal conductivity materials. Along these lines, the development of high thermal conductivity synthetic diamond and BAs have been successful. While attractive for larger power electronics (> 1 μm), their utility is limited at the < 100 nm sizes characteristic of Si-based devices. This is a consequence of phonon physics—and thus endemic to materials in general—and therefore not a defect that can be "fixed."

Thermal conductivity increases when phonons move further at higher speeds. As the size of a material decreases, phonons are effectively fenced in. They scatter off the closely spaced boundaries reducing thermal conductivity. Circumventing this so-called size-effect in the thermal conductivity requires a means of either increasing the speed of the heat carriers or in some way making them less sensitive to material boundaries.

Polaritons–quasiparticles created by the hybridization (i.e., mix) of photons and material dipoles—can do both. Their photonic character provides a path to heat transfer closer to that of the speed of light than of sound. Polaritons also localize at material boundaries and therefore skate along interfaces rather than crashing into them. Recognizing these facts, we compare the potential of several dielectrics for moving heat in extremely thin films (t<100 nm) via polartonic transport and compare their utility relative to standard phonon-based conduction. Using established analytical expressions for deriving polaritonic dispersion in conjunction with kinetic theory of polariton transport, a material map is derived linking optical properties with potential for thermal transport in ultrathin films.

SESSION SF03.06: Poster Session I
Session Chairs: Yongjie Hu and Lucas Lindsay
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SF03.06.01
Enhanced Near-Field Radiative Heat Transfer Between Planar Membranes Thinner Than the Vacuum Gap Spacing—Theory Livia Correa[1], Lei Tang[2], Chris Dames[2] and Mathieu Francoeur[1]; [1]University of Utah, United States; [2]University of California, Berkeley, United States

It is well-known that near-field radiative heat transfer (NFRHT) between two flat surfaces surpasses the blackbody limit owing to the tunneling of evanescent electromagnetic waves (e.g., Song et al., *Nature Nanotechnology* 11, 509-514, 2016; DeSutter et al., *Nature Nanotechnology* 14, 751-755, 2019; Tang et al., *ACS Photonics* 7, 1304-1311, 2020). Modeling of NFRHT in layered media relies on an exact solution valid for infinite surfaces, such that NFRHT between surfaces facing laterally smaller than the vacuum gap spacing has never been investigated. We recently developed the discrete system Green's function (DSGF) method (Walter et al., arXiv:2204.05399, 2022), which is a numerically exact framework based on fluctuational electrodynamics. The DSGF can accommodate arbitrary geometries since thermal sources are discretized into cubic subvolumes electromagnetically related to each other via a system Green's function. In this work, we analyze for the first time the impact of surface size on NFRHT. Specifically, we calculate NFRHT between two planar silicon carbide (SiC) membranes thinner than their vacuum gap spacing using the DSGF. The results show that the radiative heat transfer coefficient in the near field exceeds the predictions for two infinite surfaces when the membrane thickness to vacuum gap spacing ratio is approximately equal to or smaller than 6. For a fixed vacuum gap spacing of 100 nm, the radiative heat transfer coefficient between two 600-nm-thick SiC membranes is 165 W/m^2-K, which slightly exceeds the infinite surface predictions of 151 W/m^2-K. For 100-nm- and 10-nm-thick membranes, the radiative heat transfer coefficients are respectively 274 W/m^2-K and 1511 W/m^2-K. These are substantial enhancement of ~1.8 and ~10 with respect to the infinite surface case. We hypothesize that the enhancement is mediated by surface phonon-polaritons localized at the edges of the membranes. These localized surface phonon-polaritons are always present, but dominate NFRHT only when at least one dimension of the surfaces is smaller than the vacuum gap spacing. Furthermore, the DSGF predictions are in good agreement with experiments performed between two coplanar SiC membranes characterized by thickness and gap spacing smaller than respectively 100 nm and 500 nm. The additional enhancement of NFRHT between thin membranes may find application in energy conversion and non-contact cooling.

5:00 PM SF03.06.02
Radiative Thermal Diode Enabled by Guided-Modes of Surface Phonon-Polaritons in Silicon-Silica Heterostructures Byunggi Kim[1], Saeko Tachikawa[2], Laurent Jalabert[1,1], Jose Ordonez-Miranda[1,1], Maelie Coral[1,3], Yunhui Wu[1], Roman Anufriev[1], Sebastian Volz[1,1] and Masahiro Nomura[1]; [1]The University of Tokyo, Japan; [2]University of Basel, Switzerland; [3]Université PSL, France

A thermal diode enables the rectification of the heat flow depending on the temperature gradient, thereby playing a key role in directional thermal management. For radiative heat transport, a near-field thermal diode has been realized using materials with temperature-dependent thermophysical properties. Recently, Thomson et al. demonstrated that the Planck's black body limit can be overcome by two orders of magnitude in the far-field regime between two nanoscale membranes (Nature 561 (2018)). For membranes with thickness significantly smaller than radiation wavelengths, out-of-plane Poynting flows are greatly suppressed by guided modes. The same team showed active switching of heat flow via guided far-field radiation (Nature Nanotechnology 15, 99–104 (2020)), which hints the route for controlled far-field heat transfer. However, no experimental demonstration has yet been presented for the thermal rectification in the far-field regime. Here, we provide the experimental evidence of a far-field thermal diode using a silicon (Si)-silica (SiO$_2$) heterostructure in which guided resonant modes can be excited by the hybridization of optical phonons and photons, namely Surface Phonon-Polaritons (SPhPs).

In this study, we designed a SiO$_2$/Si/SiO$_2$ layered structure to observe the SPhP-guided radiation. We deposited 60-nm-thick SiO$_2$ layers on a 10-um-thick single-crystalline Si micromembrane. The thin SiO$_2$ layers activate SPhP-guided modes inside the Si micromembrane, which is transparent in most of the spectral range of the infrared radiation. We conducted the 3-omega measurement to obtain the gap thermal conductance between the SiO$_2$/Si/SiO$_2$-layered structure and the pristine silicon membrane. The gap size was 10 um, which satisfies the far-field criteria. We show that the gap thermal conductance from the pristine silicon to the layered structures ($G_{forward}$) is breaking the black-body limit and is three times larger than the flux in the opposite direction ($G_{backward}$), thereby showing that the rectification factor, $R = (G_{forward}-G_{backward})/G_{forward}$, is over 0.7 for temperatures ranging from 300 K to 500 K. In this temperature range, the rectification factor is outperforming the existing experimental results of the thermal diodes based on near-field heat transfer (ACS Nano 12, 6, 5774-5779 (2018)) and thermal conduction (Nano Energy 78, 105261 (2020)). We analytically derived the dispersion relation of the SiO$_2$/Si/SiO$_2$-layered structure, and calculated the in-plane Poynting flows considering the multiple branches of the SPhP-guided modes. The mid-infrared photons could be guided inside the SiO$_2$/Si/SiO$_2$-layered structure, to enhance absorption of the oblique modes generated from the pristine Si micromembrane. On the other hand, the pristine Si membrane does not absorb the SPhP-guided radiations from the SiO$_2$/Si/SiO$_2$-layered structure, which leads to the experimentally observed asymmetry of the gap thermal conductance.

In conclusion, we experimentally showed thermal rectification using a heterostructure based on a SiO$_2$ thin film and a Si micromembrane. The theoretical model attributes the diode effect to the absorption mediated by the SPhP-guided modes. Our study is the first experimental demonstration of a far-field thermal diode with a significant rectification factor larger than 0.7. Furthermore, the Si micromembrane-based design ensures incorporation in integrated circuits with better mechanical stability than sub-micron scale membrane devices. We believe that our results pave a reliable way for the control and functionalization of thermal radiation in the applications of radiative cooling and thermal circuits.

5:00 PM SF03.06.03
Impact of Molecular Weight of Conjugated Polymers on Molecular Doping Efficiency, Electrical Conductivity and Resulting Thermoelectric Performances Bomi Kim[1], Sang Eun Yoon[2], Jong Hyun Kim[2] and BongSoo Kim[1]; [1]Ulsan National Institute of Science & Technology (UNIST), Korea (the Republic of); [2]Ajou University, Korea (the Republic of)

In this study, we investigated the effect of molecular weight of a series of conjugated polymers (CPs) on the doping efficiency, electrical conductivity, and related thermoelectric properties of doped CPs. Low (L), medium (M), and high (H) molecular weight batches of PDFD-T polymers, based on difluorobenzothiadiazole and dithienosilole moieties, were synthesized and denoted as PDFD-T(L), PDFD-T(M), and PDFD-T(H), respectively. Furthermore, to compare the effects of different donor moieties, donor units of PDFD-T(L) were structurally modified from thiophene to thienothiophene (TT) and dithienothiophene (DTT), denoted as PDFD-TT(L) and PDFD-DTT(L), respectively. After doping the CPs with FeCl$_3$, doped(d) PDFD-T(H) exhibited an electrical conductivity of 402.9 S cm^{-1}, which is significantly higher than those of d-PDFD-T(L), d-PDFD-T(M), d-PDFD-TT(L), and d-PDFD-DTT(L). Furthermore, the drastic increase in σ of d-PDFD-T(H) sufficiently compensated for its reduced Seebeck coefficient, which resulted in a high power factor of up to 101.1 μWm^{-1}K^{-2} of the thermoelectric devices fabricated using d-PDFD-T(H).
Systematic characterizations were performed on both pristine and doped CPs, including spectroelectrochemical ultraviolet-visible-near infrared (UV-Vis-NIR) absorption, Raman spectroscopy, conductivity and Hall effect measurements, grazing incidence wide-angle X-ray scattering (GIWAXS), conductive atomic force microscopy (C-AFM), and so on. The doping efficiency of FeCl$_3$ on CPs was analyzed from the UV-Vis-NIR spectra of the doped CP films by Gaussian fitting, estimating the concentration of [FeCl$_4^-$] which is an indicator of the amount of generated charge carriers after doping. [FeCl$_4^-$] gradually increased from 2.67 (d-PDFD-T(L)) and 3.00 (d-PDFD-T(M)) to 6.27 M (d-PDFD-T(H)) according to the increasing order of the molecular weight. The higher molecular weight of CPs, the more charge carriers were generated in the doped CPs, implying the molecular weight of CPs affects the doping efficiency of the CPs. In addition, through GIWAXS analysis, it was revealed that the molecular weight of CPs also critically affects the crystallinity of CPs after doping, which is directly related to their charge transport properties. After doping, the crystallinity of CPs with low molecular weight decreased significantly due to structural disorders resulting from the infiltration of dopant molecules, causing low charge carrier mobility. However, d-PDFD-T(H) maintained its original crystallinity the most among the CPs and good charge transport pathways. In conclusion, these results highlight that the high molecular weight of polymers is necessary to achieve high crystallinity, high charge carrier mobility, and charge carrier concentration simultaneously.
This work demonstrates that the increased molecular weight of CPs strongly suppresses the crystallinity degradation of doped CPs and optimizes their doping efficiency and electrical conductivity. Therefore, we suggest that optimizing the molecular weight of CPs is an essential strategy for ultimately high thermoelectric performances from their doped CP films.

5:00 PM SF03.06.04
Tailored Phonon Transport in Heterogenous van der Waals Structures Zihao Qin, Man Li, Lingyun Dai, Suixuan Li, Huan Wu and Yongjie Hu; University of California, Los Angeles, United States

Heterogenous two-dimensional materials provide a unique platform study transport physics under high controllability and extreme conditions. Here through the design of layered control over van der Waals structures and atomic design at the interfaces, we find extremely anisotropic and structural dependent thermal conductivity control. In particular, our spectroscopy measurements and first-principles simulations show consistent observation of the localizations and atomic tailored phonon spectra. The resulted phonon structure provides heat transfer in a unique and controllable manner that are not available in other systems. We attribute this behavior to the enhanced coupling phase space that suppress phonon flux. This study probes complex phonon transport physics and opens the way for the understanding of microscopic energy transport mechanisms in heterogenous van der Waals structures.
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Zihao Qin, Man Li, Jessica Flohna, and Yongjie Hu, Thermal management materials for energy-efficient andsustainable future buildings, Chemical Communications 57, 12236 (2021).

5:00 PM SF03.06.05
Electrospinning-Assisted Radiative Cooling Composite Films Heegeom Jeon[1], Choyeon Park[2], Byung-il Choi[3], Seokjun Kim[3], Chanil Park[2], Sungmin Park[2], Yong Seok Kim[2] and Youngjae Yoo[1]; [1]Chung-Ang University, Korea (the Republic of); [2]Korea Research Institute of Chemical Technology, Korea (the Republic of); [3]Korea Testing & Research Institute, Korea (the Republic of)

The rapid increase in annual cooling energy demand has a significant adverse impact on global warming. To overcome this, several studies have been conducted, and interest in passive radiative cooling that can be cooled without energy consumption has increased. Recent research on passive radiative cooling using various materials to reduce energy use for cooling has been reported. Previous studies focused on solar reflection and mid-infrared (IR) emission based on photonic crystal materials that are expensive and difficult to achieve large areas. Passive radiative cooling research is shifting from inorganic materials to organic materials and requires better solar reflectivity and mid-IR selective emissivity. In this study, an experiment was conducted to increase the solar reflectance of the existing PRC cooler to generate high emission at wavelengths in the atmospheric window range. Wave-selective emitters in the atmospheric window range were fabricated using glass bubbles (GBu) and barium sulfate ($BaSO_4$) in polydimethylsiloxane (PDMS). Then, polyacrylonitrile (PAN) nanofibers were electrospun on the prepared coolers. The optical properties and cooling power according to the ratio of GBu and $BaSO_4$ contained in the cooler and PAN electrospinning conditions were analyzed. Compared with the PDMS/GBu and $BaSO_4$ cooler, the cooler with the added electrospinning layer exhibited higher reflectivity and cooling power.

5:00 PM SF03.06.06
A Three-Terminal Magnetic Thermal Transistor Lorenzo Castelli, Qing Zhu, Trevor J. Shimokusu and Geoffrey Wehmeyer; Rice University, United States

Three-terminal thermal analogies to electrical transistors have been proposed for use in thermal amplification, thermal switching, or thermal logic, but have not yet been demonstrated experimentally. Here, we design and fabricate a three-terminal magnetic thermal transistor in which the gate temperature controls the source-drain heat flow by toggling the source-drain thermal conductance from ON to OFF. The centimeter-scale thermal transistor uses gate-temperature dependent magnetic forces to actuate motion of a thermally conducting shuttle, providing thermal contact between source and drain in the ON state while breaking contact in the OFF state. We measure source-drain thermal switch ratios of in high vacuum with gate switching temperatures near . Thermal measurements show that small heat flows into the gate can be used to drive larger heat flows from source to drain, and that the switching is reversible over >150 cycles. Proof-of-concept thermal circuit demonstrations show that magnetic thermal transistors can enable passive or active heat flow routing and Boolean thermal logic gates. This work will allow thermal researchers to explore the behavior of nonlinear thermal circuits using three-terminal transistors, and motivates further research developing thermal transistors for advanced thermal control.

5:00 PM SF03.06.08
Achievement of High Thermal Conductivity in Polyphenylene Sulfide Composites by Adding Amine-Functional Polysiloxide Coated ABN and Silane Treated Graphene Oxide Dabin Park, Youngsung Cho, Jooheon Kim, Minsu Kim and Wondu Lee; Chung-Ang University, Korea (the Republic of)

Polyphenylene sulfide (PPS) is a material with strong mechanical properties and chemical stability. However, PPS has a low thermal conductivity of 0.18 W/m K, which limits its applications in fields requiring heat dissipation properties.
In this study, to improve the thermal conductivity of the PPS/GF composite, aggregated boron nitride (ABN) was selected to create a heat path between the glass fiber fillers. ABN is a material that is physically aggregated with hexagonal BN (h-BN). H-BN has a high in-plane thermal conductivity of 180–300 W/m K and high chemical resistivity, which makes h-BN suitable as a filler for the improvement in thermal conductivity of various matrices. H-BN is difficult to handle due to its poor interfacial adhesion with composite matrix. For this reason, the surface modification of BN is necessary to improve adhesion with the PPS matrix. And to prevent the destruction of the ABN morphology in the extrusion and injection molding processes, amine-functional polysiloxide was selected to cover the ABN surfaces and was heat-treated at a high temperature of 973 K to provide thermal stability to withstand the high temperatures of the molding process. In addition to adding ABN, graphene oxide (GO) was also added to the composite to improve the adhesion between the glass fiber and the PPS matrix. Glass fiber and ABN in a PPS matrix have cylindrical and spherical morphologies; therefore, 2-dimensional GO was selected to improve the interface adhesion between the two fillers and the PPS matrix. In previous reports, silane-modified GO improved the dynamic mechanical and thermal properties by improving the adhesion between the filler and matrix. Furthermore, 3-mercaptopropyl trimethoxysilane (MPTMS) is a silane coupling agent which has a thiol functional group (R-SH). The R-SH in MPTMS can induce hydrogen bonding with the sulfur from PPS. The tri-filler-contained PPS composites were fabricated, and the mechanical and thermal properties were measured.
This study improves the mechanical and thermal properties of PPS-based composites. Because ABN and GO could not endure the melting extrusion and injection molding processes at a high temperature of 573 K, it was necessary to treat ABN and GO for the successful fabrication of the composites. ABN was coated with amine-functional polysiloxide and underwent the annealing process to transform into SiOC ceramics. In addition, MPTMS silane material was attached to the surface of GO. By adding PSZABN and MGO into the PPS/GF system, the dynamic mechanical property, more specifically, the storage modulus was increased by 50 times compared with neat PPS, and the mechanical tensile strength was increased from 60 MPa to 84 MPa. The thermal conductivity of the composite was 0.7 W/m K, which is 3.8 times greater than that of neat PPS. These improvements are due to the surface modification of the matrix and the improvement in adhesion with the glass fiber and PPS matrix by adding MGO. The above results demonstrate the application potential in various fields including the automotive field, which requires heat dissipation properties, by improving the thermal conductivity of the PPS matrix containing strong mechanical properties.

5:00 PM SF03.06.09
Thermal Transport in Fluid-Filled Si Nanocomposite Films Bayan A. Kurbanova[1], Azat Abdullaev[1], Ali Belarouci[2], Vladimir Lysenko[2] and Zhandos Utegulov[1]; [1]Nazarbayev University, Kazakhstan; [2]Université de Lyon, France

Although the investigation of dynamic properties of liquids within spatially confined solid spaces has drawn a considerable amount of research and

practical interest, a comprehensive understanding of the effect of fluid confinement in solid nanoporous media on the thermal transport properties of the fluid-infiltrated nanocomposite systems is still lacking [1]. Moreover, a study of easily controllable heat transfer using hybrid-like porous materials across solid-fluid interfaces is an important technical issue in engineering nanofluidic devices and nanoelectro-mechanical systems (NEMS) infiltrated with fluids [2,3].
We demonstrate experimental results of the femtosecond pulse laser-based time-domain thermo-reflectance (TDTR) and continuum laser wave-based micro-Raman spectral thermometry techniques measuring the thermal conductivity of nano-porous Si films infiltrated with various fluids. These heat conduction measurements were employed to validate finite-element mesh (FEM) simulations of laser-induced heating temperature distribution across these fluid-filled Si nanocomposite films of various porosities (30 - 70%) and fluid fillers (silicone oil and air).
It is established that the presence of liquid in the pores leads to a significant rise in due to the increase of the specific surface area of the liquid/solid interfaces. However, the fluid infiltration into the porous solid Si network induces a substantial reduction in compared to continuous bulk single-crystalline Si due to the presence of topologically interconnected thin solid Si walls of the porous medium [4]. Also, the obtained values were found to be higher than those of Si nanogranular films owing to the lack of additional interface thermal resistance across neighboring nanoparticle boundaries [5]. Additionally, our experimental results are in good agreement with earlier theoretical molecular dynamics (MD) calculations [6] and photoacoustic (PA) measurements in liquid filled Si nanocomposites [7, 8].
This work was supported by Nazarbayev University CRP grant 11022021CRP1504.
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5:00 PM SF03.06.11
TBC Degradation Behavior Analysis Based on CMAS Sol for Evaluation of CMAS Resistance of TBC Janghyeok Pyeon, Bong-Gu Kim, Junseong Kim, Hyeryang Choi, Tserendorj Khadaa, Jung-Hun Son, Byungil Yang, Yeon-Gil Jung and SeungCheol Yang; Changwon National University, Korea (the Republic of)

Thermal barrier coatings (TBCs) have been generally applied to the blades and vanes of the gas turbine to protect alloy substrate from high temperature environment. CMAS (32CaO-7MgO-12Al2O3-49SiO2) material, existing in sand, volcanic ash, etc., is easily penetrates the pores inside the top coat under high temperature operation of gas turbine. The penetrated CMAS induces to thermal conductivity increase of top coat, and additional stress between bond coat and top coat due to the difference in their thermal expansion coefficient. Therefore, CMAS attack on TBC negatively affect the life time of the gas turbine blades and vanes. In this work, we synthesized CMAS sol, which can be uniformly penetrated in the top coat, to set up a new CMAS evaluation method. For the synthesis, the CMAS sol was prepared through pH control after dissolving the precursor of CMAS materials in nano-sized Si sol. The fixed amount of CMAS sol was uniformly applied to the surface of the YSZ specimen. Thereafter, the test piece was heat-treated at 1,300 ° C for melting the CMAS sol and infiltration of melted CMAS into the YSZ. As a result of microstructural analysis, penetration depth of the CMAS in the top coat increased with time increase of heat treatment. In addition, it was conformed that CMAS in the top coat was uniformly distributed. In addition, porosity of the YSZ top coat was decreased by a reaction between YSZ and CMAS. As a result of XRD analysis, we confirmed that monoclinic phase in YSZ increased with an amount increment of CMAS coated on YSZ.

5:00 PM SF03.06.12
Full Predictive Heat Transport Model for Electronic Devices at the 20 nm Scale Jordi Tur Prats[1], F. Xavier Alvarez[1], Lluc Sendra Molins[1], Juan Camacho[1], Javier Bafaluy[1] and Albert Beardo Ricol[1,2]; [1]Universitat Autònoma de Barcelona, Spain; [2]University of Colorado Boulder, United States

Simulation of the thermal evolution of actual electronic devices is a very challenging topic. Heat transport at the nanoscale does not behave as in the macroscale [1-2]. This is a problem for engineers, as they cannot predict the thermal response of their devices with accuracy.

In the last years, the Kinetic Collective Model (KCM) has been used to develop a finite element tool to describe the thermal evolution of electronic devices with great accuracy using the Guyer and Krumhansl hydrodynamic equation. The results obtained from this approach fit extraordinarily to experiment with characteristic scales up to 400 nm using only ab initio parameters [1-2], but for smaller devices, effective values for the parameters are required. In these situations, some corrections are required in order to predict the experiments.

We present the Higher Order Perturbation (HOPE) an improvement of the KCM-hydrodynamic approach [4-5]. This new method allows to obtain a full predictive finite element model for thermal transport at the 20nm scale. The model is obtained from the split of the Boltzmann Transport Equation (BTE) in two terms, a first one that describes the hydrodynamic behavior and a second one with the residual terms that describes the evolution of the perturbations of higher order. From the solution of the residual term using a Monte Carlo approach we derive a boundary correction term that modifies the hydrodynamic boundary conditions. With this correction, the applicability of our finite element tool is significantly improved. We compare the results obtained from our simulations with experimental data of devices in the 200-20 nm range.

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5:00 PM SF03.06.14
Effect of Mechanical Alloying Methods on Nanostructured Aluminum-Graphite Composites Fabricated by Spark Plasma Sintering—Thermal Conductivity, Microstructure, Mechanical Property Bum Soon Park, Jeong-Han Lee, Hyun-Kuk Park and Jae-Cheol Park; Korea Institute of Industrial Technology, Korea (the Republic of)

In an effort to secure superior thermal conductivity compared to conventional metal heat-dissipating materials such as copper and aluminum, aluminum-graphite (Al-Gr) composites were prepared, and then mechanical and thermal properties depending on graphite contents were closely investigated. In this study, the graphite contents were changed to 20, 30, 40, 50, and 60 vol.% in order to sinter aluminum-graphite composites having different graphite content ratios. The Al-Gr composite powders mechanically synthesized by mixer milling were sintered under the following process conditions; sintering temperature of 480 °C, sintering pressure of 40 MPa, and duration of 2 minutes at the temperature of 480 °C. The relative density of the sintered body gradually decreased as the graphite content increased and showed the highest value of 94% when the Al-Gr content ratio was 8:2. The phase change and hardness of the Al-Gr sintered body depending on the graphite contents were investigated by XRD and Vickers hardness analysis, respectively. Furthermore, thermal conductivity as a function of the graphite content, which is the most important indicator of this study, was systematically investigated.

5:00 PM SF03.06.15
Pore Size Dictates Anisotropic Thermal Conductivity of Two-Dimensional Covalent Organic Frameworks with Adsorbed Gases Muhammad Akif Rahman and Ashutosh Giri; University of Rhode Island, United States

Two-dimensional covalent organic frameworks (COFs) are an emerging class of porous crystals that have already established themselves as game-changing materials due to their exceptional physical properties such as high porosities, large surface areas and flexibility of controlling the functional building blocks which make them ideal candidates for a plethora of applications, such as gas separation, adsorption and storage, drug delivery, and as solid-state electrolytes for upcoming energy storage technologies. However, the excessive heat generation due to the adsorption of guest species is one of the major bottlenecks for their alrge scale incorporation in aforementioned applications. Therefore, it is crucial to find innovative ways to modulate the thermal properties of COFs, which is contingent upon fully comprehending the essential characteristics that dictate the effectiveness of energy transfer in these materials. Herein, we carry out a detailed analysis of the influence of pore geometry on the overall heat transfer mechanisms in 2D COFs through systematic atomistic simulations demonstrating the thermal conductivity can either be increased due to additional heat channels introduced by the gas adsorbates or decreased due to the phonon scattering resulting from the interactions between the gas and the solid pore walls of the COFs.

We perform molecular dynamics simulations on pristine and gas adsorbed COF structures by varying the pore sizes and gas densities and reveal that for COFs with relatively larger pore sizes (>2 nm), despite the reduction of the thermal conductivity of the solid framework due to solid-gas scattering, the overall cross-plane thermal conductivity dramatically increases, which is attributed to the additional heat transfer pathways introduced by the low-frequency vibrations (<0.5 THz) of the gas adsorbates. On the other hand, for COFs with relatively smaller pores (<2 nm) both the cross-plane and in-plane thermal conductivities decrease monotonically due to the increase in phonon scattering resulting from the solid-gas interactions at the pore walls. Our simulations on COF/methane systems reveal the intricate relationship among gas diffusivities, pore geometries, and solid–gas interactions dictating the modular thermal conductivities in these materials. Furthermore, our results can also help guide the design of efficient 2D polymeric crystals for applications with improved gas storage, catalysis, and separation capabilities.

5:00 PM SF03.06.17
Investigating Optical and Thermal Properties in Novel Rare Earth Zirconates for Radiative Barrier Coatings William T. Riffe[1], Hunter Schonfeld[1], Milena Milich[1], Victor Champagne[2], Jeroen Deijkers[1], Haydn Wadley[1], David R. Clarke[2] and Patrick E. Hopkins[1]; [1]University of Virginia, United States; [2]Harvard University, United States

Rare earth zirconates show promising optical and thermal properties required of next generation radiative barrier coatings (RBCs) for ultrahigh temperature (1500K+) applications. A fundamental mode of heat transfer that has been neglected in current barrier coatings is radiative heating between hot components. New research aims to mitigate both conductive and radiative heating by doping standard barrier coating materials with rare earth metals that are optically opaque in the spectral range of the emitted radiation.

In this work, we perform a series of thermal and optical studies via pump-probe thermoreflectance techniques and spectroscopic ellipsometry to elucidate temperature-dependent thermal conductivity, wavelength-resolved ultrafast electronic transitions, and optical constants of rare earth zirconates. Understanding the trends and thresholds of thermal conductivity is of utmost importance in selecting RBCs that can endure cycling to ultrahigh temperatures. Furthermore, we directly measure electronic excitations as a function of wavelength and incident fluence to relate non-equilibrium relaxation of electrons to the optical constants associated with peak blackbody emission at ultrahigh temperatures. By investigating the pertinent physical scattering mechanisms, we deconvolute key design considerations for next generation RBCs.

5:00 PM SF03.06.18
Application of Refractory Plasmonic Nanomaterials to Enhance 3D Printability of Thermoset Resins Madeline Finale, Sanchari Chowdhury and Youngmin Lee; New Mexico Institute of Mining and Technology, United States

Additive manufacturing of thermosets is attractive due to their potential for structural applications, especially for automotive and aerospace parts. However, additive manufacturing of thermosets using methods such as selective laser sintering could be challenging as the conventional thermosets do not exhibit thermoplastic-like melt flow behavior. We modify the chemistry of thermosets such as epoxy with Diels-Alder reaction to make it flowable at high temperatures. We added photothermal plasmonic refractory titanium nitride nanoparticles (TiN) to the epoxy. These photothermal nanoparticles can absorb light efficiently to generate heat instantly at the nanoscale. This can bring down the light intensity required for the printing significantly. Another important parameter for successful layer-by-layer printing is the time required to melt and solidify the thermosets. We developed an optical microscopy-based method to study the in situ melting of the epoxy composites under light and the time it takes to solidify when the light source is turned off. The nanoparticle loading, light intensity, and heat dissipation were studied to determine the optimal conditions for application in selective laser sintering. We could reach temperatures as high as 1500°C and start melting within 10 seconds with 0.78 W/cm^2 halogen lamp light source for the epoxy sample with 0.5 wt% titanium nitride nanoparticle loading. The sample without the nanoparticles could only reach 750°C when exposed to similar intensity via halogen lamp.

5:00 PM SF03.06.19
Gallium Arsenide Telescopic Nanowire-Based 'Thermal Diode' Yashpreet Kaur[1], Saeko Tachikawa[1], Miquel López-Suaréz[2], Milo Yaro Swinkels[1], Matteo Camponovo[1], Anna Fontcuberta i Morral[3], Riccardo Rurali[2] and Ilaria Zardo[1]; [1]University of Basel, Switzerland; [2]Universitat Autònoma de Barcelona (Spain), Spain; [3]EPFL, Switzerland

Photonics and electronics have reached a high level of control and sophistication in technology today, but heat manipulation continues to be a challenge. While nanoscale devices have made their way to industry, the problem of heat management still hinders their performances and is a limiting factor [1]. To achieve ultimate control over heat flow and cool down densely packed systems in current microchips, a thermal diode must be realized. A thermal diode is a device that enables heat to flow preferentially in one direction, thus, giving rectification.

Efforts have been made as early as the 1930s to study heat rectification theoretically and experimentally by exploring several mechanisms, including combining materials with the different temperature dependence of thermal conductivity [2]. Nanostructuring further helps tune the thermal conductivity due to phonon scattering effects, which was explored in nanowires for thermal rectification through molecular dynamic simulations in 2015 [3].

Here, we have exploited the size and temperature dependence of the thermal conductivity to manipulate heat flux and study thermal rectification experimentally. For this purpose, we investigate the thermal properties of semiconducting gallium arsenide nanowires with an abrupt change in diameter [4], also called telescopic nanowires. To perform precisely controlled thermal transport measurements on these nanowires, suspended silicon nitride platforms with Joule heaters are used to apply thermal gradients and measure thermal conductivity [5, 6]. Further, to obtain the temperature profile along the nanowire axis, Raman thermometry is performed upon applying a thermal gradient. Mapping the temperature of the heat channel provides us with the thermal conductivity of each section of the nanowire, as well as the interface resistance. We measured rectification values ranging from 2 to 7% at a range of ambient temperatures, with rectification values increasing for larger temperature gradients. The direction of rectification and its dependence on temperature gradient is confirmed by numerical calculations of the one-dimensional heat equation, based on thermal conductivities computed ab initio. Interface thermal resistance, calculated within the acoustic mismatch model, is explicitly accounted for. This work is the first experimental indication of rectification using a telescopic nanowire. Our findings make an impact in the direction of efficient thermal management and in the development of thermal circuit elements.

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5:00 PM SF03.06.20
Investigation of Bond Quality and Interfacial Strain at a Room Temperature Bonded GaN-Diamond Interface via Raman Spectroscopy William; Delmas, Matthew Bahr, Anthony McDonald, Wyatt Hodges, Amun Jarzembski, Zachary Piontkowski and Luke Yates; Sandia National Laboratories, United States

Vertical gallium nitride (GaN) power devices have the potential to improve power conversion efficiency in electrical circuits due to enhanced mobility and high critical electric field. Since device performance and reliability are directly related to thermal performance, there is significant interest in improving options for passive thermal management. To this end, the heterogeneous integration of diamond with vertical GaN devices is explored. In this current work, the bond quality of a bulk GaN substrate with single-crystal diamond via an intermetallic surface activated Au bond is investigated. The intermetallic layer in the GaN-diamond stack potentially creates a phonon bridge for enhanced heat dissipation out of GaN and into the diamond. However, it is unclear whether/how the bonding will introduce strain in the GaN crystal, which can negatively impact electrical performance and device reliability. Here, we use high-resolution micro-Raman spectroscopy to characterize the strain in the GaN near the interface. The quality of the interfacial bonding between GaN and diamond is evaluated via Scanning Acoustic Microscopy (C-SAM). The C-SAM images are referenced to bonded and non-bonded regions for further investigation via micro-Raman. The micro-Raman maps revealed localized regions of strain when moving from a non-bonded to bonded area. This result highlights two important aspects of the interface when optimizing for thermal boundary conductance: 1) Interfacial bonding is not necessarily uniform and requires spatial mapping for full characterization. 2) Although bonded and non-bonded regions of an interface may not show strain changes post bonding, the transition between these regions may be strained and have an impact on the device performance. Moving forward, Raman strain maps and C-SAM images of bonded and non-bonded regions will be combined with thermal mapping, via frequency-domain thermoreflectance (FDTR), to fully characterize the thermal and mechanical properties across an entire interfacial region. This work will provide additional insight into the inhomogeneity of a room temperature bonded GaN-diamond interface and the subsequent non-uniform strain profiles that exist near bonding sites. (SAND Number: SAND2022-14970 A)

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SESSION SF03.07: Quantum Thermal Phenomena
Session Chairs: Yongjie Hu and Philip Kim
Wednesday Morning, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate A

8:00 AM *SF03.07.01
Measurement of Electronic Thermal Conductance in Low Dimensional Materials with Nonlocal Noise Thermometry Philip Kim; Harvard

University, United States

In low-dimensional systems, the combination of reduced dimensionality, strong interactions, and topology has led to a growing number of many-body quantum phenomena. Thermal transport, which is sensitive to all energy-carrying degrees of freedom, provides a discriminating probe of emergent excitations in quantum materials. However, thermal transport measurements in low dimensions are dominated by the phonon contribution of the lattice. An experimental approach to isolate the electronic thermal conductance is needed. In this presentation, I will discuss how the measurement of nonlocal voltage fluctuations in a multiterminal device can reveal the electronic heat transported across a mesoscopic bridge made of low-dimensional materials. By using graphene as a noise thermometer, we demonstrate quantitative electronic thermal conductance measurements of graphene and carbon nanotubes up to 70K, achieving a precision of ~1% of the thermal conductance quantum at 5K. Employing linear and nonlinear thermal transport, we observe signatures of long-range interaction-mediated energy transport in 1D, in agreement with a theoretical model.

8:30 AM SF03.07.02
Thermoelectric and Photovoltaic Energy Conversion in Interlayer Exciton Structures Yajie Huang[1], Sizhe Weng[2], Yu Wang[2], Steve Cronin[2,2] and Li Shi[1]; [1]The University of Texas at Austin, United States; [2]University of Southern California, United States

Excitons are bound electron and hole pairs. Recent spectroscopic and electronic transport measurements have observed potential Bose-Einstein condensation signatures of interlayer excitons in van der Waals heterostructures of transition metal dichalcogenides (TMDs). Thermoelectric measurement can provide unique insight into unusual collective energy transport behaviors associated with the bosonic nature of excitons. Here, we explore thermoelectric and photovoltaic measurements in two-dimensional TMDs heterostructures separated by a hexagonal boron nitride insulating layer. With their charge carrier concentration controlled by separate bottom and top gates, an n-type material and a p-type material can be connected electrically in series and thermally in parallel, similar to a thermoelectric couple. A lateral temperature gradient drives the diffusion of the electrons and holes from the hot side to the cold side, giving rise to a thermoelectric current. These thermoelectric and optoelectronic properties are measured at different combinations of the electron and hole concentrations to search for signatures of exciton binding and improved energy conversion.

8:45 AM SF03.07.03
Engineering Spin Coherence in Core-Shell Diamond Nanocrystals Peter Maurer; The University of Chicago, United States

Diamond nanocrystals can harbor spin qubit sensors capable of probing the physical properties of biological systems with nanoscale spatial resolution. These diamond nanosensors can readily be delivered into intact cells and even living organisms. However, applications beyond current proof-of-principle experiments require a substantial increase in sensitivity, which is generally limited by surface-noise-induced spin dephasing and relaxation. In this talk, I will discuss a novel strategy to significantly reduce the surface noise by engineering core-shell structures, which on average result in a 3.5-fold increase in spin coherence and spin-lattice relaxation time. Probing qubit dynamics at a single particle level, furthermore, reveals that the noise characteristics change from a model consistent with a two dimensional dipole fluctuator model to a more dilute three dimensional bath. Our results shed light on the underlying mechanisms governing spin dephasing in diamond nanocrystals and offer an effective noise mitigation strategy based on engineered core-shell structures.

9:00 AM SF03.07.04
Tuning and Probing Interfacial Thermal Conductance between Moiré Superstructures Devika Mehta, Emma Martin, Nemin Wei, Yajie Huang, Allan MacDonald and Li Shi; The University of Texas at Austin, United States

The operating temperature of emerging two-dimensional (2D) electronic and optoelectronic devices is sensitive to the interfacial thermal conductance of the 2D layered materials. In past work, this thermal transport property has been probed by time-domain thermal reflectance (TDTR) measurements and tuned by electrochemical intercalation. Here we report an experiment that probes interfacial thermal transport between twisted bilayer graphene (TBG) moiré superstructures separated by a thin hexagonal boron nitride layer with the use of steady state resistance thermometry measurements. Besides the thin film platinum gates that can serve as the resistance thermometers, the large temperature coefficient of resistance of TBG enables sensitive measurements of the small temperature drops between the two moiré superstructures. The improved sensitivity allows for the observation of the dependence of the measured interfacial thermal conductance on the gate electric fields applied to the two moiré superstructures. The measurement results are compared to theoretical calculations to understand the field effects on the lattice contribution to the interfacial thermal conductance through the van der Waals interfaces, and to search for an additional contribution due to a predicted Coulombic interaction mechanism.

9:15 AM SF03.07.05
Universal Heat Flow Behavior in Highly-Confined Semiconductor Nanosystems Albert Beardo Ricol[1,2], Brendan McBennett[1], Emma Nelson[1], Begoña Abad Mayor[1], Travis Frazer[1], Yuka Esashi[1], Baowen Li[1], Henry Kapteyn[1], Margaret Murnane[1] and Joshua Knobloch[1]; [1]University of Colorado Boulder, United States; [2]Universitat Autònoma de Barcelona, Spain

The thermal evolution of nanostructured semiconductor devices has been shown to exhibit non-diffusive behaviors that cannot be interpreted using effective forms of Fourier's law [1]. Predicting and understanding this phenomenology using models solvable in arbitrary geometries is key to developing efficient thermal management strategies for nanoelectronic and thermoelectric applications.

Here, we study the process of energy release from nanoscale heat sources towards a silicon substrate using an infrared pump laser to excite the sample and an extreme ultraviolet probe to dynamically monitor its relaxation. We perform these experiments both in a semi-infinite substrate [1], and a 3D nanostructured metalattice substrate, consisting of a Si crystalline nanostructure with periodically distributed spherical nanovoids [2]. To develop a unifying description of heat flow from both nanoscale hotspots and in nanostructured materials, we use a hydrodynamic heat equation recently derived from the Boltzmann Transport equation (BTE) [3]. For a semi-infinite substrate, the heater temperature follows a double-exponential decay that cannot be fit using effective Fourier modeling, but can be predicted using the hydrodynamic equation with ab initio calculated parameters. For a nanostructured substrate, an analogy to rarefied gas flow in porous media can be used to distinguish a geometry-dependent *permeability* contribution to thermal conduction from an intrinsic *viscous* component, which scales universally with porosity across all systems where feature sizes are much smaller than the dominant phonon mean free paths. This leads to an analytic description of thermal conduction in highly-confined silicon nanosystems, extensible to nanomeshes, porous nanowires or nanowire networks [2], thus enabling their representation as effective media for engineering design applications.

Finally, we compare the hydrodynamic modeling of the experiments with alternative approaches such as direct solvers of the BTE with simplified forms of the Collision operator. In particular, we discuss the validity of some assumptions commonly used to solve the BTE in the presence of boundaries, which prevent the emergence of collective phonon evolution in highly-confined conditions in materials such as silicon.

[1] Albert Beardo, Josh Knobloch, et al., ACS Nano 15, 8, 13019-13030 (2021)
[2] Brendan McBennett, et al., arXiv:2209.11743 (2022)
[3] Lluc Sendra, et al., Phys. Rev. B 103, L140301 (2021)

SESSION SF03.08: Thermal Transport Under Extreme Conditions

Session Chairs: Raymond Jeanloz and Thomas Pfeifer
Wednesday Morning, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate A

10:00 AM *SF03.08.01
Ultrahigh-Pressure Experiments on Thermal Transport—Linking Theory to Applications Raymond Jeanloz and Mercedes Vasquez; University of California-Berkeley, United States

Ultrahigh-pressure experiments reveal significant changes in the stability, elasticity and transport properties of crystalline and fluid matter, challenging first-principles theory and helping in the development of new materials. Compression into the high energy-density regime (pressures exceeding 10^11 Pa or 10^6 atmospheres) causes electronic as well as crystal-structural transitions due to the thermodynamic perturbation being comparable to valence electron energies (~ eV): insulators become metals (and vice-versa), ions change shape as well as size, and chemical bonding is altered. Recently, time-domain thermoreflectance (TDTR) and other pulse-probe measurements have been integrated with diamond cells to quantify thermal transport under static high pressures. The connection between thermal and electron transport is currently receiving particular attention, the results to date being in agreement with established theory of electron and phonon scattering, and providing important constraints on our planet's early evolution. Future experiments using dynamic compression may allow measurements to be extended into the realm of atomic pressures (10^{13} Pa), at which the structure of the atom is fundamentally altered and compressional energies exceed core-electron values (keV). Experiments at such extreme conditions are part of a strategy for advancing theory and producing new materials of interest under practical, near-ambient conditions.

10:30 AM SF03.08.02
High-Pressure Thermal Transport Physics in Extreme Materials Suixuan Li, Zihao Qin, Huan Wu, Man Li and Yongjie Hu; University of California, Los Angeles, United States

High pressure represents extreme environments and provides opportunities for materials discovery. Thermal transport under high hydrostatic pressure has been investigated for more than 100 years and all measurements of crystals so far have indicated a monotonically increasing lattice thermal conductivity. Here we report in situ thermal transport measurements in the newly discovered semiconductor crystal boron arsenide, and observe an anomalous pressure dependence of the thermal conductivity. We use ultrafast optics, Raman spectroscopy and inelastic X-ray scattering measurements to examine the phonon bandstructure evolution of the optical and acoustic branches, as well as thermal conductivity under varied temperatures and pressures up to 32 gigapascals. Using atomistic theory, we attribute the anomalous high-pressure behaviour to competitive heat conduction channels from interactive high-order anharmonicity physics inherent to the unique phonon bandstructure. Our study verifies ab initio theory calculations and we show that the phonon dynamics—resulting from competing three-phonon and four-phonon scattering processes—are beyond those expected from classical models and seen in common materials. This work uses high-pressure spectroscopy combined with atomistic theory as a powerful approach to probe complex phonon physics and provide fundamental insights for understanding microscopic energy transport in materials of extreme properties.
Publication: Suixuan Li, Zihao Qin, Huan Wu, Man Li, Martin Kunz, Ahmet Alatas, Abby Kavner, Yongjie Hu, Anomalous thermal transport under high pressure in boron arsenide. Nature 612, 459–464 (2022). https://doi.org/10.1038/s41586-022-05381-x

10:45 AM SF03.08.03
Hydrodynamic Experimental Observations in Bulk Semiconductors F. Xavier Alvarez[1], Lluc Sendra Molins[1], Albert Beardo Ricol[1,2], Juan Camacho[1], Javier Bafaluy[1] and Jordi Tur Prats[1]; [1]Universitat Autonoma de Barcelona, Spain; [2]University of Colorado Boulder, United States

A large number of experimental observations incompatible with the classical Fourier description of thermal transport at the nanometer and in the picosecond scales has been reported in the last decade [1,2]. Despite the theoretical efforts done in the topic, a model able to describe the gathered data at all length and time scales is still not available.
Two different descriptions have been proposed. Phonon hydrodynamics has been used as a framework to model thermal transport in materials where momentum conservation in phonon-phonon collisions is important. For other situations, a kinetic description based on the propagation of independent phonons, in what is called quasiballistic description, has been developed. The fundamental difference between them is in the number of length or time scales required to describe the observations. While in the hydrodynamic approach, a single scale is enough, in the quasiballistic description, the full set of phonon scales is necessary.
Traditionally, for graphene and other 2D materials, the hydrodynamic approach has been the traditional main stream, while the quasiballistic approach has been more used for classical bulk semiconductors. But in the last years, some experiments and theoretical descriptions seems to be challenging this traditional splitting. On the one side, some predictions of the hydrodynamic regime for 2D materials like the second sound velocity have put on doubt the standard approach. On the other side, collective phonon behavior like the use of a single time scale to describe thermal decay in a silicon substrate [3] or the observation of second sound in germanium [4] seem to indicate that the hydrodynamic description could be used in these semiconductors. This could be an indication that a more unified framework could be proposed.
The talk will cover some of the most recent evidences in the theoretical and experimental research on thermal transport and we will analyze them in the framework of the Kinetic/Collective model (KCM) [5], developed to give a more generalized framework to describe thermal experiments.

References

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A new regime of nanoscale thermal transport: Collective diffusion increases dissipation efficiency. Proc Natl Acad Sci USA. 2015 Apr 21;112(16):4846-51. doi: 10.1073/pnas.1503449112
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11:00 AM SF03.08.04
Accurate Prediction of Thermal conductivity of Crystals at Ultra-High Temperatures Janak Tiwari and Tianli Feng; University of Utah, United States

Many cutting-edge applications have been pushing thermal transport to ultra-high temperatures (e.g., 1000 - 3000 K), such as thermal management of hypersonic aircraft and re-entry vehicles, thermal barrier coatings of the next-generation turbine systems operating at higher temperatures, and the development of next-generation higher-temperature nuclear power plants and fusion plants. However, the fundamental thermal transport processes at ultra-high temperatures in solids remain unclear and in debate, and the predicted thermal conductivity ( ) cannot match with the experiment in most materials at high temperatures. Without a good understanding or accurate prediction of thermal transport, many potential revolutions in materials and technologies may not be realized. Phonon, a quantized mode of lattice atomic vibrations, is the main heat carrier in most solids, especially in nonmetallic materials (e.g., dielectrics and insulators), where there are no free electrons. Phonons carry heat through interatomic interactions, which can be predicted from density function theory (DFT) solely based on the atomic structure. The prediction of thermal conductivity from first principles without any fitting parameter or any help from the experiment has achieved great success in recent years for a vast number of systems but usually fails at high temperatures. In this work, we used the first-principles method to predict the thermal conductivity of several crystals including UO2, ZrC, and HfC, most important ultra-high temperature ceramics, by including both three and four-phonon scattering as well as the temperature-dependent force constant, for the first time. We find that, at ultra-high temperatures, four-phonon scattering significantly reduces thermal conductivity but the temperature-dependent anharmonic force constants tend to bring it up. The predicted thermal conductivity is compared to various experimental data. The impact of grain size and defects are also studied. This work sheds important light on the fundamental thermal transport in ultra-high temperature ceramics and will pave the way towards the engineering and development of next-generation technologies with thermal management at ultra-high temperatures.

11:15 AM SF03.08.05
Nominal Negative Contact Thermal Resistance between Boron Nitride Nanotubes with a Gold Interlayer Zhiliang Pan, Guanyu Lu, Joshua D. Caldwell and Deyu Li; Vanderbilt University, United States

Thermally conductive polymer composites are competitive candidates for thermal interface materials, which find extensive applications in the thermal management of modern electronic devices. To date, numerous filler materials have been explored, including carbon nanotubes, ceramic particles, and metal nanowires. In particular, the requirement of electrical insulation in electronic devices warrants the rising attention paid to boron nitride nanotube- (BNNT) and nanosheet- (BNNS) based composites. One key issue in understanding the performance of polymer composites is the contact thermal resistance between nanofillers, with and without a polymer interlayer between the fillers. Previous studies have revealed interesting transport phenomena such as non-intrinsic ballistic contact resistance due to phonon reflection and bi-directional modulation of the contact thermal resistance from a polymer interlayer between BNNTs, which provide insights into enhancing the thermal performance for BNNT-based polymer composites.
Here we report on efforts towards further reducing the contact thermal resistance through introducing a gold interlayer at the contact region, which could help eliminate phonon reflections with minimal added diffusive thermal resistance. Systematic measurements have been done to compare the contact thermal resistance between bare BNNTs (R_{C}) with those including a gold interlayer ($R_{C,Au}$). As the low resistance gold interlayer removes phonon reflection resistance, $R_{C,Au}$ is smaller than R_{C} in the entire measurement temperature range. For example, the contact thermal conductance is enhanced by ~200% for a 50 nm BNNT at room temperature and the enhancement decreases with increasing tube diameter as the phonon reflection effect is smaller for larger tubes. Surprisingly, opposite to the trend for R_{C}, $R_{C,Au}$ starts to decrease quickly as the temperature drops below 150 K and becomes negative below 80 K for the 50 nm BNNT sample. This negative $R_{C,Au}$ indicates that some interesting transport mechanism has been introduced by the inclusion of the gold interlayer. Since the gold interlayer is not included in the thermal pathway, the observed nominally negative contact thermal resistance must occur through altering the thermal transport along the tube. One possible reason is that the gold interlayer boosts thermal transport along the tube through introducing surface phonon polaritons (SPhPs) into the tube. As a quasi-particle comprised of a photon strongly coupled with polar optical phonons, this hybrid mode benefits from the high heat capacity associated with optical phonons and the non-negligible group velocity of the optical phonons. A nominally negative $R_{C,Au}$, extracted by subtracting the thermal resistance of the corresponding bare BNNT from the total measured thermal resistance of the contact sample, could occur if the inclusion of the gold interlayer provides an additional thermal transport pathway, here we propose that the inclusion of the gold interlayer serves as a launcher for stimulating SPhPs which in turn can carry heat along the BNNT. This hypothesis is further supported by the fact that the propagation length of SPhPs increases as temperature drops. Therefore, the relative contribution of SPhPs enhances at lower temperatures and indeed, $R_{C,Au}$ becomes smaller as temperature drops and after $R_{C,Au}$ turns negative, its magnitude keeps increasing ($R_{C,Au}$ becomes more negative) as the temperature drops further. The above findings disclose rich physics in thermal transport through BNNTs and their contacts with a gold interlayer, which could be utilized to improve thermal performance of BNNT-based polymer composites.

11:30 AM SF03.08.06
A Nanoscale Thermometry Technique for the Measurement of Enthalpy of Melting Thomas W. Pfeifer, Sara Makarem and Patrick E. Hopkins; University of Virginia, United States

Differential Scanning Calorimetry (DSC) is used for the measurement of the enthalpy of melting within phase change materials (PCM), however it requires the use of semi-bulk samples, which may be difficult to obtain in the case of bleeding edge materials. In order to characterize these, as required for advancements in energy storage or novel electronic storage devices, alternative methods must be pursued.
We present the development of a nanoscale thermometry technique wherein we use a high power laser to induce a phase change in a PCM. The laser is focused to a micron-sized spot on the sample, which is elevated in temperature and eventually melted. The changes in temperature are monitored via a second laser in a similar manner as existing thermoreflectance experiments (TDTR, FDTR, SSTR). By recording the resultant temperature rise waveform, the thermal arrest due to melting can be observed, and a numerical model (capturing heating, melt pool formation and growth, and subsequent melt heating) can be used to back out the enthalpy of melting associated with the phase change.
Several additional experimental considerations are also captured. For example, as with all thermoreflectance experiments, an optically-reflective transducer is required. Similarly, thermal properties may also vary following melting. Finally, we note that this technique is not limited to solid-liquid phase changes only. While crystalline solid-solid phase changes may have a lower enthalpy associated, the fundamental principles of operation still apply.

11:45 AM SF03.08.07
Are Niobium Oxide Dihalide Materials Good Thermoelectrics—The Study Case of $NbOI_2$ Bastien F. Grosso and David O. Scanlon; University College London, United Kingdom

Thermoelectric materials offer the possibility to transform heat waste directly into electrical energy. Finding such materials is challenging since they should have simultaneously a large electrical conductivity and a low lattice thermal conductivity. These almost mutually exclusive conditions are usually encountered in materials containing Pb, making them not sustainable. Therefore, we study oxide dihalide materials as a sustainable alternate option.
We propose here to evaluate the potential for thermoelectric applications of the niobium oxide dihalide materials. Our study is motivated by the chemical abundance and ease of fabrication of oxyhalides, and the wide range of properties offered by the presence of mixed anions. We consider the case of $NbOI_2$ and find that this material has a relatively large electron affinity, making it likely to be a good n-type semiconductor. We calculate the electronic transport properties and lattice thermal conductivity through the third-order force constants and discuss its potential for thermoelectricity.

SESSION SF03.09: Nanoscopy and Non-Equilibrium Transport
Session Chairs: Costas Grigoropoulos and Amy Marconnet
Wednesday Afternoon, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate A

1:30 PM *SF03.09.01
Near-Field Ultrafast Nanoscopy of Energy Transport in Semiconductor Nanowires Jingang Li[1], Rundi Yang[1], Yoonsoo Rho[2] and Costas Grigoropoulos[1]; [1]University of California, Berkeley, United States; [2]Lawrence Livermore National Laboratory, United States

Carrier distribution and dynamics in semiconductor materials often govern their physical properties that are critical to functionalities and performance in industrial applications. Conventional pump-probe microscopy has limited spatial resolution due to the optical diffraction. Recently, ultrafast infrared-terahertz nano-spectroscopy was developed through the integration of scanning near-field optical microscopy and pump-probe optics. However, given the limited photon energy, the efforts have been primarily focused on studying carrier dynamics in narrow bandgap semiconductors or graphene plasmons. Here, we first report near-field ultrafast optical nanoscopy in the visible-near-infrared spectral region to access the carrier dynamics in silicon, one of the most prevalent materials in current semiconductor technology. Our pump beam has a wavelength of 400 nm (3.1 eV), which is sufficient to excite carriers in common optoelectronic semiconductors, including silicon (bandgap of 1.12 eV) and GaAs (bandgap of 1.42 eV). By combining ultrafast nanoscale measurements and theoretical modeling, we unravel the local photocarrier recombination dynamics in silicon nanowires. Moreover, we demonstrate the spatial mapping of carrier lifetime in silicon with a sub-50 nm resolution. Our results provide the capability to probe carrier behaviors in nanoscale materials and devices. By utlizing this experimental platform, we can experimentally access the nonequilibrium regime of energy transport in the nanoscale. In this context, we will show spatially and temporally resolved probing of transient energy transport in nanowires and nanobeams.

2:00 PM SF03.09.02
µ-Raman Thermography on Epitaxially Integrated NWs Confirms Negligible Thermal Contact Resistance Jose Manuel Sojo Gordillo[1,2], Carolina Duque Sierra[2], Yashpreet Kaur[1], Saeko Tachikawa[1], Nicolas Forrer[1], Nerea Alayo[2], Marc Salleras[3], Luis Fonseca[3], Alex Morata[2] and Albert Tarancón[2,4]; [1]University of Basel, Swaziland; [2]Catalonian Institute for Energy Research, Spain; [3]Institute of Microelectronics of Barcelona, Spain; [4]Catalan Institution for Research and Advanced Studies (ICREA), Spain

Currently employed materials in Thermoelectric Generators (TEGs) such as bismuth telluride or lead telluride are scarce, expensive, toxic, and environmentally harmful. In recent years, the thermoelectrics paradigm has changed mainly due to the introduction of low-dimensional materials able to reduce the thermal conductivity by phonon scattering. Semiconductor nanowires (NWs) have demonstrated fascinating properties with applications in various fields, including energy and information technologies. In particular, increasing attention has been focused on Si and silicon alloy NWs for applications in thermoelectric generation after recent successful implementation in miniaturized devices. Despite this interest, a proper evaluation of such nanostructures' thermoelectrical properties still represents a great challenge, especially when the complete characterization of the device-integrated NW is desired.

In this work, we describe the thermal analysis of epitaxially suspended rough Si NWs fabricated using a bottom-up approach following the Vapour-Liquid-Solid (VLS) method. The thermal analysis is carried out using a technique that simultaneously combines the Joule self-heating of the nanowire with micro-Raman thermometry for their thermal profiling. This sub-micrometer-resolved temperature profiling is achieved using a custom-made set-up for the acquisition of the Raman spectra within a temperature-controlled vacuum chamber. The high resolved signal of the nanostructure can be measured thanks to specifically devoted silicon-based microstructures with though trenches that eliminate the background signal of the substrate. This device also enables the analysis of the same NW with Transmission Electron Microscopy (TEM) for an accurate morphological and structural analysis.

This experiment allows to characterize the electrical and thermal conductivity of individual Si NWs and the effects of a high rough surface on these properties. The defect-free crystalline structure of the NWs and the nature of their roughness is studied with TEM. Complementary, the shape of the obtained thermal profiling yields information about the absence of electrical or thermal contact resistance between bulk and nanostructure, confirming the double-side epitaxial attachment expected for a VLS-grown NW. Finally, the combination of Joule and laser power tests required for the calibration permits to estimate the light absorption coefficient of such rough surfaces.

In conclusion, the combination of this set of techniques allows us to verify the integration of VLS NWs in the very same configuration as those used into micro-thermoelectric generators, yielding accurate thermoelectric property values that can be directly applied on the improvement in the output power of the latter.
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2:15 PM SF03.09.03

High-Performancee Planar-Type Nanophononic Si Thermoelectric Generator with a Double Cavity Structure Ryoto Yanagisawa[1], Patrick Ruther[2], Oliver Paul[2] and Masahiro Nomura[1]; [1]The University of Tokyo, Japan; [2]University of Freiburg, Germany

Thermoelectrics energy harvesting is one of the key technologies for carbon neutral. We demonstrate the planar-type silicon thermoelectric generator (TEG) with phononic nanostructures based on phonon-engineered design. The planar-type device was fabricated in an SOI wafer with CMOS and MEMS processes so that the device can be largely integrated. By using phononic nanostructures and three-dimensional thermal design, we achieved 200 μWcm^{-2} output power density at a temperature difference of 12.5 K, which is the highest-performing planar-type Si thermoelectric generator reported to date.
We fabricated the Si TEG in an SOI wafer with a 1.1-μm-thick n-type poly-Si device layer and a 1.5-μm-thick BOX layer. The poly-Si layer was doped with phosphorous at 2.0×10^{20} cm^{-3} carrier density, and the Seebeck coefficient is 100 μVK^{-1}. The phononic crystal (PnC) nanostructures were formed by electron beam lithography and reactive ion etching of poly-Si. The PnC structures are an array of circular holes with a period of 300 nm with a neck size between 8 and 100 nm. It was designed to reduce the thermal conductivity of poly-Si by considering the phonon mean free path spectrum. The cap wafer, which was designed for efficient cooling of the device, was fabricated and bonded on the TEG by flip-chip bonding. This double-cavity thermal design leads to a high-power density of the device. The single unit of the TEG has an area of 44 μm by 73 μm, and 2,400 units are integrated into a 2.64 mm by 2.92 mm area with 120 series and 20 times parallel connections.
The TEG performance was measured in the air around room temperature. We found that more than 30% of the temperature difference between the upper and bottom of the device was applied in the thermoelectric material thanks to the careful thermal design of the double cavity structure. Since the power density of the TEG is proportional to the square of the temperature difference, this thermal design is an important key factor, as well as the ZT of the thermoelectric material. Our TEG showed the output power density of about 200 μWcm^{-2} at a 12.5 K temperature difference between the device (about 4 K in thermoelectric material). The obtained normalized performance of 1.3 $\mu Wcm^{-2}K^{-2}$ is, to our knowledge, the highest-performing planar-type Si thermoelectric generator reported to date.

2:30 PM SF03.09.04
Differential Multi-Probe Thermal Transport Measurements of Individual Carbon Nanotubes Grown by Chemical Vapor Deposition Qianru Jia, Yuanyuan Zhou and Li Shi; University of Texas at Austin, United States

As a transport property important for thermal management applications, the solid thermal conductivity of graphitic materials can potentially exhibit peculiar behaviors that deviate from Fourier's law description of diffusive thermal transport. In nonmetallic solids, the thermal conductivity is dominated by the contribution of phonons. Ideal one-dimensional (1D) lattice can exhibit the Fermi-Pasta-Ulam-Tsingou (FPUT) paradox, for which the recurrence of excited phonon modes is accompanied by the extremely slow decay of heat flux correlation and a divergence of the effective thermal conductivity (k) with length (L) according to a power law relationship, $\sim L^{\alpha}$ with $0<\alpha<1$ even at room temperatures. In three-dimensional bulk crystals, in comparison, the divergence is reduced or removed by elastic anisotropy at low temperatures and by four-phonon scattering at high temperatures.
Carbon nanotubes (CNTs) are quasi-1D nanostructures that can behave differently from idealized 1D lattice chains and 3D crystals. According to recent theories, momentum-conserving normal scattering of phonons can dominate Umklapp processes in graphitic materials including CNTs to produce hydrodynamic phonon transport behaviors and length-dependent thermal conductivity due to the hydrodynamic entrance effect. Based on a prior theoretical study, in comparison, first-order three phonon scattering alone yields a $L^{1/2}$ divergence of the calculated k of a single-walled CNT, whereas additional higher-order phonon-phonon scattering results in a saturation of k when L is increased to about 10 μm. While there exist different theories on the length dependence, ultrahigh room-temperature thermal conductivity values, up to 6000 $Wm^{-1}K^{-1}$ at room temperature, have been calculated for individual single-walled CNTs (SWCNTs) by both first principles based phonon transport models and molecular dynamics simulations. These theoretical predictions have motivated both thermal transport measurements and thermal management applications of CNTs. However, existing reported experimental thermal conductivity values of individual SWCNTs and multi-walled (MW) CNTs vary by one order of magnitude due to the variation of sample quality and uncertainty in the measurement methods.
Here we report recent progress in differential four-probe thermal transport measurements of individual CNTs grown by methane chemical vapor deposition (CVD). Individual CNTs synthesized over long trenches are transferred and assembled on multiple suspended thin film metal resistance thermometer lines. A recently reported multi-probe thermal transport measurement method is employed to separate the thermal resistance of suspended CNT segments from the contact thermal resistance. A theoretical model is established to obtain the non-equilibrium temperature distribution along the contacted and suspended segments of the CNT and to extract the intrinsic thermal conductance of the suspended segments. The signal-to-noise ratio is enhanced with the use of a differential Wheatstone bridge based measurement scheme and Fast Fourier transform analysis of the data, which are measured with discrete heating levels in the heaters. The crystal structure and dimension of the suspended CNT segments are characterized by transmission electron microscopy. This method has been employed to measure the thermal transport properties of different suspended segments of the same CNT samples in the temperature range between room temperature and 10 K. The effects of metal coating on either the contact areas or the suspended segments of the CNTs are observed. The measurement method and obtained results help to advance the understanding of the peculiar phonon transport behaviors in quasi-1D CNTs.

2:45 PM SF03.09.05
Phase Identification in Cryopreserved Systems via Thermal Conductivity and Crystal Symmetry Effects Spencer P. Alliston and Chris Dames; UC Berkeley, United States

Long-term preservation of biological tissue is a research goal amongst biomedical researchers and bioengineers for its potential impacts such as improving efficacy of organ transplants, a problem for which incremental advances correlate to thousands of lives saved each year. In particular, there is a concentrated research push towards achieving long-term organ storage via bulk vitrification of tissues, in which tissues are rapidly cooled while suppressing ice formation. Low-temperature storage of tissues in an amorphous phase prevents ischemic cell death and enables virtually limitless storage times. Among the barriers to this goal is the lack of a non-invasive diagnostic method to determine the phase of solid biological samples. Current quantitative techniques, including X-ray diffraction and direct measurement of cell death, are time- and cost-intensive and damaging to samples. Otherwise, imprecise measures such as visual examination for cracking are used. An optimal technique for probing phase in vitreous biological systems would be non-destructive to cells, distributable for research and clinical applications, and resolvable for times and sizes used in vitrification protocols.

To achieve this, we implement the 3ω method as an *in situ* thermal method to determine phases of representative samples, made possible by the high dependance of thermal conductivity on crystal structure. To demonstrate this, solutions of water and cryoprotective agents (CPAs) are used as representative thermal systems on a temperature-controlled cryogenic stage with electrical and optical feedthroughs. By manipulating CPA concentration and cooling rate, the sample can be selectively solidified into a vitrified (amorphous) or crystalline state. This solid phase is stable and allows for exploration of a variety of potential characterization methods, including a modified 3ω method for thermal conductivity. Today, we demonstrate the viability of an alternative scheme in which a 'buried substrate' is measured allows for simplified experimentation and fabrication, which was preferred for dissemination of the technique.

A parallel study utilizes the refractive properties of crystals as an indication of phase. Ordinary ice (ice I_h) has a hexagonal crystal structure which exhibits birefringence. This causes the double refraction of incident polar excitations. As amorphous solid water, or a vitreous organ, is isotropic and therefore not birefringent, polarized light macroscopy can be used as an independent metric for the phase of representative samples. Here, we demonstrate the use of optical techniques as a means for phase identification in representative systems and explore the potential of polarized acoustics as a high-speed, volumetric probe for crystal symmetries in opaque systems.

3:00 PM SF03.09.06
Thermal Transport in Ga_2O_3 Polymorph Heterostructures Azat Abdullaev[1], Kairolla Sekerbayev[1], Alexander Azarov[2], Zhandos Utegulov[1] and Andrej Kuznetsov[2]; [1]Nazarbayev University, Kazakhstan; [2]University of Oslo, Norway

Gallium oxide (Ga_2O_3) is a very promising material that belongs to the novel class of ultra-wide bandgap semiconductors exhibiting such unique features as very high electric field breakdown, acceptable electron mobility, low-cost fabrication process, etc. However, there is a fundamental limitation of Ga_2O_3 attributed to its low thermal conductivity [1]. Therefore, effective thermal energy management is crucial for the further development of Ga_2O_3 technology. Up to now, most of the studies on Ga_2O_3 were focused on its conventional monoclinic β-phase due to its high stability, but thermal management is not limited just to this phase and there is a strong interest to explore properties of other phases [2]. The second most studied structure is corundum α-Ga_2O_3, but it is a metastable phase that converts to monoclinic β-phase at high temperatures (~650°C) [3]. Most recently it was demonstrated that ion implantation can result in the formation of highly oriented new Ga_2O_3 polymorph on the top of β-phase having sharp polymorph interfaces. This new phase was identified as orthorhombic κ-Ga_2O_3 [4] or defective cubic spinel γ-Ga_2O_3 [5]. Moreover, there is a strong demand to study the properties of phase-transformed interfaces, particularly thermal transport as it has a great impact on device performance. To the best of our knowledge, there is also no information from the literature neither on the thermal properties of κ- or γ-Ga_2O_3, nor on interfacial thermal conductance across phase-transformed interfaces, nor on phonon transport in ion beam-modified Ga_2O_3 materials.
In this work, we study the phonon thermal transport in [010] oriented β-Ga_2O_3 irradiated by 500 keV, 1 MeV, and 1.7 MeV Ga ions to a fluence of 6×10^{15} ions/cm^2. X-ray diffraction and Rutherford backscattering spectrometry techniques reveal a radiation-induced phase transformation in the implanted region. Heat transport measurements were performed using a femtosecond laser-based frequency-modulated time-domain thermoreflectance (TDTR). By controlling the penetration depth of the thermal waves using different modulation rates, we could spatially probe two different regions: first was several hundred nanometer-thick new phase and damaged β-phase. The thickness of the new phase was estimated to be in excellent agreement with the Rutherford backscattering technique, therefore demonstrating the capability of TDTR to spatially isolate the conductivities of individual phases. To validate the experimental results, the density functional theory was implemented to predict the thermal conductivity of the emerging κ-phase.
This work was supported by Nazarbayev University collaborative research program (CRP) grant 11022021CRP1504. M-ERA.NET GOFIB project (RCN project number 337627) is also acknowledged for financial support.
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SESSION SF03.10: Thermoelectrics and Thermal Conductance
Session Chairs: Yongjie Hu and Chris Van de Walle
Wednesday Afternoon, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate A

3:30 PM *SF03.10.01
First-Principles Studies of Thermal Conductivity in $AlGaO_3$ Alloys Chris G. Van de Walle; University of California, Santa Barbara, United States

Gallium oxide (Ga_2O_3) has promising applications in high-power and high-frequency electronics due to its wide band gap and excellent electronic transport properties. However, practical device applications are hampered by its low thermal conductivity. Devices also require forming heterojunctions with the wider-bandgap aluminum gallium oxide. We investigate the lattice thermal conductivity of monoclinic Ga_2O_3 and of the $AlGaO_3$ alloys using the phonon Boltzmann transport equation, with the harmonic and third-order anharmonic force constants calculated from density functional theory. Interestingly, we find that 50/50 alloys of Ga_2O_3 with Al_2O_3 can form a low-energy ordered structure [1]. We find that the thermal conductivity of this ordered $AlGaO_3$ is raised by more than 70% compared to Ga_2O_3 [2]. The enhancement is ascribed to (1) increased group velocities and (2) reduced anharmonic scattering rates due to the reduced weighted phase space. The findings offer an avenue towards improved heat dissipation from Ga_2O_3 devices.

Work performed in collaboration with Sai Mu and Hartwin Peelaers and supported by AFOSR.

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4:00 PM *SF03.10.02
The Phonon Quantum of Thermal Conductance—What Are We Calculating and What Are We Measuring? Carlos Polanco[1,2], Ambroise van Roekeghem[1,2] and Natalio Mingo[1,2]; [1]CEA, France; [2]Université Grenoble Alpes, France

Two decades after the first reported measurements and calculations of the thermal conductance quantum in suspended nanostructures[1], reconciling experiments and theory remains elusive[2]. Through calculations of phonon transport in micrometer-sized three-dimensional structures, we show that part of the disagreement between theory and experiment stems from a misconception of thermal transport at small scales and low temperatures, and a possible inadequacy of the experimental geometrical designs. After clarifying the meaning of temperature in the wave ballistic regime, we show that the spatial placement and dimensions of thermometers, heaters, and supporting micro-beams in the suspended structures, can noticeably affect the thermal conductance's measured values. In addition, diffusive transport assumptions made in the data analysis may result in measured values that considerably

differ from the actual thermal conductance of the structure.
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4:30 PM SF03.10.03
Ionic Thermoelectric Materials with Giant Thermopower and Figure of Merit Jianyong Ouyang; National University of Singapore, Singapore

Thermoelectric materials are significant for sustainable development because they can be used to directly convert heat into electricity and there is abundant waste heat on earth. The conventional thermoelectric materials are inorganic or orgnaic conductors and semiconductors. However, their thermopower due to the Seebeck effect is low, and their thermoelectric properties are not good enough for large scale application. Recently, ionic thermoelectric materials emerged as the next-generation thermoelectric materials mainly due to their high thermopower. The thermopower of ionic conductors can be higher than electronic conductors/semiconductors by 1-2 orders in magnitude. Here, I will present various methods to improve the thermpower and ionic conductivity of ionic conductors. The thermopower can be higher than 40 mV/K, and the figure of merit (ZTi) can be greater than 6 at room temperature.

4:45 PM SF03.10.04
Effect of Sb-Doping on the thermoelectric Performance of CuInTe$_2$ Sabrine Hachmioune[1,2,2], Seán R. Kavanagh[1,3], Maheswar Repaka[2], Zhai Wenhao[2], Kedar Hippalgaonkar[2,4], Michael Sullivan[2] and David O. Scanlon[1]; [1]UCL, United Kingdom; [2]Agency for Science, Technology and Research, Singapore; [3]Imperial College London, United Kingdom; [4]Nanyang Technological University, Singapore

CuInTe$_2$ is a material of interest for thermoelectric power generation and photovoltaic energy harvesting. We present a detailed experiment-theory study of all intrinsic defect species, followed by extrinsic doping by antimony (Sb), to investigate the optimal conditions for performance. Hybrid-density functional theory (DFT) with spin-orbit coupling (SOC) was used to accurately model the electronic behaviour of CuInTe$_2$. Antimony was the chosen dopant as experimental studies observed an improvement in the power factor and transport properties required for a desirable thermoelectric figure of merit (ZT).[1]
The formation of energies of Cu$_{1-x}$Sb$_x$InTe$_2$, CuIn$_{1-x}$Sb$_x$Te$_2$ and CuInTe$_{2-x}$Sb$_x$ systems were calculated to determine the lowest energy defective composition, employing the ShakeNBreak approach to identify the ground-state defect structures.[2] In addition, a ternary competing phase was included to give new insights on the true phase space of the system.
The effect of Sb-doping on the transport properties of CuInTe$_2$ was then calculated by applying the momentum relaxation time as implemented by the AMSET[3] code. Combining the theoretical and experimental results, we rationalise the effect of Sb-doping on the power factor and electrical thermal conductivity, yielding insights and design principles that can be applied to optimise performance in this and other emerging thermoelectric materials.
1. D.V.M. Repaka, Z. Wenhao (in progress)
2. I. Mosquera-Lois, S. R. Kavanagh, A. Walsh and D. O. Scanlon, 2022.
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5:00 PM SF03.10.05
Effect of Antiferromagnetic Order on Thermal Conductivity of NiO from 125 to 700 K Qiyang Sun[1], Songrui Hou[1], Bin Wei[2], Yaokun Su[1], Victor H. Ortiz[1], Bo Sun[3], Jiao Lin[4], Hillary Smith[5], Sergey Danilkin[6], Douglas L. Abernathy[4], Richard B. Wilson[1] and Chen Li[1]; [1]University of California, Riverside, China; [2]Henan Polytechnic University, China; [3]Tsinghua University, China; [4]Oak Ridge National Laboratory, United States; [5]Swarthmore College, United States; [6]Australian Nuclear Science and Technology Organisation, Australia

Thermal transport in magnetic insulators is governed by lattice dynamics, spin dynamics, and the interactions between these two systems. Thermal transport mechanisms of how phonons carry heat are well understood. However, how phonon-magnon interactions affect conduction is not well established. In this work, we use time domain thermoreflectance to measure the thermal conductivity of NiO between 125 and 700 K. Nickle oxide (NiO) is an antiferromagnetic material with Néel temperature being 523 K. We observe that the thermal conductivity (Λ) of NiO has an anomalous $T^{-1.5}$ temperature dependence between 200 and 500 K, and a more normal dependence above 550 K. To understand the origins of the anomalous temperature dependence below 500 K, we measured the phonon and magnon dispersion relations at 10, 300, 550, 640 K by inelastic neutron scattering. We observe NiO loses its long-range spin order at temperatures above its Néel temperature. And we observe no evidence of phonon softening near the Néel temperature that could explain the anomalous dependence of Λ. Therefore, we credit the temperature dependence to phonon scattering caused by spin-disorder. As spin-disorder increases near the Néel temperature, phonon lifetimes decrease. The effect of spin-disorder saturates at the Néel temperature of 523 K. To support this hypothesis, we performed first-principles calculations of Λ vs. T between 200 and 500 K that include the effects of phonon-phonon and phonon-defect scattering. Our study improves understanding of how spin-disorder in magnetic materials effects phonon lifetimes and conduction.

SESSION SF03.11: Thermal Transport of Nanostructures and Interfaces
Session Chairs: Renkun Chen and Lucas Lindsay
Thursday Morning, April 13, 2023
Marriott Marquis, B2 Level, Golden Gate A

8:00 AM *SF03.11.01
Increasing Thermal Conductivity in Assemblies of Colloidal Nanocrystals and Magic-Sized Clusters Robert Y. Wang; Arizona State University, United States

Colloidal nanocrystal assemblies are actively been explored for a variety of electronic and optical applications, and are already being commercially-used in LED displays. However, these materials also have low thermal conductivities (0.1 - 0.5 W m^{-1} K^{-1}), which will lead to heat dissipation challenges as they become used in an increasing number of applications. The low thermal conductivity in these materials stems from organic ligands that cover the surface of these nanocrystals. These organic ligands result in weak van der Waals interactions between adjacent nanocrystals that in turn rate-limit thermal transport. In this talk, I discuss my group's ongoing work to improve thermal transport in these materials. More specifically, I present three different methods for improving thermal conductivity: (i) crosslinking the organic ligands between adjacent nanocrystals, (ii) increasing nanocrystal order via superlattice formation, and (iii) improving size dispersion through the use of magic-sized clusters. We show that each approach can lead to ~3-fold improvements in thermal conductivity. To complement these thermal transport measurements we also perform materials characterization, mechanical measurements, and modeling on these materials.

8:30 AM SF03.11.02
High-Performance and Flexible Thermal Interfaces Based on Self-Assembled Boron Arsenide Ying Cui, Zihao Qin, Huan Wu, Man Li and Yongjie Hu; University of California, Los Angeles, United States

Thermal management is the most critical technology challenge for modern electronics. Recent key materials innovation focuses on developing advanced thermal interface of electronic packaging for achieving efficient heat dissipation. Here, for the first time we report a record-high performance thermal interface beyond the current state of the art, based on self-assembled manufacturing of cubic boron arsenide. The self-assembly of BAs exhibits highly desirable characteristics of high thermal conductivity up to 21 W/mK and excellent elastic compliance similar to that of soft biological tissues down to 100 kPa through the rational design of BAs microcrystals in polymer composite. In addition, the s-BAs demonstrates high flexibility and preserves the high conductivity over at least 500 bending cycles, opening up new application opportunities for flexible thermal cooling. Moreover, we demonstrated device integration with power LEDs and measured a superior cooling performance of BAs beyond the current state of the art, by up to 45 °C reduction in the hot spot temperature. Together, this study demonstrates scalable manufacturing of a new generation of energy-efficient and flexible thermal interface that holds great promise for advanced thermal management of future integrated circuits and emerging applications such as wearable electronics and soft robotics.

8:45 AM SF03.11.03
Twin Boundaries in Bi2Te3—Their Impact and Importance in Thermal Transport Aoife K. Lucid[1], Javier F. Troncoso[2], Jorge Kohanoff[2], Stephen B. Fahy[1] and Ivana Savic[1]; [1]Tyndall National Institute, Ireland; [2]Queen\'s University Belfast, United Kingdom

Highly efficient, room-temperature thermoelectric materials are key to the future of environmental energy harvesting, solid-state cooling, and the powering of the Internet of Things, among many other applications. In pursuit of such materials, the impact of nanostructure engineering on thermal transport is a factor which must be carefully considered. Nanostructured thermoelectric materials are generally highly polycrystalline, meaning extended defects such as interfaces, are prevalent. Advancing beyond the current state-of-the-art room-temperature thermoelectrics requires an atomistic-level understanding of the impact of interfaces on thermal transport in currently utilised materials, such as Bi2Te3. Ideally, interfacial properties could be linked to thermal transport, allowing targeted engineering of interfaces and leading to optimised thermoelectric materials. These insights can also be extended to new and emerging materials.

In this work, we employ reverse non-equilibrium molecular dynamics simulations (rNEMD)[1] with a recently developed classical two-body interatomic potential[2], to examine the effect of specific interfacial structures, in this case, twin boundaries, on thermal transport in Bi2Te3. The quintuple layer structure of Bi2Te3, separated by van der Waals gaps, lends itself readily to the formation of interfaces, e.g. basal plane twin boundaries[3]. The interfacial thermal resistance (Kapitza resistance) and interfacial structures are compared across a number of twin boundaries. Density-functional theory (DFT) optimised twin boundary structures and formation energies are also compared to existing interatomic potentials. Additionally, we will examine the impact and importance of finite-length effects in rNEMD simulations of interfaces as these are frequently overlooked or not discussed. We will also explore the limitations of existing classical interatomic potentials (for interfacial simulations) and consider the development of machine-learned interatomic potentials for Bi2Te3.

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This work is supported by the Irish Research Council Government of Ireland Postdoctoral Fellowship 2021/823, a research grant from Science Foundation Ireland (SFI) and the Department for the Economy Northern Ireland under the SFI-DfE Investigators Programme Partnership, Grant No. 15/IA/3160 and also by SFI Grant No. 13/RC/2077.

9:00 AM SF03.11.04
Phonon-Influenced Transport Characteristics of Superionic ThO_2 Yuqing Huang, Anant Raj and Jacob Eapen; North Carolina State University, United States

Fluorites, which belong to the class of superionic materials, exhibit a second order phase transition at a critical temperature below the melting point. Thoria (ThO_2), which is a promising oxide nuclear fuel, portrays superionic behavior at high temperatures, particularly in accident conditions. Phonon properties such as dispersion and lifetimes are crucial to understanding the thermal response of nuclear fuel under such conditions. However, the interplay between the phonon properties and anion transport in the superionic state remains as a fundamental knowledge gap. In this work, molecular dynamics simulations are performed with ThO_2 at high temperatures using the BPNN-SCAN potential [*Sci. Rep.* 12(1) (2022)]. First, the temperatures corresponding to the onset of the superionic state and the second order phase transition are determined. Then, the oxygen ion transport, which occurs through correlated hopping in the superionic state, is quantified. Lastly, the excited phonon modes and interactions are correlated to anion hopping and glass-like dynamics in the superionic state. Our work highlights how phonon dynamics influences anion transport in ThO_2 at high temperatures.

9:15 AM SF03.11.05
Low Temperature Enhancement of *Z* in Silicon "Nanoblade" Micro-Thermoelectric Coolers Mark Lee[1], Ruchika Dhawan[1,2] and Hal Edwards[2]; [1]The University of Texas at Dallas, United States; [2]Texas Instruments, United States

To improve thermal management in Si integrated circuits (ICs), micro-thermoelectric coolers (µTECs) compatible with ICs are being investigated. Most research on µTEC technology concentrates on materials having high TE factor $Z = (\alpha^2\sigma)/\kappa$, where α, σ, and κ are the thermopower, electrical conductivity, and thermal conductivity. The focus on high Z materials is because the maximum temperature reduction achievable is $\Delta T_{max} = (T_{source} - T_{sink}) = -\tfrac{1}{2}Z(T_{source})^2$, where T_{source} and T_{sink} are the temperatures of the heat source and sink. However, high Z materials can be expensive, often contain toxic or rare elements, and may be incompatible with IC processing. Si is not usually considered a viable TE material because its high phonon contribution to κ makes its $Z \sim 1\%$ of modern high Z materials.
Doped Si nanowires (SiNWs) can have Z values competitive with state-of-the-art high Z materials while being compatible with IC processing. It is believed this enhancement in Z is due to the cross-sectional dimensions of SiNWs being smaller than the phonon mean-free-path (mfp), increasing phonon surface scattering and reducing κ. However, over the past decade µTE devices incorporating SiNWs or other kinds of Si nanostructures have mostly failed to demonstrate substantial enhancements in performance that should result from higher Z.
We report on prototype µTECs using $Si_{0.97}Ge_{0.03}$ as the TE material, made on an industrial Si IC process line. The TE elements were structured by standard lithographic etching into "nanoblades" 80 nm wide by 350 nm tall by 750 nm long. By comparison, the phonon mfp near 300 K is ~ 200 nm. For T_{source} = 300 K, using bulk material parameter values the ideal $\Delta T_{max} \approx -1.5$ K, while our measured $\Delta T_{max} = -0.3$ K. The reduction from ideal value is due to parasitic series resistances. Near 300 K the inferred Z value of the nanoblades is indistinguishable from bulk material.
However, at T_{sink} = 150 K, ΔT_{max} remains nearly constant. That is, these µTECs can still reduce T_{source} by around –0.3 K below T_{sink} , and measurable

cooling of T_{source} persists to $T_{\text{sink}} \sim 100$ K. If the values of all material and device parameters were temperature independent, then we expect $\Delta T_{\max}(150\ \text{K})/\Delta T_{\max}(300\ \text{K}) = ¼$. The fact that the measured ratio is actually close to unity cannot be attributed to decreases in parasitic resistances; these tend to increase at lower temperature which should make $\Delta T_{\max}(150\ \text{K})/\Delta T_{\max}(300\ \text{K}) < ¼$.
We then infer that the nanoblades' $Z(150\ \text{K})/Z(300\ \text{K}) > 4$ to compensate for the temperature decrease. However, using bulk material properties indicates $Z(150\ \text{K})/Z(300\ \text{K})$ should be < 1. This implies a low temperature increase in Z unrelated to bulk behavior. We believe the likely cause is an increase in the phonon mfp with decreasing temperature; the mfp is estimated to be ~ 3x longer at 150 K compared to 300 K. Thus at 300 K a nanoblade is smaller than the phonon mfp in width only, whereas at 150 K it becomes smaller in both width and height. This makes phonon heat transport effectively one-dimensional, which could significantly reduce the phonon contribution to κ and enhance the nanoblade Z. Full experimental results and comparisons to theoretical analyses of low dimensional phonon transport on Z will be presented.

9:30 AM *SF03.11.06
Thermal Transport in Flowing Granular Media Renkun Chen; University of California, San Diego, United States

Granular media such as ceramic particles have been used as heat transfer media in heat exchangers for solar-thermal energy capturing and storage systems. However, thermal transport processes in flowing granular media are still not fully understood. Particularly, it is still not clear whether and how the thermal conductivity of the particles in the near-wall region could be impacted by the particle -wall interaction when the particles are flowing. While numerous models exist, there is a lack of a suitable experimental technique to directly probe the thermal transport processes of flowing granular media. In this work, we report the instrumentation development of high-temperature thermal conductivity measurement of flowing ceramic particles within a confined channel. We extend an existing technique called modulated photothermal radiometry (MPR) to high temperature measurements (up to 700 deg. C). MPR is a non-contact technique where the surface of the sample is heated by an intensity-modulated laser and it utilizes the intrinsic thermal emission from the specimens for thermometry, which is favorable for the measurement at high temperature in harsh environment. The high-temperature MPR setup is validated by measuring bulk, thin coatings, and liquids with known thermal conductivity. We then develop the technique for measuring both stationary and flowing ceramic particles. The results on the stationary particles are in good agreement with those obtained from a transient hot wire (THW) technique. The measured effective thermal conductivity of the flowing particles, however, show considerable reduction in thermal conductivity compared to the stationary ones. Further analysis of the frequency dependent data shows that this reduction in thermal conductivity is originated from the particle-wall thermal resistance. The measurement results are coupled with modeling based on the discrete element method (DEM) to understand thermal transport in both the bulk and near-wall regions of flowing particles.

SESSION SF03.12: Thermal Characterizations Under Interactions and Processing
Session Chairs: M Cynthia Hipwell and Jonathan Malen
Thursday Morning, April 13, 2023
Marriott Marquis, B2 Level, Golden Gate A

10:15 AM *SF03.12.01
High Speed Thermal Imaging of Melt Pools Reveals Underlying Thermophysics in Additive Manufacturing Processes Jonathan A. Malen, Alexander Myers and Guadalupe Quirarte; Carnegie Mellon University, United States

At its heart, additive manufacturing (AM) of metals is a heat transfer problem that depends on many nano and microscale thermophysical processes. Laser powder bed fusion, the most popular AM process uses a moving heat source (e.g. laser or an electron beam) to sinter metal powder together in predefined patterns, to build parts layer by layer. Temperature fields control the stability of the melt pool and common defect structures in laser powder bed fusion (L-PBF) parts. Experimental measurements of the melt pool temperature using conventional infrared imaging techniques or pyrometry lack the temporal and spatial resolution needed to determine melt pool temperature profiles. We have developed an alternative experimental method to measure melt pool and surrounding temperatures using a high-speed color camera (>50,000 frames per second). This method creates real-time thermal imaging AM tool leveraging the principle of two-color (a.k.a. dual-wavelength) pyrometry, where each pixel acts as a two-color pyrometer. Relative to conventional thermal imaging approaches, two-color pyrometry is advantageous because it is less sensitive to melt pool emissivity, plume transmissivity, and the camera's view factor. Our initial two-color experiments were performed using a Photron AX200 high speed color camera where the temperature given by the ratio of the red to green pixel values was validated against the NIST blackbody source.
Temperatures from melt pools of Ti-6Al-4V, Inconel, and 316L-SS were taken as a function of laser power and scan velocity offer new information about the thermophysical processes occurring in the melt pool. Our high resolution temperature images are amongst the first taken of the melt pool and suggest that temperatures peak between 3500-4000 K in these materials. These temperatures, which are directly under the laser, can surpass the metal's vaporization temperature causing the vaporization of material into a metal vapor plume. The mass loss due to vaporization, which is modified by the accommodation coefficient, results in a downward pressure on the melt pool, inducing convective flows towards the back of the melt pool. In addition, a vapor depression is formed such that the laser reflects internally, increasing the effective absorptivity for higher energy density processing conditions. Surface tension gradients can also induce convective currents in melt pools, known as Marangoni convection. Temperature-dependent specific heat, thermal conductivity, and density also impact the melt pool and surrounding temperatures. Computational fluid dynamics packages such as FLOW-3D incorporate these melt pool physics but require several input parameters that are uncharacterized. Surface temperatures measured with our high-speed two-color thermal imaging system are a starting point to fit uncharacterized parameters and validate these complex multi-physics models.

10:45 AM SF03.12.02
Ultrafast Ultraviolet Transient Grating—Tabletop Access to Nanoscale Thermal Transport in High-Bandgap Materials Joshua Knobloch, Brendan McBennett, Emma Nelson, Albert Beardo, Henry Kapteyn and Margaret Murnane; STROBE, JILA, University of Colorado Boulder, United States

Nanostructuring on length scales comparable to the fundamental length scales of phonons in materials such as silicon can provide control over thermal transport, making it possible to engineer thermal properties [1]. Finding effective thermal management strategies is critical for a host of applications, as temperature often determines the speed and efficiency, *e.g.* the clock-speed of modern processors is limited due to a heat buildup [2]. However, as devices become increasingly complex, thermal management solutions are elusive due to a lack of predictive models that span from micro-to-nano-to-atomic scale lengths. To advance our understanding of nanoscale heat flow, more precise measurements of the thermal properties of general, complex, nanostructured, and high-bandgap materials are needed, which can be used to validate predictive theories.
Specifically, recent research has shown that transient thermal grating experiments can reveal non-diffusive thermal transport [3], as well as exotic phonon behaviors such as second sound [4]. However, due to the fundamental diffraction limit of visible light, such visible-laser-based techniques cannot access the nanoscale length scales (<0.5 μm) relevant to advanced devices. Moreover, visible lasers cannot directly excite high-bandgap materials such as ceramic

materials for advanced battery applications, or diamond for quantum systems applications. Our recent work has demonstrated that tabletop, coherent short-wavelength laser-like beams can provide unique insight into the thermal transport properties of nanosystems—uncovering surprising new behaviors. These include exploring and explaining new behaviors for the cooling of periodic nanostructured heaters where close-packed hot spots cool faster than widely-spaced ones [5-7], validating novel theories using a hydrodynamic-like transport equation to predict phonon flow in general semiconductors [7], and a universal scaling of nanoscale heat flow in highly-confined geometries [8].

Here, we combine the versatility of tabletop transient thermal grating experiments with the sensitivity and precision of short-wavelength light by demonstrating a deep-ultraviolet (UV) transient grating metrology using ultrafast UV lasers with wavelengths <200 nm and with 100s of femtosecond pulse durations. We first upconvert ultrafast, infrared pulses to the deep-UV using nonlinear crystals [9], and then split and recombine the pulses to create a transient, sinusoidal interference pattern [10] of deep-UV light on the sample. The relaxation of the resulting sinusoidal thermal excitation is then observed using an ultrafast probe beam with wavelengths from the visible to UV. The short-wavelength of the light allows us to probe transport distances on the 100s of nanometer scale in both visibly-transparent and opaque materials. We then use this technique to observe non-diffusive nanoscale thermal transport in diamond on scale lengths less than dominant phonon mean free paths. We use microscopic theories and mesoscopic models to benchmark our results. This work demonstrates that tabletop sources of ultrafast, deep-UV light can reveal new insight into phonon transport at its intrinsic scales in a general set of materials allowing for the development and validation of advanced theories and for nondestructive, noncontact characterization of thermal properties of energy and quantum materials.

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11:00 AM SF03.12.03
Developing Next Generation Building Envelope Insulation Emily F. Thomas[1,2] and Peter Holliman[1]; [1]Swansea University, United Kingdom; [2]TATA Steel, United Kingdom

In 2020, an average of 67% of the total household energy consumption within the EU was used for space heating in buildings.[1] Thermal insulation is crucial to improving the thermal efficiency of buildings by reducing the heat lost through the building envelope to the outside environment.[2] Organic based materials such as polyisocyanurate (PIR) foams are the current industry leading thermal insulation material for buildings due to their low density (< 45 kgm^{-3}), suitable structural properties, and low thermal conductivity (0.024 Wm^{-1}K^{-1}). But, despite these advantageous properties, PIR is classified as combustible, with a fire rating class of B-s2 according to the European fire classification system.[3] The Grenfell Tower disaster in London in 2017 demonstrated a fire propagating in a building envelope through combustible insulation.[4] Following this fire, the UK government banned combustible materials from the exterior of buildings taller than 18m.[5] According to the European fire classification, all new insulation materials must now be classed as A1, non-combustible or A2-s1, a limited combustible material (i.e. must self-extinguish < 10 s after ignition).[6] Stone wool an inorganic thermal insulation material with excellent fire resistance (A1 rating) but, a density up to 180 kgm^{-3} which is not ideal for building insulation.[7] Therefore, the study of low-density inorganic materials is a new concept to improve the fire ratings.

This work studies adding expanded perlite (EP) and powdered aerogel into PIR foam system. Both EP and aerogel provide a low-density cellular structure with a high surface area, and a low thermal conductivity, along with heat resistance and the necessary structural properties. EP and aerogel have previously been used as insulating materials in seldom, making them ideal materials to add to the existing PIR system.[8][9]

The experiments focused on three foam formulations, a low weight addition of either EP, aerogel or a 50/50 mix of EP and aerogel, to explore the feasibility of adding solid-state materials into a liquid-based material. All foams exhibit low thermal conductivity, an average at 0.021 Wm^{-1}K^{-1}, densities below 45 kgm^{-3}, but slightly higher compression values versus PIR. Foams were also studied using two different heat sources for visual and quantitative data. First, a radiant heat furnace was ramped from ambient to 600°C with samples (25x35x20mm) removed every 50°C. Mass and dimensions were recorded at each step to quantify mass loss and expansion/shrinkage. At 600°C, masses remaining were PIR (4%), EP (15%), aerogel (12%) and 50/50 mixture (5%), respectively. Secondly, a propane flame placed below the foam to study thermal heat transfer throughout the foam by thermography with data calibrated for foam emissivity to plot temperature against time. The data suggest that inorganic particles absorb and scatter heat (IR light) causing an average decrease in temperature across the foam, when compared with pure PIR.

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11:15 AM SF03.12.04
High-Performance Modeling of First-Principles Electron and Phonon Transport Using Phoebe Jennifer Coulter[1], Andrea Cepellotti[1], Anders Johansson[1] and Boris Kozinsky[1,2]; [1]Harvard University, United States; [2]Robert Bosch LLC, United States

The theoretical prediction of electrical and thermal transport properties relies on an accurate description of the electrons, phonons, and their interactions must be considered to accurately predict transport behavior. While first-principles methods based on density functional theory can describe these material-specific quasiparticle properties, using this information to calculate transport coefficients can be computationally demanding. To address this challenge, we developed Phoebe (https://mir-group.github.io/phoebe/), which includes the effects of electron-phonon and phonon-phonon interactions to predict the transport properties of materials by solving the Boltzmann transport equation (BTE) using a full scattering matrix formalism. In this talk, I will report on ongoing new features of Phoebe, including the addition of magnetotransport calculations as well as new tutorials and updated performance benchmarks.

11:30 AM *SF03.12.05

Tunable Thermal Conductance of Termination-Engineered MXenes through Intercalation M Cynthia Hipwell and Aditya Kuchibhotla; Texas A&M University, United States

First discovered in 2011, selective etching of transition metal carbides and nitrides with general formula $M_{n+1}AX_n$ in Hydrofluoric acid (HF) or HF-forming etchants results in a new class of layered two-dimensional (2D) materials called MXenes ($M_{n+1}X_nT_z$, where T is termination group, such as –O, -F, PH, -Cl). First principle thermal conductivity calculations of monolayer MXenes have demonstrated an order of magnitude change in thermal conductivity by changing surface termination from -F to -O due to increased phonon scattering rate and reduced phonon mean free path. While extensive research on unique electrical, electrochemical, and mechanical properties of MXenes has been reported, no experimental investigations exist characterizing thermal transport performance of a stack of MXene nanosheets or large area free-standing multi-layer MXene sheets. Here I will present our current research endeavors in advancing the application of MXenes in thermal management. Combining elemental analysis tools such as XRD with AFM for chemical and structural characterization and Time-Domain Thermoreflectance (TDTR) for thermal conductance measurements, we explore the correlation between surface functionalization and thermal transport. I will also describe our efforts beyond surface functionalization to further control the thermal transport through MXenes via electrochemical intercalation. Our findings lay the groundwork for advancing the engineering thermal transport through MXenes, both actively or passively, having wide reaching impact in energy harvesting, conformal/wearable electronics, electromagnetic interference shielding, and thermal management.

12:00 PM SF03.12.06

Thermal Conductivity Enhancement Through Kinetically Arrested Dispersion—Breaking Dispersion Barriers of Highly Conductive Carbon Allotropes in Aqueous Solutions Lucas L. Cullari[1], Istvan Furo[2], Gennady Ziskind[1] and Oren Regev[1]; [1]Ben-Gurion University of the Negev, Israel; [2]KTH Royal Institute of Technology, Sweden

Carbon-based nanomaterials such as graphene are usually produced industrially as powder-like materials. Harnessing the incredible potential of these nanocarbons (e.g., high electrical and thermal conductivities) in many applications (e.g., conductive inks and heat transfer fluids) requires their dispersion. However, when the highly hydrophobic graphene sheets are dispersed in water, they tend to aggregate and precipitate due to strong van-der-Waals attraction. Surface treatment of graphene (via surfactant adsorption or chemical modification) results in a low concentration of dispersed graphene (<0.2wt%) of relatively small lateral size (<0.5µm), or in high defect density, both are detrimental for thermal management applications. In this work, we disperse graphene in water by adding fibrous clay mineral - sepiolite - a negatively charged particle, which kinetically arrests the system. The “trapped” graphene cannot re-aggregate and precipitate. The trapping mechanism makes it possible to disperse high graphene concentration (1wt%) with high lateral size (>5µm). This approach applies to all three dimensionalities of carbon, that is, 1D-carbon nanotubes, 2D-graphene and 3D-graphite. The thermal conductivity (TC) of liquids, an essential parameter in heat dissipation applications, could be enhanced by 31% via loading graphene as a filler material both in water, and in commercial cooling liquids such as water-ethylene glycol mixtures. The proposed dispersion approach is filler independent, and could be employed in enhancing composite properties both in liquid and solid states for thermal managment applications of electronics.

SESSION SF03.13: Nanoscale Imaging and Transport

Session Chairs: Amy Marconnet and Xiaoqing Pan
Thursday Afternoon, April 13, 2023
Marriott Marquis, B2 Level, Golden Gate A

1:30 PM SF03.13.01

Characterizing Highly-Confined Heat Flow, Elastic Properties and Porosity in a Semiconductor Metalattice Emma Nelson[1], Brendan McBennett[1], Albert Beardo Ricol[1], Charles Bevis[1], Sadegh Yazdi[2], Begoña Abad Mayor[1], Travis Frazer[1], Jorge Hernández-Charpak[1], Amitava Adak[1], Yuka Esashi[1], Hiu Y. Cheng[3,3], Alex J. Grede[3,3], Pratibha Mahale[3], Nabila Nova[3,3], Noel Giebink[3,3], Thomas Mallouk[3], John Badding[3,3], Baowen Li[4,2], Henry Kapteyn[1], Margaret Murnane[1] and Joshua Knobloch[1]; [1]University of Colorado, Boulder, United States; [2]University of Colorado Boulder, United States; [3]The Pennsylvania State University, United States; [4]Southern University of Science and Technology, China

Nanostructured semiconductors can exhibit thermal properties unachievable in bulk systems due to the increased influence of surfaces and interfaces. The ability to understand and fully characterize the thermal, elastic, and structural properties of these nanostructured semiconductor materials is important for developing new materials with tunable properties for applications in next-generation nanoelectronics and energy efficient devices. Managing thermal transport in nanoscale materials is critical for optimizing the performance of computer chips—however, when the critical dimensions have the same length scales as the average phonon mean free paths, traditional theories of heat flow break down. Moreover, first principles models of nanoscale thermal transport are too computationally challenging for 3D nanostructured geometries, while mechanistic approaches make overly simplistic assumptions about the nature of phonon-boundary interactions.

Here, we probe the elastic and thermal properties of a 3D nanostructured silicon metalattice, which consists of an interconnected network of nanoscale pores that dramatically alter the material properties compared to bulk crystalline silicon. We impulsively heat nickel grating transducers that are fabricated on the 3D silicon metalattice sample using an infrared pump laser pulse. This launches acoustic waves and heat into the metalattice, which we probe using diffraction from an extreme ultraviolet (EUV) probe pulse. This technique has high spatial and temporal resolution, since the ~30nm EUV light has a wavelength much shorter than that of visible light, with a pulse duration of ~10fs.

By using metallic gratings of varying linewidths and periodicities, we launch surface acoustic waves in the metalattice with wavelengths equal to the grating periodicity. These surface acoustic waves are detected by the probe as changes in the reflectivity and the surface displacement of the sample. We compare the experimental data to finite element models of the 3D silicon metalattice to nondestructively extract porosity and Young’s modulus. Also, by varying the period of the metallic grating we can vary the acoustic wave penetration depth, allowing us to characterize the 3D silicon metalattice film thickness and substrate elastic properties. To validate our extracted porosity value and the metalattice geometry models, we compare to 3D electron tomography reconstructions of the sample geometry [1].

Using the extracted porosity and elastic properties, we model heat flow in the metalattice using finite element methods and fit an apparent thermal conductivity two orders of magnitude below bulk silicon. We model the heat flow dynamics using a Fourier-like relation with an apparent conductivity indicating two key conclusions: the size of the heat source does not significantly affect the heat flow as the metalattice geometry dominates, and the transport is diffusive-like in highly-confined situations where ballistic transport is traditionally expected. We compare our results to other highly-confined nanostructured systems by separating the thermal conduction into a permeability component, which captures the geometry of the system, and a viscosity component related to the intrinsic phonon properties. This treatment reveals a universal trend in the permeability which can be used to predict the thermal conductivity in general nanostructured silicon systems—from nanomeshes, to metalattices, to porous nanowires and nanowire networks.

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1:45 PM DISCUSSION TIME

2:00 PM *SF03.13.03
Nanoscale Imaging of Phonon Dynamics Emergent from Single Defect and Interface by Electron Microscopy Xiaoqing Pan; University of California, Irvine, United States

Crystal defects and interfaces affect the thermal and heat-transport properties of materials by scattering phonons and modifying phonon spectra. Spatially resolved vibrational mapping of nanostructures and defects is indispensable to the development and understanding of thermal nanodevices, modulation of thermal transport and novel nanostructured thermoelectric materials. Through the engineering of complex structures, such as alloys, nanostructures and superlattice interfaces, one can significantly alter the propagation of phonons and suppress material thermal conductivity while maintaining electrical conductivity. There have been no correlative experiments that spatially track the modulation of phonon properties in and around individual defects and nanostructures due to spatial resolution limitations of conventional optical phonon detection techniques. In this talk, I will show that the vibrational spectra of a single defect or interface can be imaged by space- and angle-resolved vibrational electron energy-loss spectroscopy in a transmission electron microscope. It reveals a red shift of several meV in the energy of acoustic vibration modes near a single stacking fault in cubic silicon carbide, together with substantial changes in their intensity. These changes are confined to within a few nanometers of the stacking fault.[1] In a two-dimensional lateral heterostructure, new phonon modes at 27.9 and 41.1 meV are observed at the interface between monolayer thick MoS_2 and WSe_2 [2]. At a Si-Ge interface, localized interfacial phonon modes at ~48 meV.[3] Simulations show that these interfacial phonon modes contribute to the total thermal interface conductance. By tracking the variation of the Si optical mode in a phonon map from a single SiGe quantum dot, the nanoscale modification of the composition-induced red shift is observed.[4] We also developed a technique to differentially map phonon momenta, providing direct evidence that the interplay between diffuse and specular reflection largely depends on the detailed atomistic structure. Our work unveils the non-equilibrium phonon dynamics at nanoscale interfaces and can be used to study actual nanodevices and aid in the understanding of heat dissipation near nanoscale hotspots, which is crucial for future high-performance nanoelectronics.

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SESSION SF03.14: Thermal Materials with Defects and Disorders
Session Chairs: Elif Ertekin and Ivana Savic
Thursday Afternoon, April 13, 2023
Marriott Marquis, B2 Level, Golden Gate A

3:30 PM *SF03.14.01
Describing the Vibrational and Thermal Properties of "In-Between" Materials Exhibiting Dynamical Disorder—Not Quite a Crystal, Not Quite a Glass Elif Ertekin; University of Illinois at Urbana-Champaign, United States

Certain materials live in configurational phase spaces that accommodate multiple degrees of freedom and host many energetically nearly-degenerate disordered configurations, with facile hopping between them. For example, in hybrid materials like perovskite methylammonium lead iodide ($MAPbI_3$), a high-symmetry lattice is decorated by low-symmetry molecular building blocks. In ion conducting materials such as the halide lithium ion conductor Li3YCl6 an ordered anion sublattice coexists with a cation sublattice that accommodates disorder in the distribution of Li, Y cations and vacancies. While such materials are often associated with "glass-like" thermal conductivity, describing the vibrational modes and thermal transport properties of such materials remains challenging. While the periodicity of conventional crystals enables the excitation of phonons -- propagating vibrational waves that carry heat, by contrast in glasses the lack of periodicity results in more localized and less wavelike vibrational modes most typically described by the theory of Allen/Feldman. In this presentation, we will highlight our recent investigations of vibrational transport in materials exhibitting dynamical disorder. Using MAPbI3 and Li3YCl6 as examples, we explore the application and limitations of both the phononic and glassy description, as well as recently developed two-channel models, to materials that lie in between crystalline and glassy. Using molecular dynamics, spectral energy density analysis, first-principles determination of higher order force constants, and Allen/Feldman theory we describe the vibrational properties of both the ordered prototype as well as of explicitly disordered versions of each material. A microscopic framework linking anharmonicity and soft bonding arising from chemistry, to the breakdown of the wavelike picture, to the presence of dynamical disorder is presented.

4:00 PM SF03.14.02
Stereochemical Modulation of Lone-Pair Electrons and Its Impact on Lattice Thermal Conductivity Hanhwi Jang[1], Michael Toriyama[2], G. J. Snyder[2], Yeon Sik Jung[1] and Min-Wook Oh[3]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Northwestern University, United States; [3]Hanbat National University, Korea (the Republic of)

Crystalline solids containing lone-pair electrons (LPEs) are of fundamental interest because the existence of LPEs makes physical properties (e.g., mechanical, optical, electrical, and thermal properties) of materials distinct from conventional materials. Among them, thermal properties have gathered significant attention from thermoelectric researchers because of the intrinsically low lattice thermal conductivity of LPE-containing solids, which is crucial for achieving high thermoelectric conversion efficiency. Conventional thermoelectric materials were intentionally doped with several impurities to suppress a propagation of phonons and reduce the lattice thermal conductivity. However, an intrinsically low lattice thermal conductivity of LPE-containing materials provided a room for optimizing electrical properties within a limited solubility of dopants, leading to a success in discovery of high-performance thermoelectric materials such as $AgSbTe_2$.
ABX_2-type compounds (A=Cu, Ag, B=Sb, Bi, X=S, Se, Te) are one of the typical LPE-containing materials, where s-orbital electrons of B-site cations

remain unpaired. These LPEs are known to exhibit strong lattice anharmonicity, which leads to the intrinsically minimal lattice thermal conductivity at room temperature. However, a clear demonstration of the effect of LPEs on the lattice thermal conductivity has not been reported. For example, it is not obvious whether the lattice thermal conductivity increases or decreases when some LPEs are eliminated from the lattice. Identifying the consequence of aforementioned question is important in that some dopants may reduce the concentration of LPEs due to their bonding characteristics.
Here, we experimentally demonstrate a rise of the lattice thermal conductivity with doping in Cd-doped $AgSbSnSe_3$, which is contradictory to the result expected from a conventional phonon scattering theory. We found that despite of an increased point defects scattering, more LPEs become stereochemically inactive with increasing Cd concentration, and this makes the lattice more harmonic. Systematic pair distribution function analysis by powder X-ray diffraction measurements reveal that the off-centering of cations is reduced and the crystal structure changes symmetrically with Cd doping. Density functional theory calculations support that these “harmonic” environment does not allow LPEs to suppress the phonon propagation, and ironically leads to higher lattice thermal conductivities with a doping. This study corroborates an importance of preserving LPE configurations in ABX_2-type compounds for maintaining intrinsically low thermal conductivity when designing thermal-glass materials.

4:15 PM SF03.14.03
Resolution Limits of Frequency Domain Thermoreflectance for Interconnect Damage in Heterogeneously Integrated Microsystems Wyatt Hodges, Amun Jarzembski, Brenden Herkenhoff, Ben Treweek, Anthony McDonald, Matt Jordan, Tim Walsh and G. W. Pickrell; Sandia National Laboratories, United States

In both industrial and consumer electronics, there is demand for increased computational power with a smaller physical footprint. Heterogeneously Integrated (HI) microsystems, using combinations of application-specific chiplets, have emerged as a way to deliver increased performance in smaller areas. HI architectures are typically constructed using metal microbumps to connect the set of chiplets. Damage to the microbumps can be detrimental to overall microsystem performance. These interconnects can be easily harmed during manufacturing processes or use, but damage identification in the metal interconnects is challenging for existing measurement techniques because the interconnects lie beneath the surface of the chiplets. Electron microscopy techniques offer detailed pictures of damage, but require cross sectioning of the HI device to interrogate the relevant interconnects. Other techniques such as acoustic microscopy or ultrasound are less destructive, but require extremely high frequencies (GHz) to image small features, and offer more limited data on interconnect failure.

To offer more detailed assessment of HI interconnect state of health, this talk demonstrates use of Frequency Domain Thermoreflectance (FDTR) to assess these subsurface geometries. The typical implementation of FDTR is a two-laser pump-probe setup which interrogates the sample of interest in the frequency domain. A metal transducer layer is patterned onto a sample to convert the incident pump laser into heat, which diffuses into the sample. Measured changes in reflected probe signal are proportional to the temperature rise on the sample surface in response to the heating from the pump beam. Typically, an analytical heat transfer model assuming radial symmetry is used to fit for thermal properties of the sample based on the phase difference between the reflected signal and pump beam assuming radial symmetry of the sample.

To demonstrate FDTR capability to assess HI microsystem interconnect state of health a thermal finite element analysis (FEA) model is validated and used in Sandia’s structural dynamics FEA code (Sierra/SD). The FEA model frees the analysis from relying on radially symmetric geometries, and shows that FDTR can be leveraged to sense buried rectilinear features. This model is used to calculate expected phase deviation due to a damaged interconnect, and is additionally used to examine the relationship between depth and resolvable feature size. FDTR is shown to be viable for sensing HI features through silicon layer thicknesses of over 100 microns. These model predictions are compared to FDTR imaging data collected on mock HI microsystems, and effects of experimental noise floor are examined.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.

4:30 PM SF03.14.04
Impact of Static and Dynamic Disorder on Thermal Conductivity of Sodium Superoxide (NaO_2) Hariharan Ramasubramanian[1], Cheng Shao[2] and Alan McGaughey[1]; [1]Carnegie Mellon University, United States; [2]Shandong Institute of Advanced Technology, China

The pyrite phase of sodium superoxide, NaO_2, is studied using molecular dynamics simulations to understand the influence of static and dynamic disorder on its thermal conductivity at temperatures between 50 and 500 K. NaO_2 is a discharge product in sodium-air batteries that can be recharged at lower overpotentials than the expected peroxide. Understanding NaO_2 vibrational structure and thermal transport will enable specification of working conditions that favor its production.
In the pyrite structure, the Na^+ and O^-_2 ions' centers of mass form a simple cubic lattice. Three distinct structural regimes are observed over the studied temperature range based on the rotational autocorrelation function (RACF) of the O^-_2 ions. At lower temperatures, the O^-_2 ions take on an ordered configuration, with orientations aligned along the four cube diagonals, and librate at their lattice sites. In this regime, the RACF is fit to a linear combination of exponential and damped cosine functions to extract the librational frequencies and decay rates. As the temperature increases, the system enters a transition regime exhibiting static disorder, where the O^-_2 ions alternate between librating and rotating to one of the other cube diagonal orientations. At higher temperatures, the O^-_2 ions rotate freely. The RACF quickly decays to zero following a single exponential decay, whose time constant decreases with increasing temperature.
Thermal conductivity is then calculated using the Green-Kubo method to study the impact of static and dynamic disorder across the three structural regimes. The calculations include contributions from both translational and rotational heat fluxes. At low temperatures, where the O^-_2 ions librate and the system is fully ordered, the thermal conductivity shows a crystal-like temperature dependence (i.e., it decreases with increasing temperature). It reaches a value of 5.3 ± 0.2 W/m-K at a temperature of 50 K. At higher temperatures, where the O^-_2 ions freely rotate and the system is dynamically disordered, thermal conductivity increases with increasing temperature similar to a disordered material, reaching a maximum value of 4 ± 0.2 W/m-K. The thermal conductivity reaches its minimum value of 1.4 ± 0.1W/m-K at a temperature of 150 K in the transition regime, where the material is statically disordered. This robust approach is transferable to other crystals that contain molecules with rotational degrees of freedom and can quantify the contributions of molecular rotations to thermal conductivity.

SESSION SF03.15: Poster Session II
Session Chairs: Yongjie Hu and Amy Marconnet
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SF03.15.01

Persistent Hot Carrier Diffusion in Boron Arsenide Single Crystals Imaged by Ultrafast Electron Microscopy Usama Choudhry[1], Fengjiao Pan[2], Xing He[2], Basamat Shaheen[1], Taeyong Kim[1,3], Ryan Gnabasik[1], Geethal Amila Gamage[2], Haoran Sun[2], Alex Ackerman[1], Ding-Shyue Yang[2], Zhifeng Ren[2] and Bolin Liao[1]; [1]University of California, Santa Barbara, United States; [2]University of Houston, United States; [3]Seoul National University, Korea (the Republic of)

Cubic boron arsenide (BAs) is promising for microelectronics thermal management because of its high thermal conductivity. Recently, its potential as an optoelectronic material is also being explored. However, it remains challenging to measure its photocarrier transport properties because of small sizes of available high-quality crystals. Here, we use scanning ultrafast electron microscopy (SUEM) to directly visualize the diffusion of photocarriers in BAs single crystals. SUEM integrates the temporal resolution of femtosecond lasers with the spatial resolution of scanning electron microscopes (SEMs). The change in local secondary electron (SE) yield as a result of the optical excitation is measured and used to form contrast images. Given the shallow escape length of SEs (a few nanometers), SUEM is highly sensitive to surface charge dynamics and has been used to study photocarrier diffusion. We observed ambipolar diffusion at low optical fluence with persistent hot carrier dynamics for above 200 ps, which can likely be attributed to the large frequency gap between acoustic and optical phonons, the same feature that is responsible for the high thermal conductivity. At higher optical fluence, we observed spontaneous electron-hole separation. Our results show BAs is an attractive optoelectronic material combining high thermal conductivity and excellent photocarrier transport properties. Our study also demonstrates the capability of SUEM to probe photocarrier transport in emerging materials.

The work conducted at the University of California, Santa Barbara, is based on research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under award DE-SC0019244 (for the development of SUEM) and by the U.S. Army Research Office under award W911NF-19-1-0060 (for studying photocarrier dynamics in emerging materials). The growth of high-quality BAs crystals at the University of Houston was supported by the U.S. Office of Naval Research under Multidisciplinary University Research Initiative grant N00014-16-1-2436. D.-S.Y. acknowledges the support by the R. A. Welch Foundation (E-1860).

5:00 PM SF03.15.02

Thermal Conductivity of BAs under Pressure Richard B. Wilson[1], Songrui Hou[1], Chen Li[1], Fengjiao Pan[2], Zhifeng Ren[2] and Bo Sun[3]; [1]University of California, Riverside, United States; [2]University of Houston, United States; [3]Tsinghua University, China

BAs has a thermal conductivity (Λ) 10x higher than Si despite similar crystal structure, elastic constants, and density. Its unusually high thermal conductivity is explained by first-principles theory to be a result of its special phonon dispersion relation [1], which limits three phonon scattering rates. To better understand the relationship between BAs' vibrational structure and three- and four-phonon scattering rates, we report experimental measurements of its thermal conductivity vs. pressure, Λ vs. P. Thermal conductivity vs. pressure is measured by time-domain thermoreflectance with a diamond anvil cell. Compression of BAs leads to significant changes in phonon dispersion. An increase in the frequency gap between acoustic and optic phonons should suppress four-phonon scattering and increase phonon thermal conductivity. Alternatively, a decrease in acoustic bunching should increase three-phonon scattering rates and decrease thermal conductivity. Therefore, measurements of $d\Lambda/dP$ provide an experimental measure of the relative importance of three- vs. four-phonon scattering rates. We observe of ~1200 W m^{-1} K^{-1} between 0 and 30 GPa [2]. From 30 to 60 GPa, decreases monotonically to ~600 W m^{-1} K^{-1}. Brillouin scattering measurements show that the speed of sound increases monotonically across this pressure range. Therefore, the decrease in thermal conductivity at high pressures implies large changes in the average phonon lifetime. Our results corroborate first-principles predictions for how three- and four-phonon scattering rates depend on vibrational structure, and expand fundamental knowledge of phonon-physics in high thermal conductivity materials.

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5:00 PM SF03.15.03

Ultrahigh Heat-Generation Power in Ferrite Nanoparticles by Magnetization Resonance Yongsub Kim, Jae-Hyeok Lee and Sang-Koog Kim; Seoul National University, Korea (the Republic of)

Magnetic nanoparticles are increasing interesting due to their unique magnetic properties such as superparamagnetism and particle-size-dependent magnetization dynamics [1-2]. These novel properties make magnetic nanoparticles very attractive for bio-applications including hyperthermia and MRI contrast agents. Nonetheless, their applications are quite limited by their toxicity to human beings and low heating power based on conventional Néel-Brownian relaxation and hysteresis-loss mechanisms.
Here, we found a new magneto-thermal modality entailing resonantly excited magnetization dynamics followed by consequent dissipation [3-5]. We experimentally observed extraordinary high powers of heat generation using MnF_2O_4 nanoparticles: an initial temperature-increment rate of more than 670 K/s over as short a duration as 0.1 sec, with a low AC-field strength of 17 Oe. The observed high-power local heating can be applied not only for magnetic hyperthermia but also for metal ablations via a rapid melting process. Our present work provides a better understanding of the relationship between the fundamental spin dynamics of nanoparticles and their technologically useful application for rapid local heating toward a high target temperature.

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5:00 PM SF03.15.04

Low-Temperature Thermal Characteristics of Graphene Composites—Applications in Thermal Management of Quantum Technologies Zahra Ebrahimnatajmalekshah[1], Youming Xu[1], Jonas Brown[1], Jivtesh Garg[2], Xi Chen[1], Fariborz Kargar[1] and Alexander A. Balandin[1]; [1]University of California, Riverside, United States; [2]The University of Oklahoma, United States

Interfacing electrically the cryogenic superconducting quantum technologies with room-temperature semiconductor electronics requires efficient thermal insulating materials. It is important to insulate cryogenic environments efficiently and reliably while allowing for electrical connectivity. Composites consisting of epoxy with graphene and few-layer graphene fillers show significantly increased thermal conductivity as compared to the base epoxy when measured near and above room temperature [1-2]. We have previously demonstrated graphene composites with thermal conductivity reaching ~15 W/mK at room temperature [3-4]. For comparison, the thermal conductivity of pristine epoxy is ~0.2 W/mK. The thermal characteristics of graphene composites at cryogenic temperature can be strikingly different from those near room temperature. At such temperatures, the added graphene fillers can act more as scattering centers rather than heat-conducting inclusions. We established that at temperatures above 11 K the thermal conductivity increases when increasing the loading of few-layer graphene. However, at temperatures less than 11 K there is a noticeable change – the thermal conductivity of graphene composites becomes lower than that of epoxy. The effective out-of-plane thermal conductivity of few-layer graphene is responsible for the behavior in the composite with graphene loading below 20 wt. %. At the graphene loading above ~20 wt. %, the trend changes again owing to the onset of thermal percolation. Our somewhat unexpected experimental findings suggest that the epoxy composites with the low loading of graphene and few-layer graphene can act as efficient thermally insulating materials at sufficiently low temperatures. These results indicate the potential of graphene composites for applications in the thermal management of cryogenic technologies.

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5:00 PM SF03.15.05
Hygrothermal and Viscoelastic Properties of Polyurea Elastomeric Foam Mark Smeets[1], Behrad Koohbor[2] and George Youssef[1]; [1]San Diego State University, United States; [2]Rowan University, United States

The emergence of elastomeric foams for impact mitigation applications, including sports protective gear, hinges on their superior mechanical behavior as a function of various operating, environmental, and loading conditions. For example, polyurea elastomeric foams have shown exceptional potential as helmet liners, protective body pads, and shoe insole materials. It is hypothesized that polyurea foams inherit the superior environmental and mechanical behaviors of their solid constituents, *i.e.*, polyurea. This research aims to broadly investigate the hygrothermal and viscoelastic behaviors of elastomeric polyurea foams, assessing their response to moisture with different pH levels, temperatures, and mechanical loading rate. The experimental approach used in this study consist of three sets of measurements. First, the heat flow rate of in-house fabricated polyurea foam plugs is measured using differential scanning calorimetry (DSC) at temperatures ranging from -120C to 400C. The DSC thermograms are analyzed to extract the glass transition temperature, crystallization temperature, apparent melting/softening temperature, and enthalpy and latent heat. Second, foam plugs are submerged in deionized and saline water for extended periods, 2 and 4 weeks, before pyrolyzed using a thermogravimetric analyzer (TGA) from room temperature up to 700C. The TGA thermograms elucidate the hygrothermal and decomposition behavior of polyurea foams as a function of the submersion solution. Finally, the time-dependent mechanical response of polyurea foams is quantified using a dynamic mechanical analyzer (DMA) at frequencies ranging from 1 to 5 Hz, congruent with biomechanical loading scenarios at temperatures ranging from -100C to 100C, covering a broad range of loading conditions. The DMA results relate the viscoelastic properties to the stochastic microstructure of the foam. The outcomes of these investigations extend the applicability of elastomeric polyurea foams to a broad range of civilian and military applications while substantiating the process-structure-property interrelationship of stochastic elastomeric foams.

5:00 PM SF03.15.06
Atomistic Calculations of Irradiation Damage in Tungsten Improved with Temperature-Dependent Electron-Phonon Coupling Byeongchan Lee and Younggak Shin; Kyung Hee University, Korea (the Republic of)

Plasma-facing components (PFCs) in fusion reactors are exposed to extreme heat flux, making thermal management of PFCs critical to protect the entire reactor. More important, PFCs experience neutron irradiation and undergo severe microstructural damages. In the absence of true fusion environment, however, test and design of PFCs substantially depends on simulations; neutronics, magnetohydrodynamics, and atomistic calculations to name a few.

Atomistic calculations using primary knock-on atoms (PKAs) are of particular importance as the detailed information on the microstructural degradation during irradiation is readily available. To that end, it is crucial to implement a virtual environment as well as a virtual/atomistic specimen compatible or at least comparable with the true environment, and our focus is specifically on the thermal conductivity: how extreme energy density delivered locally via PKAs is dissipated through the material, and what the impact of computational settings would be on conduction.

In this talk, tungsten is studied from atomistic calculations as it is one of the candidate materials for PFCs thanks to its high melting temperature and thermal conductivity. Specifically, a two-temperature model (2TM) handling the background electron-thermal contribution associated with electron-phonon coupling is used for a quantitative improvement in the conductivity prediction. Without 2TM, the thermal conductivity only from phonons is predicted to be less than 20% of the experimental measurements. Surprisingly, the electron-phonon coupling coefficient increases over 5 times with increasing electron temperature, and the thermal conductivity at high temperature is decreased down to nearly a half of the room-temperature value. Given that an irradiation cascade results in an extreme temperature gradient, generating a range of local conditions with different thermal conductivities, it is necessary to incorporate the temperature-dependent electron-phonon coupling coefficients into atomistic calculations.

We report the results of variable electron-phonon coupling effects in irradiated damages, and also discuss the effects of defects on the thermal conductivity as damage progresses. We briefly discuss how we can predict the upper and lower bounds of the irradiated damage in terms of thermodynamic as well as numerical settings.

5:00 PM SF03.15.08
Thermal and Transport Properties of Novel Metal Oxychalcogenides for Energy Recovery Joe Willis, Katarina Brlec and David O. Scanlon; University College London, United Kingdom

It is estimated that up to half of global energy input is lost to thermal processes.[1] Harvesting this waste heat and converting it into consumable, electrical energy is a viable route towards cleaner energy, and is made possible through the use of thermoelectric materials and the Seebeck effect. Historically, thermoelectrics contain heavy, toxic metals such as Pb, and are unsuitable for use in everyday society. The discovery of non-toxic, earth-abundant thermoelectrics is therefore highly desirable, enabling widespread improvements in energy efficiency and potential climate change mitigation.
Following the recent proposal of the mixed anion system $Y_2Ti_2O_5S_2$ as an n-type thermoelectric,[2] we investigate the thermal and transport properties of a

family of related $Ln_2M_2O_5Ch_2$ oxychalcogenides (Ln = Sc, Y, La, M = Ti, Zr, Hf and Ch = S, Se, Te) for energy recovery applications. We use AMSET,[3] a package for calculating scattering rates from first principles, to assess mobility, power factor and carrier lifetimes. These results will allow us to determine the effects of simultaneous cation and anion substitution on the electronic properties of this family of materials, and to identify promising candidates for the calculation of lattice thermal conductivity and figure of merit (ZT).

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5:00 PM SF03.15.10
A Substitute Contact Layer to N-Type Nanocrystalline Diamond Surfaces Using Hafnium Evangeline Amonoo, Vishal Jha, Franz Koeck, Gabriel Munro-Ludders, Robert J. Nemanich, Trevor Thornton and Terry Alford; Arizona State University, United States

For the first time, gold, platinum, and hafnium nanofilms were grown on nanocrystalline diamond to serve as electrical contact layers. Hall effect measurements confirmed n-type conduction behavior of the nanocrystalline diamond material and hafnium was observed to form a conductive carbide after annealing at temperatures above 800 °C. After electrical measurements, a specific contact resistance in the range of 10^{-2} $\Omega.cm^2$ and a sheet resistance in the range of 6300 Ω/sq was attained.

5:00 PM SF03.15.12
Multiscale Modeling of Boltzmann Transport Equation to Study Unsteady Thermal Transport Using FEM Kunwar Abhikeern; Indian Institute of Technology Bombay, India

The **thermoelectric (TE) materials** could complement the renewable energy extraction from sources like solar energy and it can also act as an alternative to heat engines while harvesting waste heat from several electrical devices like computers. The **figure of merit *ZT*** is responsible for the thermal efficiency of TE materials which can be increased by decreasing the lattice thermal conductivity of the materials. It has been found that *ZT* is enhanced in nanostructured grains with small misorientations. It has also been observed that nanocomposites such as optimally doped Bi_2Te_3 and its solid solution with Sb_2Te_3, Bi_2Se_3 and silica powder can enhance *ZT*. These grains and nanoinclusions are of nanometer to micrometer sizes for which first principle calculations and molecular dynamics based calculations become computationally too expensive to even attempt. Therefore, not only there is a need to **understand thermal transport across interfaces**, **grain boundaries** and **naoninclusions** using known methods, but a **mutiscale modeling of Boltzmann Transport Equation (BTE)** will also help **understand thermal and electrical transport** across all these defects and composites involving several scales. We aim to **develop a multiscale framework** in which the **phonon** information coming from **molecular dynamics/DFT** simulations will be **coupled** with Finite Element Methods (**FEM**) **for solving BTE** which has advantages such as constructing a well defined boundary solution to be used to study thermal transport across the grain boundaries or phase and interface boundaries for nanoinclusions. This will be cross verified by the experiments involving nano-composites of $Bi_x\ Sb_{\{2-x\}}Te_3$. The finite volume scheme is already in use but the current work uses FEM whose accuracy could be improved by mesh refinement or by increasing the order of interpolation functions.

5:00 PM SF03.15.13
Printing 3D Cuboid Thermoelectrics Using Commercially Available Inorganic Binders Geraint Howells[1,2,3], Matthew Burton[1,4], Matthew Carnie[1,4], Shahin Mehraban[1,5] and Nicholas Lavery[1,5]; [1]Swansea University, United Kingdom; [2]Coated, United Kingdom; [3]Tata Steel UK, United Kingdom; [4]SPECIFIC, United Kingdom; [5]Materials Advanced Characterisation Centre (MACH1), United Kingdom

Rising concerns of global warming and its subsequent effects mean that energy production must move away from traditional fossil fuels to cleaner green solutions. Thermoelectric materials recycle waste heat and turn it into useful electrical energy, by utilising the Seebeck effect (a movement of charge carriers from the hot, high energy state to the cold, low energy state). Thermoelectric generators (TEGs) consist of p-type and n-type legs, combined electrically in series and thermally in parallel. Thermoelectric performance is characterized by the dimensionless figure of merit value, ZT ($ZT = \sigma S^2T/\kappa$), consisting of the Seebeck coefficient (S) electrical conductivity (σ), thermal conductivity (κ), and the absolute temperature (T).[1] Traditionally, thermoelectric materials have been dominated by tellurium based compounds, bismuth telluride and lead telluride for low and medium temperatures, respectively. These materials, however, are toxic, and tellurium itself is relatively earth scarce, with an abundance like platinum (1 $\mu g\ Kg^{-1}$).[2] To alleviate the problems surrounding these materials, new compounds must be researched. Tin selenide (SnSe) has been shown to exhibit a record high figure of merit, ZT number of 3.1 in 2021, due to its ultralow thermal conductivity and high Seebeck coefficient.[3] Manufacturing methods of making SnSe based thermoelectrics include Bridgman crystal growth and spark plasma sintering, which take a long time and are energy intensive.[3,4] As a result, there is a need to look at new manufacturing techniques for thermoelectric materials.
This work, consequently, looks at the feasibility of printing SnSe produced via ball milling constituent elements. Printing dramatically lowers the embodied energy of manufacturing, has a high production output, and lowers the cost to make thermoelectric materials.[5] Typical thermoelectric printing techniques such as screen printing or inkjet printing produce inherently thin samples (thickness <1mm) which are undesirable for efficient TEGs (>5mm). This work successfully demonstrates a method of psudo-3D printing SnSe powders using varying inorganic, industrially established binders forming samples of any desired thickness. Printing was followed by a short curing step of 1 hour in an argon atmosphere at 873 K. These results were repeatable, rapid, scalable and samples were shown to have sufficient dimensions (approximately 1 cm^2 by 2 cm) for TEG use. The materials characterisation methods of x-ray powder diffraction and energy dispersive X-ray spectroscopy displayed that the printed materials were SnSe. X-ray photoelectron spectroscopy was also employed to analyse surface chemistry of the samples. Characterization of thermoelectric performance was done on a ULVAC ZEM3 system and showed a peak power factor of 127.9 $\mu W\ m^{-1}\ K^{-1}$ at 850 K. The samples also showed no sign of thermal degradation, even after five thermal cycles up to 850 K. The peak ZT observed was 0.3 at 823 K, higher than most printed thermoelectric materials within the literature.[5] Proof of concept p-type only TEGs were produced from the samples, which produced 467 µW at 789 K, which is the highest of any printed SnSe based TEG to date.[6]
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5:00 PM SF03.15.15
Investigation of the Thermal Conductivities of Single Nickel Nanowires Wei-Tsu Peng[1], Jiun-Hung Yi[2], Kuan-Ju Yu[1], Tien-Kan Chung[1] and Ming-Chang Lu[2]; [1]National Yang Ming Chiao Tung University, Taiwan; [2]National Taiwan University, Taiwan

Magnetoresistive random-access memory (MRAM) is an emerging memory device technology with the advantages of consuming less power, fast reading and writing, and being a non-volatile memory. Therefore, it has the promising potential to replace dynamic random-access memory (DRAM) and static random-access memory (SRAM) devices. MRAM stores the data in the magnetic domains, and operates by changing the resistance of a magnetic tunnel junction (MTJ). The resistance change in an MTJ is usually accomplished by applying a spin current to switch the magnetization of the MTJ. The operation of an MRAM involves coupling a magnetic field and electron transport; in the meantime, Joule heating is also induced by the applied spin current.
Given that Ni is the most common material in MRAM devices; therefore, this study investigates the effect of magnetic field on heat transfer and current transport in single Ni nanowires (NiNWs). The NiNWs were fabricated by electroplating Ni into a porous anodic aluminum oxide (AAO) template. The Halbach magnets were employed to apply the external magnetic fields with different magnitudes and orientations on the NiNWs. The X-ray diffraction (XRD), transmission electron microscopy (TEM), selected-area electron diffraction (SAED), energy-dispersive x-ray spectroscopy (EDS), and superconducting quantum interference device (SQUID) were conducted for the characterization of the NiNWs. It was found that the NiNWs were polycrystalline with a face-center cubic (FCC) crystal structure and a grain size of approximately 21 nm. The SQUID revealed that the magnetization of the NiNW array increased with an increasing magnetic field and was saturated at approximately 3 kOe.
The measurement results showed that the orientation of magnetic fields had little influence on the thermal conductivities (*k*s) and electrical resistivities of the NiNWs. On the other hand, the *k*s of the NiNW were reduced significantly by the applied magnetic field, whereas their electrical resistivities were almost unaffected. These results indicate that the magnetic field has a relatively profound influence on magnon transport compared with electron transport. In addition, the magnon-contributed k at a magnetic field was retrieved from the difference between the *k* at a zero magnetic field and at the applied magnetic field. It was found the magnon-contributed *k* accounted for 20%–30% of the total *k* at room temperature.
In addition, a theoretical model based on the Boltzmann transport equation was developed for the magnon thermal conductivity. Four scattering mechanisms, including boundary scattering, defect scattering, magnon-magnon scattering, and magnon-phonon scattering, were considered in the model. The theoretical modeling revealed that magnon-defect and magnon-boundary scatterings played the most critical roles in magnon transport compared to the magnon-magnon and magnon phonon scatterings.

5:00 PM SF03.15.16
Thermal, Electrical and Mechanical Characterizations of Aligned Copper Nanowires Array Long Zhu, Weixiao Gao and Fei Ren; Temple University, United States

High performance and reliable thermal interface and electrical contact materials are in great demand for high power density electromechanical devices in semiconductor industry. Vertically aligned Cu nanowire (NWs) arrays exhibit remarkable thermal, electrical conductivity and mechanical compliance, and have been used in a variety of applications, such as liquid-vapor phase-change heat transfer enhancement, selective electrochemical sensor, enhanced field emission, thermal interface materials (TIMs), lithium-ion battery, etc. In this study, double sided Cu NWs array on Cu substrate were prepared via template assisted electrodeposition and used as TIMs and electrical contact material for electrical interconnection. The thermal and electrical transport properties of the double-sided Cu NWs array were systematically investigated.
In addition to their functional properties, the reliability of the devices depends on the robust bonding between the metal structures to the underneath substrates. Quantitively evaluating the mechanical properties and the bonding strength between the metal structures and substrates can provide guidance for the design, fabrication, and failure analysis of the devices. Here, nanoindentation and nanoscratch tests were performed on Cu NWs to investigate the mechanical properties and bonding strength of Cu NWs to the Cu substrate, respectively.

5:00 PM SF03.15.17
Silicon-Based TEM Grids for the Complete Thermoelectrical Characterization of Individual Nanowires Jose Manuel Sojo Gordillo[1,2], Carolina Duque Sierra[2], Nerea Alayo[2], Marc Salleras[3], Yashpreet Kaur[1], Saeko Tachikawa[1], Nicolas Forrer[1], Luis Fonseca[3], Ilaria Zardo[1], Alex Morata[2] and Albert Tarancón[2,4]; [1]University of Basel, Swaziland; [2]Catalonian Institute for Energy Research (IREC), Spain; [3]Institute of Microelectronics of Barcelona, IMB-CNM (CSIC), Spain; [4]Catalan Institution for Research and Advanced Studies (ICREA), Spain

Currently employed materials in Thermoelectric Generators (TEGs) such as bismuth telluride or lead telluride are scarce, expensive, toxic, and environmentally harmful, relegating this technology to specific niches. However, in recent years, the thermoelectrics paradigm has changed mainly due to the introduction of low-dimensional materials. This miniaturization enabled tailoring some properties of materials, such as reducing thermal conductivity by phonon scattering. Consequently, materials previously discarded due to a large bulk thermal conductivity have gained significant interest. Semiconductor nanowires (NWs) – in particular Si and SiGe NWs – have demonstrated fascinating properties with applications in a wide range of fields, including energy and information technologies. Despite this interest, a proper evaluation of the compositional, morphological, and thermoelectrical properties in such nanostructures still represents a great challenge.

Typically, the study of individual integrated NWs following the bottom-up approach faces two main issues. The first one is the need for catalyst nanoparticle precursor deposition to grow them, usually performed by colloidal solution depositions. The randomness of this process dramatically hinders the precise allocation of the desired NW into the employed test microdevices. The second challenge relates to the different architectures of test microdevices devoted to measuring one nanomaterial property. These challenges often result in the use of different NW to measure each of the studied properties, being one of the primary sources of error in the characterization of NWs.

This work presents the conceptual design, simulation, fabrication, and testing process of a micro-machined device for the complete evaluation of a single bottom-up integrated NW. In the exhibited design, the NWs can grow between multiple pairs of breakable cantilevers. This approach allows the user to select the most suitable sample among the available in the chip after the random deposition of the catalyst precursor and discard the rest. The design also incorporates though micro-trenches. This feature, added to the nominal device diameter of 3 mm, enables the use of Transmission Electron Microscopy for detailed morphology analysis and compositional characterization techniques such as EELS or EDX. In the same architecture, electrical collectors and isolated heaters are available at both ends of the trenches for thermoelectrical measurements of the NW. Moreover, through micro-Raman measurements, thermal conductivity evaluation is improved thanks to the lack of substrate below the NW and the electrical and thermal access to the NW for in-operando analysis. Finally, the fabrication process is designed without using anisotropic etching processes, allowing the chip to be fabricated in any crystallographic direction needed.

The device presented here shows remarkable utility in the challenging thermoelectrical characterization of integrated nanostructures and in the development of multiple devices such as thermoelectric generators.

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5:00 PM SF03.15.18
Dynamically Stable Cubic-Phase MAPbI$_3$ Structure and Its Phonon Particle-/Wave-Nature Jin Yang[1], Ankit Jain[2] and Wee-Liat Ong[1,1]; [1]Zhejiang University, China; [2]IIT Bombay, India

Hybrid halide perovskites, with their favorable carrier recombination time and ultrashort phonon mean-free paths, are potential candidates for numerous energy conversion applications like photovoltaics and thermoelectrics. The origin of the ultralow thermal conductivity in the prototypical methylammonium lead triiodide (MAPbI$_3$) is of intense research interest for improving its energy conversion performance.[1] So far, such an understanding remains elusive in the MAPbI$_3$ above room temperatures (c-MAPbI$_3$) despite numerous efforts due to the unstable modes in its phonon dispersion. [2]

Using molecular dynamics and the Wigner-transformed Boltzmann transport equation,[3] we report the discovery of several c-MAPbI$_3$ local energy minimum structures.[4] These stable structures are amenable to lattice dynamics-based calculations to produce totally positive phonon dispersions. Our results reveal a coherence-channel-dominated thermal transport mechanism in the c-MAPbI$_3$ crystals. Interestingly, an inter-conversion between the population- and coherence-channel occurs when the c-MAPbI$_3$ changes across these energetically equivalent structures at the same temperature. Such an effect is yet to be observed in simple atomic crystals. Our work also shows that existing thermal transport intuitions based on the phonon gas model can be misleading in such hybrid crystals. Further, the dominance of the non-traditional coherence-channel of phonons can affect the interpretation of other phonon-mediated processes in MAPbI$_3$ and other hybrid perovskites.

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5:00 PM SF03.15.19
Aluminum Nitride Microstructures by UV Laser Processing for Two Phase Heat Transfer Applications Muhammad Shattique[1], Roman Giglio[1], Ercan M. Dede[2], Mehdi R. Asheghi[3], Kenneth E. Goodson[3] and James W. Palko[1]; [1]University of California, Merced, United States; [2]Toyota Research Institute of North America, United States; [3]Stanford University, United States

With the increase of power electronics applications, the demand for higher heat flux cooling is increasing. The high thermal conductivity and electrical resistivity of AlN make it an effective substrate material in power electronics applications. Here we present nano second pulsed UV laser processing approaches under ambient atmospheres for the production of AlN microstructures for two-phase heat transfer applications. Scanning electron microscopy reveals that laser micromachining enables creation of high surface area micro pin fin type arrays in a single processing step compared to the complex processing protocols employed in traditional micromachining. The surface roughness of these laser machined micropillars is measured to be ~6 μm. The micropillar structures and high surface roughness enables capillary wicking and superior wetting of applicable working fluids. We observe that the laser exposure of the AlN surface causes metallization of AlN to Al. Conductivity measurement of the machined substrate reveals the sheet resistance to be 2.5-4 Ω/square with a corresponding thickness of the resulting aluminum layer deduced to be 6-8 nm. XPS analysis confirms the AlN Al transformation with the N signal disappearing from the laser micromachined surface. The laser machined pin fin arrays have been characterized for heat transfer performance and exhibit a critical heat flux of 145 W/cm^2 with a superheat of 20°C. We analyze the resulting performance in terms of structural and surface property modification imparted by the laser processing approach. Facile processing of AlN holds significant promise to further the use of two phase heat transfer applications at large scale.

5:00 PM SF03.15.20
Innovative Swaging-Drawing ATF Tube of Thermal Stability Evaluation by LOCA Situation for PWR Unho Lee, Ji Hyeok Choi, Jisu Na, Jeong Hye Jo and Young Soo Yoon; Gachon University, Korea (the Republic of)

After Eu-taxonomy in 2022, PWR (Pressurized Water Reactor) is scheduled to be treated with verification technology applied with ATF (Accident tolerant fuels) technology until 2028. Among nuclear power plant materials, nuclear fuel tubes must have resistance to accident situations as well as pressurized and high-temperature environments. In order to delay the accident of Zr-alloy tube in LOCA (loss-of-coolant accident) situation, research on surface coating and composition change is in progress. However, since Zr-alloy is used as the base material, it is very difficult to provide dramatic changes to overcome the nuclear accident. This Korean research team shows excellent thermal stability in the LOCA simulation situation for the swaging-drawing technology, which is the core technology to which the ATF technology is applied. In addition, SS-Zr-SS tube (SS316L/Zr-alloy/SS316L) exactly match the specifications of commercial Zr-alloy tubes for nuclear fuel and has the advantage of being a room temperature and mass production process. A swaging-drawing of an ultra-thin SS tube of about 70 micrometers was performed inside and outside, and thermal stability evaluation was performed in the LOCA simulation situation at 1,200°C. Oxidation was inhibited by the formation of Zr-nitride in the interfacial environment of SS and Zr. In theory, it was also confirmed that there was no decrease in the power generation output of a Fe-based alloy having a high neutron absorption cross-sectional area. In conclusion, the innovative swaging-drawing triple tube is expected to be an ATF application technology candidate for PWR, which has not only thermal stability but also accident resistance in the LOCA simulation situation.

5:00 PM SF03.15.21
Tuning Polymer Thermal Conductivity by Molecular Alignment Yoko Tomo[1,2] and Zhenan Bao[2]; [1]Kyushu University, Japan; [2]Stanford University, United States

Polymer is a widely used material in industrial and personal applications due to its low cost, high formability, lightweight and chemical stability. Its ultralow electrical conductivity is also an important feature. In many electronic devices, polymers are used as electrical insulators in the form of interfacial materials and flexible substrates. However, the low thermal conductivity is a disadvantage for thermal management because it hinders the thermal dissipation in electrically-heating devices and causes a significantly high-temperature rise. A molecular dynamics simulation study showed that single polymer chains could have as high thermal conductivity as metals. Recent experimental research also reported high thermal conductivity polymers up to

104 $Wm^{-1}K^{-1}$ by drawing polymer fibers or films. However, this high thermal conductivity is usually fixed once the polymer elongated because the polymer structures are irreversible. In this work, we measured the in-plane thermal conductivity of shape memory polymer using home-developed sensors. We discovered that the thermal conductivity was enhanced by drawing films because it induced molecular structure alignment. Moreover, the thermal conductivity decreased when the films became at the original length. Our results showed that the thermal conductivity of shape memory polymer is tunable by molecular alignment and also suggested that shape memory polymer could be prospective materials for a thermal switch.

SESSION SF03.16: Thermal Transport at Interfaces and Surfaces
Session Chairs: Tianli Feng and Lucas Lindsay
Friday Morning, April 14, 2023
Marriott Marquis, B2 Level, Golden Gate A

8:00 AM SF03.16.01
A Bio-Inspired Artificial Butterfly Wing-Like Membrane for Thermal and Optical Management Yeongju Jung, Seongmin Jeong and Seung Hwan Ko; Seoul National University, Korea (the Republic of)

Natural species often introduce novel functionalities or offer viable solutions for the current technologies as the species evolved through genetic mutations over time to adapt to the specific environment. Similarly, a large number of butterfly species in the warmer climate have evolved to attain interesting properties on their wing scales which exhibit dual functionalities of optical property (structural coloration) and thermal management (radiative cooling). The Archaeoprepona demophoon dorsal wing scale exemplifies such functionalities due to its nanostructure that is characterized by the periodic ridge grating and random nano pore matrix. Despite the fascinating properties that can be translated into practical thermal and optical management applications, there has been no report that reconstructed the physical nanostructure of the butterfly wing scale, although several studies have investigated the origin of functionalities.
Inspired by the fascinating characteristics that the natural species exhibit, we introduce the bio-inspired artificial membrane that artificially reconstructs the wing scale nanostructure of Archaeoprepona demophoon to replicate the thermal and optical management functionalities. To replicate the optical property (iridescent structural coloration) of the butterfly species, PDMS ridge grating structure was fabricated by laser interference lithography. The ridge structure is able to generate of the large color gamut that is capable of expressing 91.8 % of sRGB. For the thermal management property (radiative cooling), the hierarchical PVDF-HFP nano pore membrane was fabricated using SiO_2 nanoparticle etching process. PVDF-HFP nanoporous membrane demonstrates desirable optical properties for radiative cooling: reflectivity = 0.99 (in the range from ultraviolet to visible) and emissivity = 0.95 (in the range of atmospheric window). In this study, we fabricated the artificial bioinspired butterfly wings for thermal and optical management to translate dual functionalities of the butterfly wing into real-world applications. The membrane exhibited the effective radiative cooling with maximum temperature reduction of 8.45 °C. We expect that this study will not only provide the experimental platform that clarifies the optical structure-functionality correlation of the Archaeoprepona demophoon wing scale but it would also share useful insights into the current optics and heat-transfer technologies.

8:15 AM SF03.16.02
Longitudinal Sound Speed and Thermal Properties of Atomic Layer Deposition-Grown Amorphous AlN/Al2O3 Multilayers with Varying Oxygen Composition Md Shafkat Bin Hoque[1], Ian Brummel[1], Eric R. Hoglund[1], Jaymes Dionne[2], Kiumars Aryana[1], John Tomko[1], John T. Gaskins[1], Daniel Hirt[1], Sean W. Smith[3], Thomas Beechem[4], James M. Howe[1], Ashutosh Giri[2], Jon Ihlefeld[1] and Patrick E. Hopkins[1]; [1]University of Virginia, United States; [2]University of Rhode Island, United States; [3]Radiant Technologies, United States; [4]Purdue University, United States

Dielectric AMLs are currently being used in a wide array of applications such as optical coatings, nanoelectronic, energy harvesting, and recovery devices. The relatively low thermal conductivity of AMLs makes it particularly challenging to effectively dissipate the waste heat generated during these applications. The problem is further compounded in AMLs with high interface densities as the non-negligible role of the interfaces leads to additional thermal conductivity reductions. Thus, it is of vital interest to find pathways of modulating interface density of AMLs without sacrificing thermal conductivity. Here, we report on the sound speed and thermal conductivity of a series of amorphous AlN/Al_2O_3 multilayers grown via plasma enhanced atomic layer deposition. To introduce compositional disorder in the AMLs, the oxygen content of the multilayers is systematically varied as function of interface density. The longitudinal sound speed of the AMLs is solely dictated by the composition. The thermal conductivity, on the other hand, is dictated by both composition and interface density. The oxygen content and interfaces act to increase and decrease the thermal conductivity, respectively. Due to such competing influences of the two parameters, the thermal conductivity of the AMLs remains nearly constant as a function of interface density.

8:30 AM SF03.16.03
Synthesis of Nanostructured Mott insulator La_2CuO_4 and Its Magnon Thermal Transport Properties Shucheng Guo[1], Hongze Li[2], Shuchen Li[1], Jianshi Zhou[2] and Xi Chen[1]; [1]University of California, Riverside, United States; [2]The University of Texas at Austin, United States

The Mott insulator La_2CuO_4, which crystalizes in a two-dimensional layered structure with strong antiferromagnetic coupling, is a promising material for thermal management applications due to its large magnon thermal conductivity. Although bulk La_2CuO_4 crystals have been synthesized and studied extensively, there have been few reports on the synthesis of the nanostructures and studying their magnon thermal transport properties . Here, we study the synthesis of La_2CuO_4 nanostructures and measure their thermal transport properties. Nanorods and nanoparticles of La_2CuO_4 have been prepared by a wet chemical method. The growth mechanism of these nanostructures has been investigated by electron microscopy and energy dispersive X-ray spectroscopy studies. Moreover, nanostructured bulk samples were prepared by consolidating as-synthesized powders. The role of grain size and shape on magnon thermal transport was determined by the thermal conductivity measurements. These results provide useful insights into the development of magnetic nanomaterials for spin caloritronic and thermal management applications.

8:45 AM SF03.16.04
Interfacial Thermal Resistance from Non-Equilibrium Phonons and Electrons Jinchen Han and Sangyeop Lee; University of Pittsburgh, United States

Large interfacial thermal resistance challenges thermal management in nanostructured devices and opens opportunities for developing ultralow-thermal conductivity materials. However, interfacial thermal transport remains poorly understood due to complex physics and limited methodologies. For example, the complex interplay between the interfacial scattering and intrinsic phonon-phonon and electron-phonon scattering in nano-to-microscale has not been comprehensively studied. Methods that have been widely used in the past include the Landauer's formalism ignoring the intrinsic scattering of phonons and molecular dynamics simulation having a much smaller length scale than the typical mean free paths of phonons. To explore the role of intrinsic scattering of phonons on the interfacial thermal resistance at microscale, we solve the Boltzmann transport equation in both reciprocal and real spaces using a Monte Carlo method with *ab initio* inputs.

Our simulation indicates a significant non-equilibrium of phonon distribution near the interface due to the interfacial scattering in Si-Ge and III-V semiconductor interfaces. The process in which intrinsic phonon scattering attempts to relax the non-equilibrium distribution to a local equilibrium distribution generates a large amount of entropy according to the Boltzmann's H-theorem and leads to excessive thermal resistance. The non-equilibrium effect is observed to contribute more thermal resistance than the interfacial scattering itself in many interfaces. The III-V compound semiconductor interfaces were comprehensively studied to search for general rules of non-equilibrium resistance between two constituent materials. We further involve the electron-phonon scattering in the metal side of the Al-Si interface to investigate its effect on metal-semiconductor interfacial thermal transport. Our study brings a new insight into the significant role of intrinsic phonon-phonon scattering and electron-phonon scattering on interfacial thermal resistance above the atomistic scale.

9:00 AM SF03.16.05
Impacts of Various Interfacial Nanostructures on Spectral Phonon Thermal Boundary Conductance Rui Xie, Janak Tiwari and Tianli Feng; University of Utah, United States

Nanoengineering of interfaces has become an effective way to tune the thermal boundary conductance (TBC) of heterostructures. However, the same nanostructure design can have opposite impacts on TBCs for different systems. To provide a clue toward a unified explanation, in this work, we directly and explicitly reveal the impacts of nanostructures on mode-dependent phonon TBC contributions. We study four representative types of nanostructures, i.e., (1) an intermediate layer, (2) interfacial interlaced teeth, (3) interfacial atomic mixing, and (4) interfacial atomic defects on two example heterostructures: 28Si/Ge and 6Si/Ge, which have moderate and large phonon frequency mismatches, respectively. We find that most of these nanostructures reduce the TBC of 28Si/Ge while increasing the TBC of 6Si/Ge. Each nanostructure is found to have two competing impacts on an interface—one tends to increase TBC while the other tends to decrease TBC. For example, adding an intermediate layer provides a phonon bridging effect, which tends to increase both elastic and inelastic phonon transmission, but it adds one more interface and, thus, more phonon reflection. As a result, an interlayer decreases the TBC of the 28Si/Ge interface by decreasing the inelastic transmission while increasing both elastic and inelastic transmissions of the 6Si/Ge interface. Other nanostructures with atomic disorder can increase transmission by increasing the contact area but can also decrease transmission by phonon-disorder backscattering. This work unveils the fundamental thermal transport physics across interfaces with nanostructures and sheds light on future interface nanoengineering for electronic devices such as high-power transistors, photodiodes, and supercomputing architectures.

9:15 AM SF03.16.06
The Significant Effect of Intrinsic Defects on the Performance of Novel Lightweight Thermoelectric, MgB_4 Sabrine Hachmioune[1,2,2], Alex M. Ganose[3] and David O. Scanlon[1]; [1]UCL, United Kingdom; [2]Agency for Science, Technology and Research, Singapore; [3]Imperial College London, United Kingdom

Thermoelectric materials are being explored as an avenue for alternative power generation. They are typically composed of heavy elements such as Bi, Pb and Te, and are used for large-scale applications. By contrast, this work explores a promising lightweight thermoelectric, MgB_4, with the potential to power wearable electronics, mobile phones, and sensors.[1] We use hybrid-density functional theory (DFT), AMSET[2] and Phono3py[3] to explore the thermal and carrier transport properties of MgB_4, followed by a full defect study to understand its doping limits.

MgB_4 has never been studied before as a thermoelectric material and this work reports ZT's greater than 1, above 900 K under n-type doping, with reduced ZT's under similar p-type doping. The material exhibits an average lattice thermal conductivity of 4.20 $Wm^{-1}K^{-1}$ at 900 K, that reduces upon nano-structuring. The defect study reveals the key role of the intrinsic defects and ionic charge compensation in the dopability and achievable thermoelectric performance of this system.

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9:30 AM SF03.16.08
Orientation Effects on Near-Field Radiative Heat Transfer Between Complex-Shaped SiO_2 Particles Lindsay Walter and Mathieu Francoeur; The University of Utah, United States

Near-field radiative heat transfer between micro/nanoscale dielectric particles is often characterized by shape-dependent, localized surface phonon-polariton resonances. These localized resonances are of interest because they typically dominate near-field radiative heat transfer and may be modified through alteration of particle geometry to shift the spectrum of heat transfer. In addition to geometry effects, a few theoretical studies have predicted that the orientation of particles may be used as a method for tuning the heat flux by as much as two orders of magnitude, opening the possibility of developing particle-based thermal switches (R. Incardone *et al*., *Europhys. Lett*. **106**, 41001, 2014; M. Nikbakht, *J. Appl. Phys*. **116**, 094307, 2014). These previous studies on particle orientation, however, have been limited to a small range of geometries encompassing spheroidal point dipoles, gold cylinders (A. W. Rodriguez *et al*., *Phys. Rev. B* **88**, 054305, 2013), and graphene dimers (F. V. Ramirez *et al*., *Phys. Rev. B* **96**, 165427, 2017). The work presented here is not restricted to the point dipole approximation and goes beyond these previous studies to address the knowledge gap concerning orientation effects on near-field radiative heat transfer between more complex-shaped particles. Specifically, we model systems of two 50-nm-radius SiO_2 superellipsoid particles of variable concavity and orientation (L. P. Walter and M. Francoeur, *Appl. Phys. Lett.* **121**, in press, 2022). The analysis is conducted using the discrete system Green's function (DSGF) method for radiative heat transfer (L. P. Walter *et al*., arXiv:2204.05399, 2022). The DSGF method is a volume integral approach for solving the equations of fluctuational electrodynamics where particles are discretized into cubic subvolumes. In this way, all electromagnetic interactions are accounted for throughout the volume of each particle, and location-dependent power dissipation is resolved. The key results of this work are: (1) the range in the total conductance of the complex-shaped superellipsoid particles over variable orientation is significantly less than that predicted from spheroidal dipole models; (2) orientation effects are strongly correlated with the minimum vacuum gap distance between particles; and (3) the center-of-mass separation distance at which orientation effects on near-field radiative heat transfer are negligible is related to the particle topology. The results and insight from this work are important for engineering effective thermal management in real-world particle devices that may contain a variety of complex particle shapes and orientations, such as Mie-resonance-based metamaterials.

SESSION SF03.17: Nanoscale Microscopy
Session Chairs: Irena Knezevic and Andrea Pickel
Friday Morning, April 14, 2023
Marriott Marquis, B2 Level, Golden Gate A

10:30 AM SF03.17.01
Combining Ratiometric Thermometry and Super-Resolution Imaging of Upconverting Nanoparticles Ziyang Ye and Andrea Pickel; University of Rochester, United States

Modern electronic, data storage, and energy conversion devices increasingly combine nanoscale dimensions with challenging operating conditions, including extreme temperatures, high pressures, large electromagnetic fields, and harsh chemical environments. In tandem, thermal properties play an outsize role in determining the overall performance of these technologies. Engineering improved performance thus requires the ability to visualize heat flow using non- invasive thermometry techniques with nanoscale spatial resolution. Conventional far-field optical techniques enable non-contact measurements, but such approaches fundamentally lack the spatial resolution required to resolve nanoscale temperature heterogeneities. Upconverting nanoparticles (UCNPs) are popular luminescent thermometers with Boltzmann-distributed emission intensity that facilitates thermometry via temperature-dependent spectral peak intensity ratios, an approach known as "ratiometric" thermometry. UCNP coatings have been applied for temperature mapping with diffraction limited spatial resolution. Additionally, single-UCNP measurements have been used to circumvent the diffraction limit, but this approach only allows for single-point nanothermometry. Recently, heavily (~10%) Tm-doped UCNPs were shown to enable a super-resolution imaging method called stimulated emission depletion (STED) that has been widely used in biological imaging to circumvent the optical diffraction limit. Compared with other common STED imaging probes, UCNPs require much lower STED laser powers. Separately, this same UCNP composition, but with a much lower Tm concentration of ~1%, has been used for diffraction-limited ratiometric thermometry, suggesting the possibility of adapting STED imaging for far-field optical temperature mapping with sub-diffraction limited spatial resolution.

Here, we demonstrate that individual heavily Tm-doped UCNPs can be applied both for ratiometric thermometry and STED imaging. We measure temperature-dependent emission spectra of individual UCNPs as function of temperature, and we identify several temperature-dependent peak intensity ratios. While the temperature dependence deviates from the Boltzmann-distributed emission intensity that has been observed for lightly Tm-doped UCNPs, these ratios show sensitive, repeatable temperature dependence with good particle-to-particle uniformity. Using a custom-built STED imaging and spectroscopy system, we successfully demonstrate single-UCNP spectroscopic depletion for the first time, a key requirement for ratiometric STED nanothermometry. We also show that the sub-diffraction limited imaging resolution of our system is maintained from room temperature up to 400 K. Using an interfacial self-assembly method, we demonstrate the ability to create uniform UCNP monolayers spanning regions many microns wide, which can subsequently be placed on a sample surface. We then scan the surface of a monolayer-coated substrate that is heated to different uniform temperatures and successfully generate uniform temperature maps by recording temperature-dependent ratios at each pixel. These results indicate that temperature-dependent STED imaging of heavily Tm-doped UCNP monolayers has excellent potential to facilitate optical super-resolution thermometry of structures with nanoscale temperature heterogeneities in the near future.

10:45 AM SF03.17.02
Probing Performance Improvements in Thermophotovoltaic Energy Conversion at Nanoscale Gaps Rohith Mittapally[1,2], Byungjun Lee[1], Ju Won Lim[1], Linxiao Zhu[3], Stephen R. Forrest[1], Pramod Sangi Reddy[1] and Edgar Meyhofer[1]; [1]University of Michigan, United States; [2]Massachusetts Institute of Technology, United States; [3]The Pennsylvania State University, United States

Thermophotovoltaic systems enable the direct conversion of heat into useful electrical power. A typical TPV system consists of a hot emitter facing a cold photovoltaic cell (PV), where the emitted electromagnetic radiation generates electron-hole pairs in the PV cell. When such an emitter and a PV cell are separated by gaps larger than the thermal wavelength—said to be in the far field of each other— a blackbody limit bounds the power output density. Theoretical studies in the last decade predict that large enhancements in power output beyond the blackbody limit are possible by reducing the gaps to nanometric distances, i.e., by placing them in the near-field (NF) of each other. Experimental validation and precise characterization of this phenomenon have been challenging because accurately positioning a hot body at nanometric distances from a PV while quantifying the heat flux to the PV cell is demanding. Here, we will first describe how we experimentally establish an NF-TPV system's temperature- and gap-dependent performance and demonstrate a ~40-fold enhancement in power output in the NF compared to the far field[1]. Next, we report experimental techniques that allowed us to maintain a hot silicon emitter (at 1300 K) at gaps as small as 100 nm away from an InGaAs-based PV cell at 300 K. Aided by the development of doped silicon emitters that could be heated to temperatures as high as 1300 K and high-quality InGaAs PV cells equipped with a back surface reflector, our NF-TPV system supports a record-high power density output of 0.5 W/cm^2 at an efficiency of 6.7% [2]. Further, we will discuss our theoretical model based on a combination of fluctuational electrodynamics and PV cell modeling, which agrees with the measurements at different temperatures and gap sizes. We will conclude the talk by discussing ideas of how to (further) improve the performance of NF-TPV systems.

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11:00 AM SF03.17.03
Quantitative Temperature Measurement of Self-Heating in Non-Linear Devices Using Scanning Thermal Microscopy Nele Harnack, Pengyan Wen, Olivier Maher, Siegfried Karg and Bernd Gotsmann; IBM Research Europe - Zurich, Switzerland

Self-heating in electronic devices relates to rich and unexplored transport physics of heat and charge. Phenomena range from hot spots causing device failure [1], to exploiting self-heating as a new platform for computing by utilizing electro-thermal processes [2]. Imaging and understanding thermal transport and thermal processes at the nanoscale enables thermal management and new ways of computing, making it highly relevant in today's integrated microelectronic devices.

Scanning Thermal Microscopy (SThM) has become a valuable method to investigate device states and failure mechanisms due to its high spacial and temperature resolution. However, quantitative SThM thermometry is so far mostly limited to devices with linear current-voltage characteristics [3]. We have extended the method to investigate non-linear devices, broadening the application range to include many of the functional device types used in today's microelectronics. For instance, devices for logic or sensing involve complex interfaces that may lead to energy barriers and energy filtering.
In this method, the non-linear device under study is driven to an elevated temperature with a periodic and constant part using an applied oscillating and offset voltage. The applied amplitude allows the simultaneous estimation of temperature and thermal resistance, while the applied offset is used to set the

device state. These lead to an oscillating and constant temperature rise in the heated sensing element, which are detected through resistance changes via a Wheatstone-bridge and lock-in amplifier.

The constant temperature rise in the device can then be inferred using

$\Delta T_{DC} = T_{sensor,0} * \Delta V_{AC,n\omega} / (\Delta V_{AC,n\omega} - \beta_n * \Delta V_{DC})$ (1)

Where $T_{sensor,0}$ is the heater temperature out of contact with the device, ΔV are the heater's constant and oscillating voltage rise measured over the Wheatstone-bridge and n refers to the harmonic under investigation. The newly introduced non-linearity factor β_n accounts for the changing device resistance and is estimated numerically from its I-V characteristics. Our new technique was verified mapping the temperature of exemplary linear (ohmic) and non-linear (memristive and logical) devices.

In conclusion, the method developed here can be used to investigate non-linear devices and materials, including volatile and non-volatile phase-change materials. The combination of an AC voltage with a DC bias allows the separate investigation of different voltage-dependent device states. The method will therefore be crucial to understand dynamics in operating devices and to shine light on reliability issues and break-down mechanisms.

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11:15 AM SF03.17.04

Comparing Near-Field Thermal Radiation Between Different Materials Including III-V Semiconductors Mathieu Thomas[1], Christophe Lucchesi[1], Julien Legendre[1], Natasha Gruginskie[2], Rodolphe Vaillon[3] and Pierre-Olivier Chapuis[1]; [1]CNRS-CETHIL, France; [2]Radboud University, Netherlands; [3]CNRS IES, France

When the distance between objects decreases below the characteristic wavelength of thermal radiation (few micrometers in the 300-1000 K range), the radiative heat exchanged between these objects is increased beyond the blackbody limit imposed by Planck's law in the far field. This increase of thermal radiation, which takes place in the near field, can reach several orders of magnitude. Explained by the additional contribution of evanescent waves to the radiative transfer, this phenomenon, which is now well documented theoretically and experimentally, can be of interest for thermal-energy harvesting. For instance, thermophotovoltaics (TPV) can take advantage of this enhancement of the radiative heat flux in order to increase the electrical output power density when the emitter is brought closer to the cell [1]. A further improvement of such a device is to place a light–emitting diode (LED) on the heated emitter side, which allows controlling the emission spectrum; such device is termed thermophotonic (TPX).

Some of us have demonstrated recently that Stefan-Boltzmann's law is modified in the near field [2] and that the temperature dependence of near-field radiative heat transfer varies with the material considered. Here, we analyse the near-field radiative heat transfer between a heated emitter and different types of samples of interest for energy harvesting. For TPV and TPX devices, III-V semiconductors such as InSb, GaAs, InGaP or AlGaAs are key materials. We report on the experiments, which consist in executing several approaches of a heated micrometric spherical emitter close to the flat studied sample in order to obtain the near-field radiative conductance as a function of distance. Since the increase in the radiative flux depends dramatically on distance, we also report on our recent efforts to determine the flux more accurately in the last 50 nm before contact by means of combined analysis of laser deflection, fiber interferometry and resistive thermometry.

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This work has received funding from project EU H2020 FETProactive-2019-2020/GA951976 (TPX-Power).

11:30 AM SF03.17.05

***Ab Initio* Simulation of Swift Heavy Ion-Driven Damage on Nanoscale Thermal Transport in ZnO** Kairolla Sekerbayev[1], Azat Abdullaev[1], Bekdaulet Shukirgaliyev[1], S. Mehdi V. Allaei[2], Yanwei Wang[1,3] and Zhandos Utegulov[1]; [1]Nazarbayev University, Kazakhstan; [2]University of Tehran, Iran (the Islamic Republic of); [3]National Laboratory Astana, Kazakhstan

Swift heavy ion (SHI) irradiation of non-metallic materials is a promising approach to engineering their thermal transport properties at the nanometer scale. SHI damage can be imparted into host semiconducting and insulating solid lattices in the form of cylindrical ion tracks or near-surface point defects[1]. However, there is a lack of clear understanding of the effect of SHI damage on nanoscale thermal transport in irradiated solids.

In this work, we analyze the *SHI-induced damage* to wide-bandgap semiconducting ZnO single crystal by a hybrid simulation technique combining *ab initio* Monte-Carlo Time-Resolved Electron Kinetics (TREKIS) and molecular dynamics (MD), which is free from fitting parameters[2]. In this approach, the evolution of electron dynamics of host Zn and O atoms is simulated following the initial impact of Bi ion on the ZnO lattice within the first 100 fs. The radial energy density distributed by ion to the lattice is obtained from TREKIS, the output of which is used to set the initial velocities for the classical MD model in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code[3] to predict the 3D damage pattern to the initial zinc oxide hexagonal lattice during its relaxation on a time scale from 100 fs to hundreds of ps. Four different Zn-O interatomic potentials (IAPs) are considered in MD simulations. IAP determines both the ion-induced defect formation and the subsequent thermal conductivity (k) calculations. This TREKIS-MD method is compared with randomly distributed atomic displacements in the crystal formed by the Atomsk software[4].

Then the phonon thermal conductivity of the ion-damaged subsurface region of the ZnO lattice along the (0001) direction obtained from TREKIS-MD is calculated with equilibrium molecular dynamics (EMD) and is compared with the results from the Boltzmann transport equation relaxation time approximation (BTE-RTA), semi-analytical Klemens-Callaway and Rayleigh effective medium approximation models. The k of pristine ZnO obtained by BTE-RTA matches that found by EMD. The difference between the TREKIS-MD and randomly introduced point defects model is seen at high ion doses due to overlapped impinging ions. The *random defects model* fails at high ion doses and predicts further k decrease. On the contrary, the TREKIS-MD model demonstrates k saturation observed experimentally but overestimates the saturated k value. The convergence between TREKIS-MD and spatially-controlled time-domain thermoreflectance measurements of k can be tailored by the appropriate selection of the IAP. The described computational approach opens up an avenue for the design of thermal nanomaterials by controlling the radiation damage via monitoring the electronic excitation by SHIs and subsequent electron-lattice phonon relaxation.

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R. Shan, M. J. Stevens, J. Tranchida, C. Trott, S. J. Plimpton, *Comput Phys Commun*. **271** (2022), doi:10.1016/j.cpc.2021.108171.
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11:45 AM *SF03.17.06
Dynamics of Long-Wavelength Phonons Near Boundaries and Interfaces in Nanomaterials Irena Knezevic; University of Wisconsin-Madison, United States

Long-wavelength phonons undergo infrequent phonon-phonon scattering and thus tend to propagate ballistically over long distances in single-crystalline, high-quality bulk materials, thereby making a major contribution to thermal conductivity in these systems. The dynamics of long-wavelength phonons and their interaction with boundaries and interfaces can be accurately modeled within the elastic-continuum limit. I will present recent work, combining experiment and theory, that shows phenomena such as the incoherent-to-coherent transition in thermal transport in III-V superlattices and the changes in the power-law dependence of phonon lifetime on frequency for rough nanowires and membranes with varying correlation types. The work illustrates the complexity of phonon interaction with disorder, and the utility and flexibility of numerical techniques such as the finite-difference time-domain (FDTD) method for elucidating the dynamics of phonons in nanomaterials.

12:15 PM SF03.17.07
Enhanced Near-Field Radiative Heat Transfer Between Planar Membranes Thinner Than the Vacuum Gap Spacing—Experiment Lei Tang[1], Livia Correa[2], Mathieu Francoeur[2] and Chris Dames[1]; [1]UC Berkeley, United States; [2]The University of Utah, United States

Several experiments have demonstrated that near-field radiative heat transfer (NFRHT) between two flat surfaces can exceed Planck’s blackbody limit (e.g., Song et al., *Nature Nanotechnology* 11, 509-514, 2016; DeSutter et al., *Nature Nanotechnology* 14, 751-755, 2019; Tang et al., *ACS Photonics* 7, 1304-1311, 2020). Recent simulations based on the discrete system Green’s function (DSGF) method (Walter et al., arXiv:2204.05399, 2022) used for modeling NFRHT in arbitrary 3D geometries suggest that the radiative heat transfer coefficient can be further enhanced when the two surfaces facing laterally are thinner than their separation gap. To date there has been no experimental work in this regime, which here we address by measuring NFRHT between the edges of two planar silicon carbide (SiC) membranes thinner than their vacuum gap spacing. More specifically we measured the NFRHT between a series of suspended microdevices consisting of pairs of coplanar SiC membranes with thickness and gap spacing respectively smaller than 100 nm and 500 nm. The measured radiative heat transfer coefficients are large and exceed predictions for two infinite surfaces at the same gap. For instance, at a fixed separation gap of an estimated ~ 100 nm, the measured near-room-temperature radiative heat transfer coefficient for 50-nm-thick SiC membranes is 470 W/m^2-K, which is around 3.1 times larger than calculations for two infinite surfaces of SiC at the same gap, ~ 30 times larger than the far-field results of Thompson et al. for 270-nm-thick SiN membranes (*Nature* 561, 216-221, 2018), and ~ 320 times higher than predicted from a classical blackbody heat transfer calculation for the same geometry. The measurements also agree reasonably well with simulations using the DSGF method. These findings may help inform various applications such as energy conversion, radiative cooling, and thermal rectification.

SESSION SF03.18: Microstructures for Energy Harvesting
Session Chairs: Ying Chen and Lucas Lindsay
Friday Afternoon, April 14, 2023
Marriott Marquis, B2 Level, Golden Gate A

1:30 PM SF03.18.01
Thermal Conductivity of GaAs-GaP Superlattices Nanowires Chaitanya Arya[1], Johannes Trautvetter[1], Yashpreet Kaur[1], Valentina Zannier[2], Omer Arif[2], Riccardo Rurali[3], Lucia Sorba[2] and Ilaria Zardo[1]; [1]Universität Basel, Switzerland; [2]NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Italy; [3]Institut de Ciencia de Materials de Barcelona (ICMAB−CSIC), Spain

In the last decades, continuous efforts have been made to understand and control phonons with great potential for numerous technological applications [1]. The objective of this work is to investigate phonons interference and different phonon transport regimes, which is crucial for phonons manipulation. Nanowires are promising candidates for studying phonons interference effects because they offer unique possibilities in terms of heterostructuring and also enable the growth of high-quality nanowire junctions. In this respect, a superlattice (a lattice made by different materials periodically alternated) can be used to investigate the behavior of phonons scattered from interfaces. Phonons scattered from single interfaces lose their phase information, leading to diffusive thermal transport. However, scattered phonons can interfere before losing their phase information resulting in a modified phonon dispersion and thermal conductivity in case of periodic repetition of interfaces with a lengthscale comparable to the phonon mean free path [2,3].
In this work, we are investigating the phonon interference effect in superlattice (SL) nanowires through thermal conductivity measurements. Thermal conductivity of SL nanowires is measured using thermal bridge method using a microdevice which consists of two SiNx suspended platforms with platinum coils that act as a heater and sensor. These platforms aresupported by 0.5mm long suspended SiNx beams, onto which gold lines are deposited, to ensure thermal isolation [4]. The nanowire is suspended between the two platforms using a micromanipulator. To measure the thermal conductance, the temperature is raised on one platform while the change in temperature on the second platform is measured as a function of heating power. To assess the temperature, the resistance of meanders is measured by four-point probe technique and the heat flux across the nanowire is calculated by measuring the power dissipated in the meanders [5].

The thermal conductivity of GaAs-GaP superlattice nanowires is measured for various SL periods from 4.8 to 23.3 nm. The nanowire sample consists of a GaAs-GaP superlattice embedded between two GaP segments. It is observed that the thermal conductivity decreases with decreasing period length and there is a minimum around the period of 8 nm, afterwards the thermal conductivity increases for smaller periods. The minimum in thermal conductivity occurs at the transition between particle-like and wave-like behavior of phonons. In the incoherent regime (i.e. particle-like behavior), the thermal conductivity decreases due to scattering from the increasing number of interfaces. When the period length is comparable to the phonons coherence length in the system, phonons scattered from the interfaces start to interfere consequently increasing the thermal conductivity. This work is a promising step toward using SL nanowires as a powerful platform for exploiting coherent phonons in thermal applications.

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1:45 PM SF03.18.03
Architecture-Induced Control of the Heat Front Propagation in Ni/Al Reactive Multilayers Nensi Toncich, Fabian Schwarz and Ralph Spolenak; ETH Zürich, Switzerland

Reactive multilayers are metastable heterogeneous nanostructures consisting of the stacking of several layered thin films that have a strong tendency toward mixing. The constituents are characterized by a large negative enthalpy of mixing and a high adiabatic reaction temperature. Upon ignition, the alternating metal thin films react in a highly exothermic reaction front that propagates through the entire system in a self-sustaining manner. Taking advantage of their nanometer size, on-demand ignition, high temperatures reached, and many other features, these materials find application as intrinsic heat sources in many fields, such as thermal batteries, joining, thin-film healing, and in the microelectronics industry. Depending on the application, different propagation velocities and temperatures are required, and for this reason, many investigations on the control of the reaction behavior have been conducted in recent decades [1]. However, to expand their scope and enable these materials to perform in more specific applications, further studies need to be carried out. In our work, we analyze the thermal management of Ni/Al reactive multilayers through architecture design. To this end, molecular dynamics simulations [2] and experimental studies were performed on the effect of the presence of a premixed layer between the two reactants, the presence of interface roughness, and the stoichiometric variation on the heat front propagation velocity and the temperature reached. Molecular dynamics simulations demonstrated a direct correlation between the premixed layer thickness and the heat front propagation velocity. An increase in the premixed layer thickness leads to a decrease in the heat front propagation velocity. The same trend, with a decrease in the combustion temperature, was observed experimentally. A second simulation showed that the introduction of an interface roughness speeds up the heat front propagation. Contrary to modeling predictions, experimentally the reaction behavior appears to be unaffected to variations in roughness. Finally, a stoichiometric variation showed a change in the reaction front behavior in both simulation and experiment. For the experimental study, Ni/Al multilayers were deposited via magnetron sputtering, and the reaction was triggered by a low-power pulse. High-speed IR imaging was performed on the samples as well as structural and compositional characterization.
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2:00 PM SF03.18.04
Thermal Conductivity and Application of Boron Nitride Nanosheets Qiran Cai[1], Hongbo Jiang[1], Srikanth Mateti[1], Elton J. Santos[2], Luhua Li[1] and Ying Chen[1]; [1]Deakin University, Australia; [2]The University of Edinburgh, United Kingdom

Heat dissipation becomes increasingly critical, especially in miniaturised modern devices, and boron nitride (BN) nanosheets are considered as a promising material for heat dissipation because of high thermal conductivity yet electrical insulation. Here, we firstly report the intrinsic thermal conductivity of atomically thin BN, and the density functional theory calculation reveals the thickness and isotope effects on the heat transport *(1-2)*. To improve the dispersibility of BN nanosheets for the fabrication of advanced composites, we develop a simple, yet efficient mechanochemical exfoliation technique to prepare functionalised BN nanosheets with excellent dispersibility in water and organic solvents *(3)*. Using the high-quality BN nanosheet dispersion as a precursor, BN spheres with high, isotropic thermal conductivity are fabricated, which can isotropically enhance the thermal conductivity of poly(vinyl alcohol) by ~3700%, and address the challenge that BN reinforced polymer offers a highly anisotropic thermal conductivity *(4)*. This study provides not only the important insight into the heat transport and phonon scattering mechanism, but also a practical route to fabricate BN-enhanced thermal interface materials with high isotropic thermal conductivity and promising materials that are valuable for heat dissipation in new-era advanced electronics and related applications.
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2:15 PM SF03.18.06
A Data-Driven Exploration of Structure-Property Relationships of Thermal Transport in Metal-Organic Frameworks Meiirbek Islamov[1], Hasan Babaei[2], Jeffrey Long[2,3], Alan McGaughey[4], Diego Gómez-Gualdrón[5] and Christopher E. Wilmer[1]; [1]University of Pittsburgh, United States; [2]University of California, Berkeley, United States; [3]Lawrence Berkeley National Laboratory, United States; [4]Carnegie Mellon University, United States; [5]Colorado School of Mines, United States

Metal-Organic Frameworks (MOFs) are a class of nanoporous materials that have been heralded as revolutionary materials for gas adsorption applications. However, the usefulness of MOFs depends on how quickly they can dissipate the enormous amount of heat generated during the exothermic adsorption process. Despite its importance, thermal energy management in MOFs has been frequently neglected, which resulted in a limited understanding of the structure-thermal transport relationships in MOFs. To shed a data-driven perspective into these relationships, we performed the first large-scale computational screening of 10,194 hypothetical MOFs for thermal conductivity using classical molecular dynamics (MD) simulations and the equilibrium Green-Kubo method. We found that high thermal conductivity is favored by small pores, high density, and four-connected metal nodes. Moreover, we discovered six hypothetical MOFs that exhibit very high thermal conductivity. Interestingly, these six MOFs have in common square planar metal nodes that are each connected to four perpendicular organic linkers, indicating that topology may be particularly important for heat conduction in MOFs.

2:30 PM SF03.18.08
Computational Analysis of Plastic Crystals as Solid-Solid Phase-Change Materials—Insight into the Molecular Mechanism of Thermal Energy Storage Atta Muhammad[1,2], Eliodoro Chiavazzo[1] and Matteo Fasano[1]; [1]Politecnico di Torino, Italy; [2]Mehran University of Engineering and Technology, SZAB Campus, Pakistan

Plastic crystals are promising candidates for solid-solid phase-change materials (PCMs) in thermal energy storage components and systems. The peculiar feature is the fact that they remain solid throughout the phase transition temperature range, thus reducing the need for containment and possible additivation [1]. Plastic crystals are organic molecular crystals that display solid-solid phase transitions at temperatures ranging from 310 K to 463 K with relatively large latent heat (over 100 J/g-K). Plastic crystals transform from a low-symmetry crystal structure to a high-symmetry one at a set temperature while absorbing a significant amount of heat (and vice versa).
In this work, we perform theoretical investigations based on classical molecular dynamics (MD) simulations to obtain new physical insights into plastic crystals as PCMs and provide useful information for the rational design of new solid-solid PCMs [2]. We calculate the latent heat, density, number of hydrogen bonds, the energy of hydrogen bonds, radial distribution function, specific heat capacity, and thermal conductivity of three polyalcohols (Pentaerythritol, Pentaglycerine, and Neopentylglycol). MD simulations are also performed to elucidate the relationship between the thermophysical

characteristics of polyalcohols and their crystalline structures at the atomic level. These plastic crystals are selected because relevant thermophysical properties have been reported being phase transition temperature and latent heat for pentaerythritol much higher than those for pentaglycerine and neopentylglycol. Our MD simulation results quantitively reproduce the properties of polyalcohols obtained in recent experiments for the first time [3]. Based on the analysis, we find that their latent heat originates mainly from the decrease in the number and strength of intermolecular hydrogen bonds upon solid-solid phase transition. Furthermore, we also examine the origin of the difference in latent heat between these three polyalcohols.
Overall, this work reveals the molecular mechanism of thermal energy storage of solid-solid PCMs and provides valuable insights for the development of new materials with high latent heat without the need for encapsulation, with a prospected impact in the development of a new class of thermal energy storage systems based on solid-solid PCMs [4].

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SESSION SF03.19: Nanostructures for Modulating Energy Transport

Session Chairs: Lucas Lindsay and Qichen Song
Friday Afternoon, April 14, 2023
Marriott Marquis, B2 Level, Golden Gate A

3:30 PM SF03.19.02
Study of Carrier and Thermal Transport in Semiconductors Using Frequency Domain Thermoreflectance Qichen Song[1] and Samuel Huberman[2]; [1]Harvard University, United States; [2]McGill University, Canada

Frequency domain thermoreflectance (FDTR) is a versatile and powerful characterization technique to study thermal transport in materials. A metallic transducer is often coated on top of the sample to convert laser irradiation into lattice heating. However, the additional layer complicates the heat transfer analysis, and it is thus tempting to conduct the FDTR without the transducer layer. To properly interpret the transducerless FDTR, the non-thermal processes after photon absorption must be modeled. Here, we solved the coupled carrier and heat diffusion equations, which capture the physical processes including ambipolar diffusion, electron-phonon coupling and carrier recombination. Our transducerless FDTR measurements in Si, Ge and GaAs corroborate our model and reveal that the contribution of carrier transport to the signal varies with the dopant concentration. Our study offers insights in understanding the energy dissipation processes in semiconductor devices.

3:45 PM SF03.19.03
Tunability of Thermal Conductivity in Porous 2D-Covalent Organic Frameworks Emma Tiernan[1], Zoheb Hirani[2], John Tomko[1], Lidia Kuo[2], Nathan Bradshaw[2], Nicholas Williams[2], David Burke[2], Austin Evans[3], Mark C. Hersam[2], Patrick E. Hopkins[1] and William Dichtel[2]; [1]University of Virginia, United States; [2]Northwestern University, United States; [3]Columbia University, United States

Covalent organic frameworks (COFs) are a unique class of porous material, in which chemists can easily modulate multiple properties of the COFs by varying the nodes and linkers that make up the framework. The interchangeability of these organic building blocks allows for the structures to have a multitude of applications such as gas separation, catalysis, sensing, electronic devices, energy storage, and more. Conversely, the ability to implement COFs in these applications was limited due to the COFs polycrystalline powder form. In recent years, there has been a large effort to grow 2D COF thin films, which resulted in films with thermal conductivities of 1.0 W m^{-1} K^{-1}. In this presentation, we will use both time-domain thermoreflectance (TDTR) and steady state thermoreflectance (SSTR) to measure thermal and mechanical properties of a variety of COF thin films, including boronate-ester and imine-linked 2D COFs. TDTR and SSTR are non-contact, laser-based, pump-probe measurement techniques, which relate the change in reflectivity of the sample surface, to the thermal conductivities of the COF films below. We will discuss the effects of film thickness, connectivity, and pore functionality on the thermal properties of COF thin films.

4:00 PM SF03.19.04
Near-Field Thermal Radiation vs Near-Field Electroluminescence—Conditions for a Nanothermophotonic Refrigerator Thomas Châtelet, Julien Legendre, Pierre-Olivier Chapuis and Olivier Merchiers; Univ Lyon, CNRS, INSA-Lyon, Université Claude Bernard Lyon 1, CETHIL UMR5008, France

Fluid-based refrigerating devices are known to be noisy, involve polluting refrigerants and cannot be miniaturized easily, so solid-state coolers are especially promising to replace them. Peltier thermoelectric coolers are well-established devices that are smaller, vibration-free heat pumps, but they suffer from low efficiency at room temperature and are difficult to miniaturize further without reducing the temperature difference between the hot and cold sides. Light-emitting diodes (LED), which are also thermodynamic machines, are another category of solid-state coolers [1]. Under particular conditions, LEDs are expected to emit larger radiative power than the supplied electrical power, by pumping heat from their crystalline lattice, resulting in a cooling of the LED and its contacting environment: this effect is called electroluminescent cooling [2]. Since this effect is small, two improvements have been suggested. First, harvesting the radiation emitted by the LED by converting it into electricity in a photovoltaic (PV) cell and sending it back to the LED allows reducing the need for external powering and therefore increases the coefficient of performance of the device. Such combined device is termed thermophotonic (TPX) [1, 3]. Second, the emitted radiation can be enhanced by placing the PV cell in close proximity of the PV cell, in order to allow additional (evanescent) photons to tunnel through the separation gap: the device works then in the near field [4].
A key issue in such device is that the warmer PV cell can also radiate thermally towards the LED, reducing the net power transferred by the LED towards its surrounding. The issue is particularly significant when the two components are in the near field. By means of accurate nanoscale radiative computation

(fluctuational electrodynamics) and detailed balance, we investigate the effect of internal quantum efficiency, temperature, and vacuum gap distance on the potential performances of near-field TPX refrigerators made of GaAs-based materials. In a second step, the drift-diffusion equations are solved to analyse the charge carrier behaviour in a more realistic TPX system [4]. Finally, we analyse how surface roughness impacts the light extraction efficiency and the radiative heat transport in the device.

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This work has received funding from project EU H2020 FETOpen-2018-2019-01/GA964698 (OPTAGON).

4:15 PM SF03.19.05
Heat Transfer by Nonequilibrium Electrons in Nanoscale Metal Thin Films and Bilayers Xinping Shi and Richard Wilson; University of California, Riverside, United States

Photoexcitation of a metal drives electrons into a high energy nonequilibrium state. Relaxation of the excited electrons back to equilibrium is often treated with a two-temperature model framework. In the two-temperature model, nonthermal effects are ignored, and transport is assumed to be diffusive. Alternatively, nonequilibrium electron dynamics can be modelled with the Boltzmann transport equation [1]. The Boltzmann transport equation predicts different energy relaxation time-scales and predicts different energy transport length-scales than the two-temperature model. Clear criteria for when the two-temperature model vs. Boltzmann transport equation apply have not been experimentally established. In this talk, we report experimental measurements of nonequilibrium energy dynamics in Al, Cu, Ag, and Au. Our goal is to understand how electron-phonon interaction strengths effect the applicability of two-temperature model vs. Boltzmann transport equation. Measurements of Al, Cu, Ag, and Au are a good test for this because these four metals have systematically different electron-phonon interaction strengths due to differences in atomic mass. We perform a series of time domain thermoreflectance measurements on Al, Cu, Ag, and Au wedge thin-films and Al/Fe, Cu/Pt, Ag/Pt and Au/Pt wedge bilayers. The wedge samples have thicknesses that vary between 0 and 500 nm as a function of position. By performing measurements at different sample locations with different thicknesses, we can accurately measure how far nonequilibrium electrons carry heat before thermalizing with phonons in different material systems. We perform experiments both in a standard front/front and a front/back laser flash geometry. Our experiments show that, while the energy dynamics in Au after photoexcitation are nonthermal, heat transport by nonequilibrium electrons is almost entirely diffusive. We establish simple heuristics that describe how nonequilibrium processes effect energy dynamics in metal heterostructures on time-scales from 10 fs to 10 ns. Our work provides benchmark knowledge about nonequilibrium electron dynamics that will aid applications in nanoscale thermal engineering, photocatalysis, and spintronics.
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4:30 PM SF03.19.06
Thermal, Mechanical and Electronic Tunability in Polymerized Fullerene Structures Jaymes Dionne, Muhammad Akif Rahman and Ashutosh Giri; University of Rhode Island, United States

Recently, polymerized fullerene crystals have been synthesized through the intercalation of alkaline earth metals, avoiding the costly fabrication process involving high pressure conditions. In this study, we show that this polymerization and the introduction of intermolecular bonds between fullerene molecules offers tunable control over their mechanical, thermal, and electronic properties. The superatomic crystals polymerize in tetragonal and rhombohedral phases, or T- and R-phase, respectively, where the molecules are arranged in uniquely layered sheets, similar to that of graphene and its' bulk structure graphite. By utilizing molecular dynamics (MD) simulations and density functional theory (DFT) calculations to investigate the thermal, mechanical, and electronic properties of these phases of polymerized fullerene crystals, we find a drastic enhancement of the thermal conductivity in the in-plane direction when compared to the nonbonded FCC fullerite structure. Moreover. we find that the intercalation of magnesium atoms results in a higher thermal conductivity at room temperature compared to the pristine polymerized structure, which we attribute to the competing mechanisms of temperature-independent impurity scattering and temperature-dependent Umklapp scattering.
In terms of the mechanical properties when compared to other condensed carbon phases, the polymerized fullerenes are relatively more flexible, with a Young's modulus of 110-170 GPa, and are comparatively softer with a bulk modulus of 38.5 GPa. Moreover, the R-phase structure is more flexible than the T-phase structure thus providing an avenue for tunability in their mechanical properties. For both structures, we visualize the von Mises strain distributions and discover that the bulk of the strain is localized in sp^2 carbon atoms near the sp^3 carbon atoms forming the intermolecular bonds, rather than the sp^3 carbon atoms themselves.
For their electronic properties, we find a strain dependent band gap for which the electronic band gap reduces from 0.54 to 0.31 eV under a 4% applied strain. By visualizing the electronic localization function, we attribute this reduction in band gap to increased overlap of covalently bonded atoms forming the intermolecular bonds. As these phases of polymerized fullerenes have the potential to be used as next-generation battery materials, these results highlight their mechanical and electronic similarities to current battery electrodes, as well as the opportunity to potentially improve their heat transfer properties for better thermal management of battery systems.

SESSION SF03.20: Emerging Thermal Materials—From Nanoscale Heat Transport, Devices and Applications, to Theories I
Session Chairs: Lucas Lindsay and Nuo Yang
Tuesday Afternoon, April 25, 2023
SF03-virtual

1:30 PM *SF03.20.01
Fundamental Study on Phonon Engineering Nuo Yang; Huazhong Univ of S&T, China

Recently, with the rapid development of smart society, our demand for new functional materials and hardware is urgent. Thermal functional materials play an important role in thermal management, energy storage and energy conversion. Phonons are lattice vibrational waves, which are the main energy carriers in dielectric solids. After electronic engineering and photonic engineering, the research progress of phonon engineering has attracted much attention. Phonon engineering is the discipline of designing and controlling phonon transport and conversion by using phonon devices with micro/nano structure,

which plays a leading role in the design of thermal functional materials. The research objects of phonon engineering include lattice wave quantum transport, thermoelectric conversion, phonon devices and so on. The progress of nanotechnology has also promoted the development of phonon engineering, so there is an urgent need to understand the mechanism of phonon regulation and transport.
Professor Nuo YANG and the Nano Heat Group [1] focus on the fundamental and applied research of heat transfer, thermal control and energy conversion in micro/nano- and multi- scale [2-5]. The report will introduce the research progress of the Nano Heat Group in the following aspects: nanoscale heat conduction, thermal control, thermal interface conduction, hotspot, size effect, etc.

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2:00 PM SF03.20.03
Synergistic Experimental and Computational Research on New Multinary Chalcogenides with Earth Abundant Constituents George S. Nolas and Lilia Woods; Univ of South Florida, United States

Multinary metal chalcogenides are known to form in a variety of structure types and exhibit varying properties depending on composition, crystal structure, chemical bonding, and processing conditions. Nevertheless, providing new avenues for discovery allows for pathways towards the design of new materials, and processing techniques, with targeted properties for specific applications of interest. One such approach is by cation substitution methods, where one can “build” a variety of materials with different chemical formulas while maintaining the valence electron count. Moreover, knowledge of the thermal properties is essential for any application of interest, particularly for thermoelectric, thermophotovoltaic, thermos-acoustic and thermal barrier materials, where low thermal conductivity is obtained when specific features, such as weak bonding, coordination preferences, lone pair electrons, large number of atoms per unit cell, nanoscale effects and strong anharmonicity, are realized. Motivated by these considerations and our continued interest in the effect of complex structure and disorder on the thermal properties of multinary chalcogenides, we investigated the thermal and electronic properties of several new chalcogenides employing cationic substitution. We expand on the techniques we’ve previously employed in investigating Kesterites and Stannites, and will present our most recent work on the structure-property relationships of materials with Adamantine, Sphalerite and Aikinite crystal structures. An intrinsically low thermal conductivity is typical in these materials, and a result of lattice anharmonicity as well as the particular bonding and, in some cases, defects these materials possess. Our research provides a better understanding of the fundamental properties of these materials, with an eye towards determining their suitability for use in thermoelectric applications.

2:15 PM SF03.20.04
Near-Field Radiative Enhancements—Benefits and Drawbacks for Thermophotonic Energy Harvesting Julien Legendre and Pierre-Olivier Chapuis; CNRS-CETHIL, France

Thermophotonics (TPX) [1] is a technology close to thermophotovoltaics (TPV), where a heated light-emitting diode (LED) is used as the active emitter. Interestingly, an LED is physically similar to a TPV cell, but used in the opposite fashion, i.e. it emits light from electrical power. With such a device, the emission profile can be tuned: initially in the infrared range, it can be shifted by means of electroluminescence to a spectral range matching better the gap of efficient TPV cells. With the development of LEDs and the increase of their achievable quantum efficiency, TPX has come out as an attractive concept for both energy harvesting and refrigeration [2]. One advantage is that the emitter temperature can stay moderate, close to few hundreds of degrees Celsius, in contrast to usual TPV emitters. The many studies on near-field (NF) thermal radiation and their application into efficient NF-TPV devices [3] highlight the possibility to extend the concept to near-field thermophotonics (NF-TPX), where enhanced energy conversion is due to both electrical control and wave tunneling.

In order to model accurately the device and deduce the electrical power output, we couple a radiative transfer solver based on fluctuational electrodynamics - a framework allowing to deal with thermal and nonthermal (electroluminescent) emission within the medium - with a drift-diffusion equations (DDE) solver used for both the LED and the cell [4,5]. This reveals that an electrical power density as high as 2.2 W/cm^2 (~7 mW/cm^{2}K) can be obtained from the NF-TPX device by using realistic AlGaAs PIN homojunctions with the emitter at 300°C. Through a thorough analysis of this device, we point out that such high power can only be achieved in the near-field regime, which is mandatory to extract any power [5]. However, going to the near field also largely increases thermal radiation due to below-bandgap energy surface plasmon/phonon polaritons, which potentially gives rise to large temperature deviation in both LED and cell components and thus induce a significant performance drop. A thermal study performed on TPX devices shows that for a given thermal management system, there is an optimal separation distance that results from a trade-off between increased above-bandgap power transmission and worsened thermal management.

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2:30 PM SF03.20.05
Chemically Induced Tuning of Interfacial Thermal Resistance in Porous Silicon/Hexadecane Nanocomposite Oksana Makukha[1], Vladimir Lysenko[2] and Ali Belarouci[1]; [1]Institute of Nanotechnology of Lyon, France; [2]Light-Matter Institute, France

During the last decade, the rapid evolution of elaboration methods for new nanomaterials and nano-architectured devices and systems requires deep understanding and technological mastering of fundamental mechanisms responsible for heat transport at the nanoscale [1]. A specific scientific interest is focused on thermal phenomena taking place across multiphase nanoscale interfaces, such as liquid-solid interfaces. The presence of liquids confined in nanopores of a solid-state material strongly affects heat transfer at the nanoscale as well as the global thermal properties of the liquid-solid nanocomposites. In a porous crystalline matrix with large specific surface areas up to 600-800 m^2/g (such as porous silicon, for example) containing a liquid confined in the nanopore network, one should absolutely consider heat transfer phenomena through the solid-liquid interfaces described in terms of interfacial thermal resistances. Surface chemistry modification of the nanoporous solid skeleton may lead to significant changes in thermal resistance. The thermal mismatch at the interface can be reduced by appropriate surface functionalization, whose thermal properties, hydrophilicity, and wettability characteristics match better those of the surrounding liquid [2].
There are numerous approaches for the chemical functionalization of Si surfaces. The most common methods rely on: (i) formation of Si–C

(hydrosilylation, carbonization, etc.) or (ii) Si–O bonds (e.g., silanization). A wide range of existing chemical functionalities allows tuning surface properties according to a specific application. In particular, an outstanding versatility of silanization enables to vary wetting properties in a wide range, from hydrophilic to super-hydrophobic. At the same time, monolayer and crosslinked multilayers are achievable, grafted either to the whole surface or with some patterns. Among the strongest advantages of silanization are mild conditions of the reaction permitting deposition of molecules with active or sensitive functional groups, such as –SH, –CN, –COOH, –COH, –C(O)C, –NH2, etc.
In the current work, the photo-induced temperature growth estimated from micro-Raman measurements was correlated with the steady-state heat transport finite element modeling (FEM) to estimate thermal conductivity values of porous silicon/hexadecane nanocomposite. To illustrate the impact of surface chemistry at silicon/hexadecane interface on the corresponding interfacial thermal resistance, silanization with alkyl and amino silanes was performed. In order to prevent any significant changes of porous silicon morphology, soft wet chemical oxidation was carried out. Contribution of the formed oxide and grafted silanes to the heat conduction in the porous silicon/hexadecane nanocomposites were studied.

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SESSION SF03.21: Emerging Thermal Materials—From Nanoscale Heat Transport, Devices and Applications, to Theories II
Session Chair: Lucas Lindsay
Tuesday Afternoon, April 25, 2023
SF03-virtual

4:00 PM SF03.21.02
Testing and Modeling of an *In Situ* Shear Exfoliated 2D Nanocomposite Coating Casing Material for the Suppression of Li-Ion Battery Fires in Electric Vehicles Md Ashiqur Rahman[1], MD Abdur Rahman Bin Abdus Salam[1], Humaun Kabir[2], Elmmer Vera Alvarado[1], Tousif Sadman[3], Rajib Mahamud[4], Kibria K. Roman[5], Mohammad Nahid[6] and Ali Ashraf[1]; [1]University of Texas Rio Grande Valley, United States; [2]Chittagong University of Engineering and Technology, Bangladesh; [3]Bangladesh University of Engineering & Technology, Bangladesh; [4]Idaho State University, United States; [5]The State University of New York at Canton, United States; [6]FCA Fiat Chrysler Automobiles, United States

The requirements of high energy density Li-ion battery along with its flammable electrolyte in electric and hybrid electric vehicles makes it susceptible to abusive operating conditions leading to thermal runaway, gas venting, fires, and explosions. Though there are external cooling and in-situ measures (e.g., coating of cathode with inert materials) for the prevention of thermal runaway, initiation of thermal runaway in one cell can easily propagate to adjacent cells, the entire pack assembly, and the vehicle. The commercial application generally focuses on water mist for the suppression of fire, the effectiveness of which depends on the types of fire encountered or the particular event scenarios. In this study, a 2D nanocomposite coating material, a mixture of dragon skin® (flame-resistant silicone elastomer from Smooth on, Inc.) and hexagonal boron nitride (DS/hBN), was applied on the traditional polycarbonate casing material to study its effect on flame retardancy. Dragon skin polymer precursor (dragon skin part A) and curing agent (dragon skin part B) with 5% low-cost layered hBN were mixed separately in a Hauschild planetary mixer to get homogenous mixing (at 2500 rpm for 2 minutes). A micro batch mixer was used to simultaneously exfoliate hBN nanosheets from bulk layered hBN raw materials and disperse these nanolayers into both dragon skin polymer precursor and curing agent separately (at 100 rpm for 10 minutes). Dragon skin polymer precursor and curing agent with exfoliated hBN were mixed in a 1:1 weight ratio to coat the polycarbonate and dried for 24 hours. Scanning electron microscopy (SEM) images confirmed the uniform dispersibility of these nanosheets. Standard 'UL94 Flammability Test' protocol was followed to measure the flame retardancy of the prepared sample. Here, Tests were conducted in both the horizontal and vertical testing arrangement specified in the standard. Besides, for the control experiment, another sample containing a coating of only dragon skin (DS) was prepared and tested. In the horizontal test, uncoated polycarbonate was found to burn extensively (labeled as "Failed"), whereas DS-coated and DS/hBN-coated polycarbonate slowed the burning rate by 33 mm/min and 9 mm/min, respectively. The burning rate of DS-coated and DS/hBN-coated samples is lower than 75 mm/min, so these can be categorized as "HB". In the vertical test, after the initial flame exposure, the flame was extinguished within 5 sec and 15 sec for the DS/hBN-coated and the DS-coated sample, respectively. During the burning, no dripping was observed for the DS/hBN-coated sample, whereas the DS-coated sample showed severe dripping and crack propagation in the coating layer. Moreover, during the vertical test of the DS-coated sample, the fire spread quickly and reached the clamp before extinguishment. So, DS-coated and DS/hBN-coated sample was rated as 'Failed' and 'V-1', respectively. These promising findings show the potential hBN nanosheets-based nanocomposites prepared from low-cost materials by in-situ shear exfoliation, which can form three-dimensional networks to rapidly disperse heat and build an efficient char layer for insulating the exposed polymer and forming a thermal barrier. Additionally, A multiphysics model is developed and applied to study the effect of butane fire on a traditional casing material and the 2D nanocomposite-coated material.

4:15 PM SF03.21.03
Subnanometer-Scale Visualization of Interaction Forces at Self-Assembled Molecules/Water Interfaces with 3D-AFM Moe Ogasawara, Masayuki Morimoto and Hitoshi Asakawa; Kanazawa University, Japan

The formation of self-assembled structures with organic building blocks on solid materials through a bottom-up process has been studied by many researchers. Three-dimensional (3D) self-assembled structures are promising for functional devices such as separation and storage. Molecular recognition utilizing nanospaces in self-assembled structures is an important research topic for their applications. However, understanding the recognition mechanism, for example, how the nanospace in a host structure interacts with the guest molecule, is still challenging. One of the main obstacles is a lack of analytical methods for investigating interaction forces acting in 3D nanospaces. 3D scanning atomic force microscopy (3D-AFM) has been developed as a "structural measurement" technique that allows us to visualize the spatial distributions of hydration and surface fluctuating structures in the nanospaces at the solid/liquid interfaces. Tip scanning of conventional AFMs is only in the XY direction, whereas the tip is scanned in the Z direction in addition to the XY direction in the 3D-AFM imaging. The Z + XY tip scanning makes it possible to obtain 3D force distribution images. Combining the 3D-AFM with a frequency-shift detection method, the interaction forces acting on the tip are detectable at the pico-Newton (pN) level. Based on the principle and performance, we believe that the 3D-AFM technique can be applied as an analytical tool for not only "structural measurement " but also "interaction force measurement."
In this study, we demonstrated the direct visualization of the interaction forces in 3D nanospaces at self-assembled molecules/water interfaces with the 3D-AFM technique. Two types of tetrakis4-ethynylphenylmethane (TEPM) derivatives with oligo(ethyleneglycol) (EG$_n$) chain (EG$_2$-TEPM, EG$_4$-TEPM) were used as the building blocks. The TEPM derivatives form self-assembled monolayers on graphite. In the monolayers, there are hydrophobic pockets

(diameter: approx. 1.7 nm) surrounded by the aromatic structure of the TEPM derivatives. The interaction forces in hydrophobic pockets were measured by the 3D-AFM in water. As a result, characteristic localized attractive interaction was visualized only at the EG_2-TEPM monolayer/water interface, and analysis of the 3D-AFM images suggests that the attractive interactions originate from hydrophobic pockets. The number of hydrogen bond networks of water in the hydrophobic pockets of EG_2-TEPM monolayer is small compared to bulk water, resulting in the low density of water molecules. The attractive interactions are likely caused by the low density of water molecules in the hydrophobic pockets. Our results demonstrate that the 3D-AFM technique has the capability of visualizing the characteristic interaction forces at the single molecule level, suggesting future contributions to the elucidation of the molecular recognition mechanisms.

4:20 PM SF03.21.04
Thermal Properties and Phase Transformation Behavior of YSZ Co-Doped by Rare Earth Oxides (La2O3, Gd2O3, Yb2O3) Tserendorj Khadaa, Junseong Kim, Janghyeok Pyeon, Hyeryang Choi, Bong-Gu Kim, Byungil Yang, Yeon-Gil Jung and SeungCheol Yang; Changwon National University, Korea (the Republic of)

Thermal barrier coating (TBC) materials were used to the application at high operating temperature component of gas turbine engines. Recently, 6-8 wt.% yttria-stabilized zirconia (8YSZ) has been widely used material for TBC. However, 8YSZ deteriorates at temperatures above 1200 °C due to their sintering phenomena and phase transition, which limiting its use as the TBC material for high temperature gas turbine. Co-doped YSZ powders containing rare earth oxides have recently been the subject of ongoing research. So, we recommend improved three types of YSZ compositions co-doped with La, Gd, and Yb. The YSZ co-doped with the compositions were prepared by ball milling and then made pellets and sintered. Then, we analyzed microstructure, thermal properties, mechanical properties and phase transformation behavior with various tools. The addition of La, Gd and Yb into YSZ effectively make thermal conductivity low and improve phase stability and mechanical properties of the YSZ which would improve the performances of thermal barrier coating. Therefore, we suggest that three types of compositions can be used instead of 8YSZ as materials for next-generation gas turbine engines.

4:25 PM SF03.15.07
Enhancement of Thermoelectric Performances by Aliovalent Bi and Sb Doping in SnTe-Based Material Wenxuan Wang[1], Chen Chen[2] and Yue Chen[1]; [1]The University of Hong Kong, Hong Kong; [2]Great Bay University, China

Thermoelectric materials are considered as a potential replacement of fossil fuels for their ability of directly converting heat to electricity. The Pb-free SnTe-based materials show high thermoelectric performances and attract much research attention. However, only few of the optimizations focused on the high carrier concentration attributed to the intrinsic Sn vacancies. In this work, we demonstrate that bismuth and antimony doping in an SnTe-based material, where Ge and Mn are added to manipulate the band structure, and self-compensation of Sn decrease the carrier concentration. The doping of bismuth and antimony further reduce the carrier concentration and contribute to the enhancement of Seebeck coefficient and thermoelectric performance. The highest dimensionless figure of merit (zT_{max}) reaches ~1.2 at 823 K, showing the influence of Sn vacancy compensation on thermoelectric performance.

4:30 PM SF03.13.02
Structural Evolution Mechanisms of Anticorrosion Coatings on Steel Using Raman Mapping Microscopy Jixi Zhang and Rodney Smith; University of Waterloo, Canada

Micron-scale coatings are widely used to protect steel plates from oxidation during hot stamping, which is a particularly important manufacturing protocol for the automotive industry. These coatings effectively protect the steel, but they also melt at the necessary temperatures for steel processing. The high-temperature liquids can then transfer to furnace components and damage the manufacturing line, incurring high costs through maintenance and production line downtime. Once melted, however, these coatings are also known as leech Fe from the steel to form intermetallic phases. This leeching leads to a change in composition, inducing a complex multi-step chain of reactions that ultimately yield a solid coating. The identity of these intermetallic phases and the series of phase evolutions have been studied extensively by electron microscopy and energy dispersive X-ray spectroscopy. We introduce Raman microscopic mapping as a simple, rapid, and complementary technique for phase transition analysis. Samples were prepared by heating a series of 22MnB5 steel coupons to set temperatures between 570 to 900°C to simulate the industrial hot stamping conditions. Raman microscopic mapping of cross-sections of each sample reveals the phase transitions with increasing temperatures. This analysis reveals a structural evolution mechanism slightly different than that suggested by electron microscopy. New insights gained through Raman microscopic mapping show that it is a powerful tool to identify the underlying chemical problems that lead to the destruction of industrial infrastructure, and to test the viability of strategies to overcome these problems.

SYMPOSIUM

April 11 - April 25, 2023

Symposium Organizers
Michael Frazier, University of California, San Diego
Xiaoyue Ni, Duke University
Carlos Portela, Massachusetts Institute of Technology
Xiaoxing Xia, Lawrence Livermore National Laboratory

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* Invited Paper
\+ Distinguished Invited

SESSION SF04.01: Wave Phenomena in Architected Materials
Session Chairs: Michael Frazier and Carlos Portela
Tuesday Morning, April 11, 2023
Marriott Marquis, B2 Level, Golden Gate C3

10:30 AM *SF04.01.01
Extreme Wave Phenomena in Mechanical Metamaterials Andrea Alu; City University of New York, United States

In this talk I will discuss our recent progress in the area of mechanical architected metamaterials, showcasing extreme examples of wave manipulation of elastic waves. In addition to discussing the general opportunities stemming from architected materials for extreme wave manipulation, I will also present examples in which reconfigurability, wave interference and geometric transformations offer new opportunities for extreme and dynamic wave control, with a broad range of applications.

11:00 AM *SF04.01.02
Elastodyanmic Properties of Architected Metamaterials Yun Jing; The Pennsylvania State University, United States

While architected metamaterials have been well studied for their quasi-static properties, their elastodynamic properties have been largely unexplored. In this talk, I will give an overview of our recent theoretical and experimental works pertaining to how architected metamaterials interact with vibration. I will first introduce a class of metamaterials that achieve low-frequency band gaps with a volume fraction as low as 3% (mass density as low as 0.034 g/cm^3). The working of the proposed design hinges on a 3D trampoline-like mode behavior that gives rise to wide, omnidirectional, and low-frequency band gaps for elastic waves despite very low-mass densities. Such a 3D trampoline effect is derived from a network of overhanging nodal microarchitectures that act as locally resonating elements, which give rise to band gaps at low frequencies. I will then present results on architected metamaterials made of a periodic arrangement of octet truss units with alternating circular strut diameters. The octet truss endows the meta-structure with a high effective stiffness and a low effective density, while alternating the units with different struts radii enables the opening of a band gap for elastic waves. For both types of metamaterials, samples were 3D printed and experimentally validated using a shaker and accelerometer. Unidirectional compression test was also performed to characterize the mechanical properties of the octet truss lattice.

SESSION SF04.02: Advancement in Fabrication of Architected Materials
Session Chairs: Xiaoyue Ni and Xiaoxing Xia
Tuesday Afternoon, April 11, 2023
Marriott Marquis, B2 Level, Golden Gate C3

1:30 PM *SF04.02.01
Intelligentsia of Nano-Architected Hierarchical Materials Julia R. Greer[1], Seola Lee[1], Max A. Saccone[2], Widianto P. Moestopo[3] and Seneca Velling[1]; [1]California Institute of Technology, United States; [2]Stanford University, United States; [3]Lawrence Livermore National Laboratory, United States

Creation of reconfigurable and multi-functional materials can be achieved by incorporating architecture into material design. In our research,we design and fabricate three-dimensional (3D) nano-architected materials that can exhibit superior and often tunable thermal, photonic, electrochemical, biochemical, and mechanical properties at extremely low mass densities (lighter than aerogels), which renders them useful and enabling in many technological applications. Dominant properties of such meta-materials are driven by their multi-scale nature: from characteristic material microstructure (atoms) to individual constituents (nanometers) to structural components (microns) to overall architectures (millimeters and above).
Our research is focused on fabrication and synthesis of nano- and micro-architected materials using 3D lithography, nanofabrication, and additive manufacturing (AM) techniques, as well as on investigating their mechanical, biochemical, electromechanical, and thermal properties as a function of architecture, constituent materials, and microstructural detail. Additive manufacturing (AM) represents a set of processes that fabricate complex 3D structures using a layer-by-layer approach, with some advanced methods attaining nanometer resolution and the creation of unique, multifunctional materials and shapes derived from a *photoinitiation-based chemical reaction* of custom synthesized resins and thermal post-processing. A type of AM, vat polymerization, has allowed for using hydrogels as precursors, and exploiting novel material properties, especially those that arise at the nano-scale and do not occur in conventional materials. The focus of this talk is on additive manufacturing via vat polymerization and function-containing chemical synthesis to create 3D nano- and micro-architected metals, ceramics, multifunctional metal oxides (nano-photonics, photocatalytic, piezoelectric, etc.), and metal-containing polymer complexes, etc., as well as demonstrate their potential in some real-use biomedical, protective, and sensing applications. I will describe how the choice of architecture, material, and external stimulus can elicit stimulus-responsive, reconfigurable, and multifunctional response.

2:00 PM *SF04.02.02
3D and 4D Printing: High Performance and Stimuli-Responsive Polymer Materials Rigoberto C. Advincula; The University of Tennessee/Oak Ridge National Laboratory, United States

The advent of 3D printing has enabled prototypes and devices of high-performance polymeric materials which have appended functionality based on composition and macromolecular design. 3D printed polymers can be further classified into thermoplastics, thermosetsond elastomers based with their corresponding thermo-mechanical properties. However, using multi-materials and 4D printing allows the design of new materials and applications based on integrating conversion chemistry with the printing mode. This talk will demonstrate stimuli-responsive properties and 4D fabrication of multi-materials, including epoxy and benzoxazine thermosets and silicone elastomers with concept objects and elastomeric properties exhibiting stimuli-response. While most of the method focuses on DIW or viscous solution printing (VSP), other works using SLA, SLS, and FDM 3D Printing will also be revealed.

2:30 PM SF04.02.04
Universal Way to 'Glue' Capsules, Gels and Tissues in 3D Using Electric Fields Leah K. Borden[1,2] and Srinivasa R. Raghavan[1]; [1]University of

Maryland, United States; [2]Massachusetts Institute of Technology, United States

This work will demonstrate the use of an adhesion induced by an electric field, i.e., Electro-adhesion (EA) to connect a variety of soft materials into 3D structures. EA requires a cationic and an anionic material, but these can be of diverse origin. For example, these can include covalently crosslinked hydrogels made by polymerizing charged monomers as well as physical gels/capsules formed by the ionic crosslinking of biopolymers (e.g., alginate and chitosan). In addition, the anionic material could be electroadhered to naturally occurring soft materials such as animal and plant tissues [1].

Between each cationic/anionic pair, EA is induced rapidly (in ~ 10 s) by low voltages (~ 10 V DC) - and the adhesion is permanent after the field is turned off. This adhesion is strong enough to allow millimeter-scale capsules/gels to be assembled in 3D into robust structures such as capsule-capsule chains, capsule arrays on a base gel, and a 3D cube of capsules. EA-based assembly of spherical building blocks can be done more precisely, rapidly, and easily than by any alternative techniques. Moreover, the adhesion can be reversed (by switching the polarity of the field) - hence any errors during assembly can be undone and fixed.

EA can also be used for selective sorting of charged soft matter - for example, a 'finger robot' can selectively 'pick up' capsules of the opposite charge by EA and subsequently 'drop off' these structures by reversing the polarity. In this talk we will also explore various experimental results that shed light on the mechanism of EA. Overall, our work shows how electric fields can be used to connect soft matter without the need for an adhesive or glue.

[1] L. K. Borden, A. Gargava and S. R. Raghavan
Reversible Electroadhesion of Hydrogels to Animal Tissues for Suture-less Repair of Cuts or Tears.
Nature Communications, 12, 4419 (2021)

2:45 PM SF04.02.05
Additive Manufacturing of Micro-Architected Metals via Hydrogel Infusion Max Saccone[1,2], Rebecca A. Gallivan[3,2], Kai Narita[2], Daryl W. Yee[4,2] and Julia R. Greer[2]; [1]Stanford University, United States; [2]California Institute of Technology, United States; [3]ETH Zürich, Switzerland; [4]École Polytechnique Fédérale de Lausanne, Switzerland

Metal additive manufacturing (AM) has emerged as a uniquely powerful tool to produce complex and high-performance parts with applications from the aerospace to biomedical fields. Most existing metal AM techniques use heat to define part shape via thermally initiated melting or sintering. In contrast, we report an AM technique, coined hydrogel infusion additive manufacturing (HIAM), that produces metals and alloys with microscale resolution via vat photopolymerization (VP). To fabricate micro-architected metal structures, we infuse 3D-architected hydrogels with aqueous metal precursors, then calcine and reduce the infused hydrogel scaffolds to create miniaturized metal replicas. Unlike existing VP strategies, which incorporate target materials or precursors into the photoresin during printing, HIAM does not require re-optimization of resins and curing parameters for different materials, enabling quick iteration, compositional tuning, and the ability to fabricate multimaterials. We demonstrate HIAM of micro-architected metals such as copper, nickel, silver, cobalt, cupronickel alloys, high entropy alloys, and tungsten with critical dimensions of ~50 µm. Hydrogel scaffolds can be considered responsive architected materials—we demonstrate how a single architected gel can respond to a variety of chemical and thermal stimuli to transform into a vast array of metals, providing a pathway to create advanced micro-architected metals.

3:00 PM SF04.02.06
Metallized Ultraporus 3D Printed Lattices Nihan Sengokmen Ozsoz and Frederik Claeyssens; The University of Sheffield, United Kingdom

High internal phase emulsions (HIPEs) are potential stereolithography-based inks for producing innovative light-weight porous materials. However, the use of these resins has only been shown in bespoke stereolithography set-ups. From these studies, it can be learnt that stereolithography-based polyHIPE structures tend to be overcured due to their inherent light scattering nature, but that the inclusion of light absorbers can drastically increase the printing resolution. In this study, we focus on the inclusion of biocompatible light absorbers within the resin and the compatibility of those resins with commercial vat photopolymerization additive manufacturing (or stereolithography) set-ups. A surfactant (hypermer) stabilized water-in-oil emulsion based on ethylhexyl acrylate and isobornyl acrylate was used. For the light absorbers, both hydrophobic (beta-carotene) and hydrophilic (tartrazine) molecules were used, which dissolve in the organic phase and aqueous phase, respectively. It was found that using a combination of both beta-carotene and tartrazine provided the best stereolithography-based 3D printing resolution. Additionally, the emulsion was stable for the duration of the printing experiment and showed a polyHIPE pore structure with open surface porosity. The formulation of these HIPE-based resins permits them to be used in a wide range of applications since complex structures can be fabricated from HIPEs.
Architected truss structures with inherent porosity were 3D printed to be used as scaffolds for innovative applications. The mechanical properties of these structures have been improved four times by applying electroless nickel plating. This result showed that HIPEs could be used as scaffolds thanks to electroless metal deposition for innovative applications.

3:15 PM BREAK

3:45 PM SF04.02.08
A Free-Standing Organogel That Spontaneously Degrades to a Thin Sol After a Set Time Faraz Burni and Srinivasa R. Raghavan; University of Maryland, United States

Many applications in the oilfield industry utilize a nonpolar organic solvent (i.e., an oil) to be gelled. The gel must be a shear-thinning fluid so that it can be pumped into an oil well. When the fluid reaches its destination in the oil-bearing formation, it must set into a gel. From a rheological perspective, this organogel must be sufficiently strong (high elastic modulus G' as well as yield stress) so that it can act as an effective plug to block the flow of fluid (oil or water). However, the gel-like nature (and thus the plugging ability) may become undesirable after a period of time (2 to 4 weeks). Thus, after this time, there is a need for the gel to be degraded or dissolved. Numerous 'degrading agents' have been examined by the oilfield industry for a given type of gel, but they all have their drawbacks. Here, we present a solution to this vexing problem by designing a *self-degrading molecular organogel*. We use a small-molecule gelator, dibenzylidende sorbitol (DBS), that self-assembles into nanoscale fibrils in oils like n-alkanes or mineral oil, thereby gelling the oils. DBS organogels are highly robust and exhibit G' above 10,000 Pa for just 2 wt% of added gelator – indeed the gels are free-standing, i.e., strong enough to manipulate between one's fingers or place vertically on a countertop. At the same time, we have found that certain acid moieties can be introduced into the DBS organogel and induce slow degradation. Thus, the same strong organogel degrades into a thin liquid over a period of time, which can be tuned to be hours to days to weeks. In other words, we can formulate the gel with an in-built clock that sets in the degradation time. This avoids the need for injecting a degrading agent into the oil well. Our approach could be a game-changer for the oilfield industry.

4:00 PM SF04.02.09
Knots are Not for Naught—Design, Properties and Topology of Hierarchical Intertwined Micro-Architected Materials Widianto P. Moestopo[1,2],

Sammy Shaker[2], Weiting Deng[2] and Julia R. Greer[2]; [1]Lawrence Livermore National Laboratory, United States; [2]California Institute of Technology, United States

Lightweight and tough engineered materials are often designed with three-dimensional (3D) hierarchy and interconnected structural members whose junctions are detrimental to their performance because they serve as stress concentrations for damage accumulation and lower mechanical resilience. We introduce a new class of architected materials, whose components are interwoven and contain no junctions, and incorporate micro-knots as building blocks within these hierarchical networks. Tensile experiments, which agree with an analytical model for overhand knots, reveal that knot topology allows a new regime of deformation capable of shape-retention, leading to ~92% increase in absorbed energy and up to ~107% increase in failure strain compared to woven structures. Our exploration unlocks knotting and frictional contact to create highly extensible low-density materials with tunable shape reconfiguration and energy absorption capabilities.

SESSION SF04.04: Mechanical Instability and Multi-Stability
Session Chairs: Michael Frazier and Carlos Portela
Wednesday Morning, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate C3

10:00 AM SF04.04.01
Multi-Planar Printing and Control of Liquid Crystal Elastomers Devin J. Roach[1], Jeremy Herman[1,2], Samuel C. Leguizamon[1], Erik Linde[1], Adam Cook[1], Timothy White[2] and Bryan Kaehr[1]; [1]Sandia National Laboratories, United States; [2]University of Colorado Boulder, United States

Liquid crystal elastomers (LCE) are an active material that can provide rapid, reversible, and programmable actuation. In recent years, the additive manufacturing (AM) of LCE has gained attention as a facile means to both fabricate and program the actuation response. Nonetheless, LCE printing patterns and subsequent actuation directions have been limited to planar structures or simple geometries. To overcome this, we propose a method for printing of LCE in a laponite support gel which enables multi-planar, complex LCE structures. Furthermore, the LCE printing process can be monitored using in-situ measurements to build a machine learning model which will inform print parameters and final actuation properties. Lastly, we will provide demonstrations of how using machine learned printing parameters on multi-planar geometries will enable unprecedented multi-dimensional actuation profiles.

10:15 AM SF04.04.02
Tailoring the Multistability of Reconfigurable 3D Magnetic Mesostructures Xueju Wang and Yi Li; University of Connecticut, United States

Three-dimensional (3D) mesostructures that can reversibly change their geometries and thereby their functionalities are promising for a wide range of applications such as deployable devices, soft robotics, etc. The multistability of such structures is critical for their applications but is challenging to manipulate due to the highly nonlinear deformations and complex configurations of the structures. In this talk, I will present a comprehensive experimental and computational study to tailor the multistable states of continuous 3D mesostructures and origami-inspired, buckled ferromagnetic structures as well as their reconfiguration paths. Using table/ribbon structures as an example, a design phase diagram is constructed as a function of the geometry, crease number, and compressive assembly strain. For example, in origami-inspired ribbon structures, as the crease number increases from 0 to 7, the number of distinct stable states first increases and then decreases. The multistability is also shown to be actively tuned by varying the strain from 0% to 40%. Furthermore, analyzing energy barriers for reconfiguration among the stable states reveals dynamic changes in reconfiguration paths with increasing strain. Guided by the studies above, diverse examples are designed and demonstrated, from programmable structure arrays to soft robots. These studies lay out the foundation for the rational design of functional, multistable structures.

10:30 AM *SF04.04.03
Ultra-Fast, Programmable and Electronics-Free Soft Robots Enabled by Snapping Metacaps Lishuai Jin[1], Yueying Yang[1], Bryan O. Torres Maldonado[1], Sebastian Lee[2], Nadia Figueroa[1], Robert Full[2] and Shu Yang[1]; [1]University of Pennsylvania, United States; [2]University of California, Berkeley, United States

Soft robots have a myriad of potentials because of their intrinsically compliant bodies, enabling safe interactions with humans and adaptability to unpredictable environments. However, most of them have limited actuation speeds, require complex control systems, and lack sensing capabilities. To address these challenges, here we geometrically design a class of metacaps whose rich nonlinear mechanical behaviors can be harnessed to create soft robots with unprecedented functionalities. Specifically, we demonstrate a sensor-less metacap gripper that can grasp objects in 3.75 ms upon physical contact and a pneumatically actuated gripper with tunable actuation behaviors that have little dependence on the rate of input. Both grippers can be readily integrated into a robotic platform for practical applications. Furthermore, we demonstrate that the metacap enables propelling of a swimming robot, exhibiting amplified swimming speed as well as untethered, electronics-free swimming with tunable speeds. Our metacaps provide new strategies to design the next generation soft robots that require high transient output energy and are capable of autonomous and electronics-free maneuvering.

11:00 AM SF04.04.04
Domain Wall Manipulation by Hierarchy in Multi-Stable Metamaterials Chongan Wang and Michael J. Frazier; University of California, San Diego, United States

The manipulation of domains is critical to emerging functionalities in multi-stable metamaterials; however, the available strategies for domain control -- especially, those applicable in two-dimensional environments -- are few and, often, limited in their ability to sculpt and stabilize the domain contours. Here, we analyze domain wall motion in hierarchical metamaterial architectures formed by intersecting chains of elastically-coupled multi-stable elements, which establish a tailorable, non-uniform energy landscape for producing the sought-after behavior. The intersections create an energy barrier that impedes (even halts) domain wall motion and, thus, are mechanisms of control of the same. In tailoring the hierarchical structure, an assortment of unusual and complex domain contours can be realized and stabilized. We highlight some applications facilitated by the hierarchical structure.

11:15 AM *SF04.04.05
Functional Architected Materials by Harnessing Structure Instabilities Lihua Jin; University of California, Los Angeles, United States

Architected materials are materials with micro-architectures, which give rise to unusual mechanical properties and functions that are difficult or impossible to achieve in homogeneous materials. In this work, new types of architected materials are developed to demonstrate energy absorption and spatiotemporal shape morphing by harnessing structure instabilities. Subjected to an axial compression, a wide hyperelastic column can discontinuously buckle, snapping from one stable equilibrium state to another, leading to energy dissipation, while upon unloading, it can completely recover its undeformed state. Making use of this property, we design an energy-absorbing architected material by stacking layers of wide hyperelastic columns, and fabricate it by multi-material 3D printing and sacrificial molding. Characterized by quasi-static and drop tests, the material shows the capability of energy dissipation and impact force mitigation in a reusable, self-recoverable, and rate-independent manner. In a second example, we achieve spatiotemporally programmable and reconfigurable metasurfaces with simple control by exploiting pseudobistability of viscoelastic shells, which are pneumatically actuated to a concave state, held for a certain period, and recover the initial convex state after a delay time when the load is removed. We computationally and experimentally show that the recovery time can be widely tuned by the geometry and material viscoelasticity of the shells. By assembling such shells with different recovery time into arrays, we build metasurfaces with pre-programmed spatiotemporal textural morphing under simple pneumatic actuation, and demonstrate temporal evolution of patterns, such as digit numbers and emoji, and spatiotemporal control of friction. Our work opens up new avenues in designing functional architected materials by harnessing structure instabilities.

SESSION SF04.05: Mechanical Intelligence by Design
Session Chairs: Xiaoyue Ni and Xiaoxing Xia
Wednesday Afternoon, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate C3

1:30 PM *SF04.05.01
Reconfigurable Matter – From Wave Control to Mechano-Intelligence Kon-Well Wang; University of Michigan, United States

In recent years, the concept of reconfigurable matter developed based on nature-inspired modular architectures has been explored to create advanced engineering systems. For example, inspired by the observation that some of skeletal muscle's intriguing macroscale functionalities result from the assembly of nanoscale cross-bridge constituents with metastability, the idea of synthesizing metastructures from the integration of mechanical metastable modules has been pursued. In another example, inspired by the physics behind the plant nastic movements and the rich designs of origami folding, a class of metastructures is created building on the innovation of fluidic-origami modular elements. Overall, the modules are designed to be reconfigurable in their shape, mechanical properties, and stability features, so to produce synergistic and intriguing dynamic functionalities at the system level, such as programmable phononic bandgap control and nontraditional wave steering. More recently, with the rapid advances in high-performance intelligent systems, we are witnessing a prominent demand for the next generation of mechanical matter to have much more built-in intelligence and autonomy. An emerging direction is to pioneer and harness the metastructures' high dimensionality, multiply stability, and nonlinearity for mechano-intelligence via physical computing. That is, we aim to concurrently embed computing power and functional intelligence, such as observation, learning, memorizing, decision-making and execution, directly in the mechanical domain, advancing from conventional systems that solely rely on add-on digital computers to achieve intelligence. This presentation will highlight some of these advancements in harnessing reconfigurable matter for structural dynamics tailoring, from wave control to self-learning-self-tuning intelligence.

2:00 PM *SF04.05.02
Artificial Intelligent Architected Materials That Learn Their Properties Jonathan Hopkins; University of California, Los Angeles, United States

The objective of this work is to apply the concept of artificial neural networks (ANNs) to enable the creation of a new kind of architected material, called a mechanical neural-network (MNN) architected material, that can learn desired properties via a complex web of active flexible elements (AFEs) that constitute the materials' microstructure. These AFEs, which are joined together by rigid nodes, constitute an analogous physical embodiment of the mathematical weights that determine the values that are summed together by the neurons within traditional ANNs. By actively tuning the stiffness of these AFEs in a similar fashion to how weights are trained within ANNs, the new kind of architected material can learn desired mechanical properties and thus enable a variety of applications. Such applications include: (i) aircraft wings that can learn to optimally change their shape and stiffness at select locations as flight conditions change, (ii) aircraft exteriors that can learn to compensate for damage that may occur during combat or overuse by maintaining their designed properties regardless of defects or ware, and (iii) electrical, optical, or other components within aircraft that cannot be made of zero-thermal-expansion-coefficient materials but can learn to maintain their shape regardless of fluctuating temperatures.

2:30 PM SF04.05.03
Architected Mechanologics and Design Rules for Integrated Mechanical Computing Junghwan Byun[1,2,3], Aniket Pal[1], Seungjun Chung[2], Kyu-Jin Cho[3] and Metin Sitti[1]; [1]Max Planck Institute for Intelligent Systems, Germany; [2]Korea Institute of Science and Technology, Korea (the Republic of); [3]Seoul National University, Korea (the Republic of)

Mechanical computing is an unconventional domain of computation where computational operations are made solely by mechanical components and mechanisms. Recent studies in this direction harness built-in material responsiveness and structural intelligence to achieve seamless, monolithic integration between the computing process and input/output agents that can be directly coupled to surrounding environments. Specifically, digital abstractions of mechanical information (i.e., mechanical bits) have been realized by multistable configurations of mechanical elements that are able to change their shapes along with origami kinematics and/or nonlinear buckling dynamics of thin soft beams or shells. Pioneering studies have further demonstrated that architected design and engineered assembly of the multistable elements can accomplish stable transmission of elastic waves, mathematical computations, programmable metamaterials, and robotic mechanisms, all of which form the basis of mechanical computing. Despite these achievements, however, an understanding of mechanical computing has still been limited to the implementation of standalone computing units or mechanical transition waves lacking the rational design for deterministic computational functions.
In this work, we introduce a basic design principle of soft bistable beams with engineered potential energy profiles, and show how the strategic topological assembly of these engineered bistable elements can form into a monolithic computational platform in which nondispersive elastic solitary waves autonomously propagate with deterministic computational functions. Drawing inspiration from a mature design architecture of conventional electrical computing systems, we first postulate the design and functional requirements for integrated mechanical computing as follows: (i) stable transmission of mechanical signals without loss of information, (ii) a complete set of functional computing units with form factors matched with the transmission line, and (iii) lossless, computational cascades of mechanical signals through multiple computing units. The designs of transmission line units and mechanologics are physically implemented by topological assemblies of bistable building blocks into a unit square lattice frame. The resulting lattice-unit connection between fundamental mechanical components (i.e., transmission line units and mechanologics) allows us to investigate propagation behaviors of mechanical signals not only through a homogeneous elastic medium (transmission line), but also through a medium containing a computing unit with

structural heterogeneity. Based on an extensive set of experimental and numerical studies on the proposed mechanical system, we generalize a design rule for computational propagation of mechanical signals through networked computing units, and implement this decisive principle in realizing integrated mechanical computing. Proof-of-concept demonstrations of Mimosa plant-inspired soft machines show how the developed integrated mechanical computing can direct mechanical instructions across environmental inputs, computational operations and actuator modules in a seamless and monolithic form.

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2:45 PM SF04.05.04
A Soft Shape-Morphing Surface with Embedded Shape Sensing Function Yuxin Pan[1], Yun Bai[1], Yuxuan Liu[2], Yong Zhu[2], Heling Wang[3] and Xiaoyue Ni[1,1]; [1]Duke University, United States; [2]North Carolina State University, United States; [3]Tsinghua University, China

Soft robotic materials that can autonomously morph into desired shapes can enhance human-robot interaction. Recent advances in soft electronics and data-driven inverse design strategies have allowed for the creation of rapidly reprogrammable shape-morphing soft matter. To control these surfaces accurately and robustly, a shape-sensing capability is necessary. Current shape sensing methods heavily rely on exteroception, which can compromise the accuracy, reliability, flexibility, and speed of shape reconstruction in a deployed environment. In this work, we introduce a shape-morphing surface that can sense its own shape. The soft surface is constructed from silicone-based membranes containing interconnected stretchable silver nanowire conductors. The conducting meshes serve as both electromagnetic actuation elements in the presence of a magnetic field for shape-morphing and a resistive strain sensor for shape-sensing. We investigate the mechanics and materials of the soft composites and flexible sensors for optimized surface design for complex shape-morphing. Combining a mechanical model, finite-element analysis (FEA), and a machine learning pipeline with high-throughput experimentation enabled by the robotic surface, we develop a theoretical framework to describe the relationships between the input control voltages and output shapes, as well as the relationship between the deformed shapes and output sensing voltages. Stereo-imaging provides a ground-truth surface reconstruction and validates the accuracy of the embedded sensing with a maximum error of 5%. With the sensing and actuation functions closely integrated at the material level, the robotic surface is able to perform real-time closed-loop shape morphing in various changing environments.

3:00 PM SF04.05.05
Shape Morphing Mechanical Metamaterials for Multifunctional Machines Michael D. Bartlett, Edward J. Barron III, Dohgyu Hwang, A B M Tahidul Haque and Ravi Tutika; Virginia Tech, United States

Biological organisms are rich with the ability to reconfigure their shape and properties to perform diverse tasks. These capabilities are inspiring emerging soft robots and intelligent matter that have the potential to display biological capabilities through material and physical intelligence. However, soft machines and intelligent matter struggle to achieve multiple complex configurations, quickly lock into shape to support loads, and go between multiple states reversibly. In this presentation we will introduce a multifunctional shape morphing mechanical metamaterial with reversible, rapid, and lockable polymorphic reconfigurability. We couple elastomeric kirigami with an unconventional reversible plasticity mechanism in metal alloys to rapidly (< 0.1 s) lock-in complex, load bearing shapes, with reversibility and self-healing through phase-change. Large deformations and complex morphologies are demonstrated where we show the ability to exhibit positive, zero, and negative Gaussian curvatures and conformally wrap complex surfaces. This approach overcomes trade-offs in deformability and load bearing capacity while eliminating power requirements to lock in shapes. This combination of properties is enabling for creating multifunctional soft robots. We demonstrate this material through integration with onboard control, motors, and power, to create a soft robotic morphing drone which autonomously transforms from a ground to air vehicle and an underwater morphing machine which can be reversibly deployed to collect cargo.

3:15 PM SF04.05.06
Effect of Form and Architecture on the Actuation Performance of Stimuli-Responsive Polymers Frank Gardea[1], Sevketcan Sarikaya[2], Bradley Lawrence[1], Todd Henry[1] and Mohammad Naraghi[2]; [1]DEVCOM Army Research Laboratory, United States; [2]Texas A&M University, United States

Soft actuators provide a promising alternative to conventional actuators by addressing the need for adaptability, flexibility, and tunability. Stimuli-responsive soft materials are viable candidates for actuation due to their ease of tunability of actuation performance by control of not only composition but by variation of architecture or form factor. Here, we report a study on the effect of architecture and form on the responsiveness and actuation performance of various soft materials. Specifically, the size dependence on rate of actuation, stroke, and strength of stimuli-responsive polymer fibers is presented. Additionally, a comparison between a coiled and aligned architecture of the fiber actuators is made with respect to actuation performance. Performance tunability is explored by varying architecture parameters, such as coil index and degree of twist. Polymers responsive to various stimuli (pH, humidity, temperature) are studied. Finally, the usability of these soft actuators is demonstrated by integrating them into viable structures. This work demonstrates the potential of soft polymer materials for use in responsive structures and how actuation performance can be enhanced and tuned by structural design.

3:30 PM BREAK

4:00 PM *SF04.05.07
Disordered Mechanical Metamaterials Stefano Zapperi[1,2]; [1]University of Milan, Italy; [2]Consiglio Nazionale delle Ricerche, Italy

Mechanical metamaterials, or architechted materials, are a class of artificial materials engineered to have exceptional mechanical properties that are difficult to find in conventional materials. Often inspired by biological systems, mechanical metamaterials are typically designed with an internal structure composed of multiple elements arranged in periodic patterns. The ordered geometries employed in mechanical metamaterials contrast with the disordered structures encountered in biological systems, formed through self-assembly in response to environmental pressures. In this talk, I will argue that there is a value in considering disorder in the design of mechanical metamaterials and discuss the emergence of novel features induced by disorder. I will then present a computational method for the automatic design of disordered mechanical metamaterial actuators that combines a reinforced Monte Carlo method with discrete element simulations. 3D printing of selected mechanical metamaterial actuators shows that the machine-generated structures can reach high efficiency, exceeding human-designed structures. I will also show that it is possible to design efficient actuators by training a deep neural network which is then able to predict the efficiency from the image of a structure and identify its functional regions.

4:30 PM SF04.05.08
Toward Elastically and Inelastically Isotropic Multiphase Interpenetrating Network Jehoon Moon, Suyoun Ma, Gisoo Lee and Hansohl Cho; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Heterogeneous or cellular materials architected on various crystal lattices have been extensively explored for a broad variety of engineering functionalities involving photonics, acoustics and mechanics with the recent advances in additive manufacturing and three-dimensional (3D) printing technologies. Long-range order in the heterogeneous materials architected on crystal lattices often culminates in undesirable, intrinsic anisotropy in elasticity and inelasticity in diverse mechanical loading scenarios. In this work, we propose a simple yet efficient design strategy to generate heterogeneous materials that exhibit nearly isotropic elasticity and inelasticity in extreme mechanical deformation events. Furthermore, we combine experiments and numerical simulations to explore how geometric connectivity (dispersed-particle vs. interpenetrating morphologies) throughout dissimilar domains influences shape recovery as well as energy dissipation in the disordered heterogeneous materials.

We design two types of disordered morphologies: dispersed-particle morphology and its interpenetrating counterpart. Representative volume element (RVE) for dispersed-particle morphology is generated by distributing a finite number of spheres in the unit cube. The centers of the spheres are randomly placed inside the unit cube. When placing the spheres, newly inserted spheres does not overlap the existing spheres under three-dimensional periodic boundary conditions (PBC)[1]. In order to generate an interpenetrating counterpart, we perform a Voronoi tessellation on the unit cube via the spatial random points seeded for the dispersed-particle morphology. We then perform rod-connecting the center point and the Voronoi neighbor points for each of the tessellated polyhedra in the RVE. Therefore, the RVE with interpenetrating morphology has randomly connected local microstructures throughout the tessellated polyhedral network.

We then fabricated prototypes for the RVEs of both disordered morphologies using a high-resolution, multi-material 3D printer. A plastomeric material exhibiting large flow stresses and hysteresis under cyclic loading conditions was used for the hard domains (particles or rod-connected network) while a hyperelastic, elastomeric material was used for the soft domains. We then conducted large strain mechanical tests on the 3D-printed prototypes under diverse cyclic loading scenarios. Altering the connectivity throughout the disordered network was found to impact significantly on key elastic and inelastic features including initial stiffness, flow stresses, energy dissipation and elastic-inelastic shape recovery in the two morphologies upon cyclic loading and unloading conditions. Furthermore, the 3D-printed prototypes with interpenetrating morphology exhibited more robust performance in resilience and energy dissipation under repeated loading and unloading cycles. Last, we examined anisotropy in both morphologies in experiments and numerical simulations, by which the universal anisotropy index[2] was calculated. Interestingly, though altering the connectivity from dispersed-particle to interpenetrating morphologies resulted in a slight increase in anisotropy, the universal anisotropy indices for both morphologies were found to be below 0.05 (nearly isotropic behavior). In addition to the elastic isotropy, our experimental data and numerical simulation results reveal that these disordered heterogeneous materials exhibit nearly isotropic behaviors in inelastic features involving energy dissipation and shape recovery in extreme deformation conditions.

This work was funded by National Research Foundation of Korea (Grant No. 2021R1A4A103278312)

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4:45 PM SF04.05.09
A Novel Digital Manufacturing Strategy to Print Magnetically Responsive Soft Continuum Robots in a Sustainable Supporting Medium Jaemin Lee, Dmitrijs Kozminihs, Vittorio Francescon, Alistair Bacchetti, James Chandler, Pietro Valdastri and Russell Harris; University of Leeds, United Kingdom

In this talk, a breakthrough in the development of an aqueous solution-based printing medium that enables a novel direct-write method for printing microscale soft continuum robots composed of magnetic metamaterials will be described. The new cost-effective, biocompatible, sustainable printing medium offers exceptional rheological properties to keep the printed high-density magnetic tentacles securely floated in the medium and to maintain the cylindrical cross-section of the printed microscale continuum robots along the length; securing cylindrical cross-section in this scale has been a major bottleneck in additive manufacturing of soft continuum robots. With the utility in direct writing, the outstanding digital printing capability can now dramatically enhance multi-axis navigation capabilities to improve surgical efficacy during operation and reduce patient trauma,[1] making this technology more widely accessible. Simultaneously, the new development addresses major challenges such as a considerably limited polymer-based material catalog,[2] the high demands for complex chemistry to surround the printed objects in this type of medium-based printing[3, 4] and sophisticated modifications of composites to control the printing behavior.[5] The latest device performance investigation will also be presented, in conjunction with computational modeling and practical demonstration in physical organ phantoms for surgical interventions in organs such as the pancreas, heart, and brain.[1, 6, 7] Here, an external magnetic field via the dual-robot-arm approach will be utilized to remotely manipulate the printed continuum magnetic robots, which will be benchmarked against traditional robots based on molding fabrication methods.

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SESSION SF04.06: Mechanical Actuation, Morphing and Reconfiguration
Session Chairs: Xiaoyue Ni and Carlos Portela
Thursday Morning, April 13, 2023
Marriott Marquis, B2 Level, Golden Gate C3

10:00 AM *SF04.06.01
Variable-Stiffness and Shape-Morphing Architected Materials Yifan Wang; Nanyang Technological University, Singapore

Architected lattices are materials that derive their properties from the selection of both their constitutive materials and the geometry of their micro- and meso-structure. Most existing architected lattices are intrinsically passive, with properties fixed once manufactured. These limit their applications in areas where material adaptivity and tunability are required. In contrast, the tight coupling of shape transformation and stiffness tuning in biological organisms have long served as inspiration for next-generation smart material design. In this talk, I will present the development of architected materials whose mechanical properties and geometry can be controlled and adapted to varying environmental conditions. First of all, I will demonstrate a structured fabric with interlocking particles that has controllable stiffness and reconfigurable shape, which can be used for wearable robotics. Then, I will present a robotic structure from architected particle assemblies that combine shape-morphing, stiffness variation and self-sensing into one monolithic body. These works open routes towards creating the next generation of architected materials that mimics the functions of biological organisms and adapt to varying environmental conditions.

10:30 AM SF04.06.03
3D Shape-Morphing Display Based on Electrothermally-Responsive Variable Stiffness Composite Subin Oh, Sunwoo Lee, Jiheong Kang and Jae-Woong Jeong; KAIST, Korea (the Republic of)

Three-dimensional (3D) displays are being considered for the next-generation displays in terms of enhancing the realism of visual information and possibly integrating displays on curvilinear surfaces. One promising approach for implementing 3D displays is to transform a two-dimensional (2D) display into a 3D display, which can incorporate the merits of 2D display technologies. However, existing rigid displays and emerging flexible/stretchable displays are challenging to freely realize and maintain complex 3D structures and can only be used for specific purposes due to the inherent static mechanical properties of constituent materials. The stiffness-tuning technology can be of use to enable multi-purpose displays that encompass all the advantages of the current display form factor to realize customizable 3D shapes.
In this study, we propose a shape-morphing display (SMD) that can realize complex 3D configurations through electrothermal operation, firmly retain its deformed shapes with cooling and achieve reversible multi-morphological reconfiguration. The SMD is fabricated by integrating a stretchable alternating current electroluminescent (ACEL) device with an electrothermal shape-morphing platform (eSMP). The unique variable stiffness mechanism emerges from eSMP that is constructed using Field's metal (FM)-Graphene nanoplatelet (GNP)-elastomer composite. Field's metal is a key material for eSMP design, which can convert from a solid state with a high elastic modulus (9.25 GPa) to a liquid state at its melting temperature (62 °C). Based on the thermomechanical characteristic of FM, the platform exhibits shape-memory behavior with excellent shape-fixing and restoring abilities under deformation including not only stretching but also non-uniform 3D morphing. To allow rapid, reliable shape reconfiguration through electrothermal operation, GNPs are incorporated into the platform for enhancing electrical and thermal conductivities. The stretchable ACEL device featuring stable electroluminescence and deformability is beneficial to the reliable light-emitting performance of SMDs under 3D reconfiguration. The SMD can be used to realize various unusual 3D structures for a wide variety of applications. We envision that the versatile, user-friendly SMDs can bring out innovative form factors for the next generation display, and open many new opportunities for 3D art displays, transformative wearable electronics, visio-tactile automotive interfaces, and many others.

10:45 AM SF04.06.04
Cottonid—An Old Material for Autonomous Actuation Matthias Langhansl and Cordt Zollfrank; Technische Universität München, Germany

Many material systems have already been developed, which are able to respond to external stimuli such as temperature, light, electric fields, such as temperature, light, electric fields, pH-value or humidity by means of dimensional changes. These materials can react in an energy-efficient way to kinetic energy or mechanical force through volume expansion.

One material in such a system could be Cottonid, one of the oldest known (bio-)plastics. In 1859, the Englishman Thomas Taylor described for the first time the production of this material on the basis of rag paper, which he produced by soaking cellulose fibers in a zinc dichloride bath and pressing several layers under heat. Nowadays, unsized specialty paper made from cotton, pulp or a mixture of both serves as a renewable raw material for industrial production. The treatment with zinc dichloride should only last until the fibers have reacted superficially, otherwise the cellulose chains are degraded and the material is damaged. The exact mechanism of this vegetable parchmentization has not yet been identified in detail. During the process, a tremendous swelling can be observed followed by the decomposition of the paper sheet. The result of this conversion process of the cellulose fibers is a considerable change in the material properties, from soft and flexible to horn-like and hard.

The manufacturing process and the material itself is very sustainable. The zinc dichloride, used as a catalyst, can be completely recycled. The washing water is also almost completely reused. The finished material is free from chemical residues and consists only of cellulose and, for marketing purposes in some cases, pigments. In addition, zinc dichloride is a cost effective and a safe "solvent" compared to commonly used solvent systems for dissolving cellulose. The resulting material is quite hygroscopic and can be perfectly used for sustainable actuators due its dimensional changes in response to environmental humidity.

The presented talk will provide an overview of the possibilities of Cottonid in a bilayered material system for autonomous actuations. Inspired by nature we fabricated actuators with Cottonid as an active layer together with different passive layers and investigated the actuation potential of different systems. Different bio-based and non-bio-based materials and adhesives were usedt to build up a two-layered material. The autonomously actuation potential was investigated inside a climate chamber by alternating humidity. The bending motion was captured with a camera and evaluated. The resulting curvature angles reach from 1° up to 70° depending on the change of the relative humidity and the system itself. We generated a portfolio of different material systems for a wide range of possible applications for which a directed autonomous humidity driven actuation is required.

In summary, Cottonid is a promising material in the field of bioderived and sustainable materials. Due to the topicality of the issues of environmental protection and sustainability, these materials are currently experiencing a renaissance. It has great potential to replace conventional petroleum-based materials with a green alternative. Additionally, the reaction route via zinc dichloride can be transferred to the wide area of all cellulose composites and might lead to a new, even more sustainable way for their fabrication. A possible future field of application for Cottonid-based bilayer actuators could be the so-called bio-architecture. It would be conceivable to use Cottonid-based actuators as an intelligent building envelope, which reacts autonomously to the environment. Even with complex architectural geometries shading systems could be applied In addition to this function as a shading element, combination systems with solar modules, for example, would also be conceivable, in which the Cottonid bilayer adjusts the panel to the position of the sun and follows it.

11:00 AM SF04.06.05
A Study on the Intrinsic Grain Size Effect of FeMnSi-Based Shape Memory Alloys Ji Young Kim, Wook Ha Ryu and Eun Soo Park; Seoul National University, Korea (the Republic of)

Iron-based shape memory alloys (SMAs), especially Fe-Mn-Si alloys, have great potential in civil engineering structures because of their low cost and shape memory properties based on stress-induced epsilon martensitic transformation (SIEM). In Fe-SMAs, previous researchers have tried to strengthen the parent austenite phase to enlarge the plastic deformation strain range, leading to enhanced recovery strain. Herein, we suggested Fe-SMA with ultra-fine grain to strengthen the austenite phase based on the study of the intrinsic grain size effect. Moreover, to overcome the disadvantage of high annealing twin boundaries density, which is known as an obstacle to reverse martensitic transformation, we fabricated the Fe-SMA with low annealing twin boundaries through subsequent thermomechanical treatment. This study is the first to improve recovery strain through grain refinement, especially with a low density of annealing twin boundaries. Therefore, we expect that this study has both the scientific significance of revealing the intrinsic grain size effect of non-thermoelastic martensitic transformation and the engineering significance of offering a guideline for designing Fe-SMA with high recovery strain.

11:15 AM SF04.06.06
Prestrain Programmable 4D Printing of Nanoceramic Composites with Bioinspired Microstructure Wei Zhai, Tian Li, Quyang Liu and Haobo Qi; National University of Singapore, Singapore

Four-dimensional (4D) printing enables programmable, predictable, and precise shape changes of responsive materials to achieve desirable behaviors beyond conventional three-dimensional (3D) printing. However, applying 4D printing to ceramics remains challenging due to their intrinsic brittleness and inadequate stimuli-responsive ability. One can draw inspiration from Nature. Concentric cylinder structure is common in biological systems such as scallion, the tracheid of wood, the spicule of Euplectella aspergillum, and the bone Haversian system due to their unique growth organism. Such kind of structure plays a significant role in improving their strength and toughness by increasing the fracture path and energy absorption. Here, this work proposes a conceptional combination of bioinspired microstructure design and a programmable prestrain approach for 4D printing of nanoceramics. To overcome the flexibility limitation, the bioinspired concentric cylinder structure in the struts of 3D printed lattices is replicated to develop origami nanoceramic composites with high inorganic content (95 wt%). Furthermore, 4D printing is achieved by applying a programmed prestrain to the printed lattices, enabling the desired deformation when the prestrain is released. Due to the bioinspired concentric cylinder microstructures, the printed flexible nanoceramic composites exhibit superior mechanical performance and anisotropic thermal management capability. Further, by introducing oxygen vacancies to the ceramic nanosheets, conductive nanoceramic composites are prepared with a unique sensing capability for various sensing applications. Hence, this research introduces a type of high-performance shape-morphing materials for applications under extreme conditions, such as space exploration and high-temperature systems.

SESSION SF04.07: Stimulus-Responsive Architected Materials
Session Chairs: Michael Frazier and Xiaoxing Xia
Thursday Afternoon, April 13, 2023
Marriott Marquis, B2 Level, Golden Gate C3

1:30 PM SF04.07.02
3D-Printed Permanent and Impermanent Magnetic Elastomer Architectures—Identifying Key Structure and Processing Parameters for Enhanced Magnetoactive Performance Brittany Nelson-Cheeseman, James Michael Ennis, William Howell, Daniel P. Fagan, Jacob Schewe, Jimmy (Dingming) Lu and Thomas Hoft; University of St. Thomas, United States

Magnetic elastomers are of interest for soft robotic applications where remote contactless activation is desired. These composite smart materials are made of magnetic particulate embedded in an elastomeric matrix and respond to applied magnetic fields with mechanical deformation, termed magnetoaction. It’s been shown that anisotropic structures and properties within these materials leads to increased magnetoactive performance. Magnetic annealing is the main processing technique that has been used to increase magnetoactive performance through the introduction of local anisotropy. For further enhancements to magnetoaction, the 3D-printing technique, Fused Filament Fabrication (FFF), can be used to create additional anisotropy in the structures and properties of magnetic elastomers. FFF architectures create anisotropic sub-structures within a part by extruding 1D lines of the molten material (termed "infill") in 2D patterns that build up to a 3D part. This infill pattern is entirely customizable with respect to orientation and percentage filling allowing for one to readily tune the properties of the resulting part. While it’s been clearly shown that these parameters significantly influence the resulting mechanical and magnetic properties of FFF-printed parts, their influence on magnetoaction (the confluence of mechanical and magnetic responses) has yet to be reported.

Here, we investigate how a variety of parameters on multiple length-scales influence magnetoaction in FFF-printed magnetic elastomers. In particular, we study how FFF *infill percentage* and *infill orientation* relative to applied magnetic field influences magnetoaction of the printed part. We also study a variety of *soft vs. hard magnetic particulates* in order to understand how these distinct magnetic material properties interact with the various 3D printed structural features.

A custom setup and approach has been developed to meticulously measure resulting magnetoactive effects by isolating the deflection and rotational components of any complex motion observed. For both modes, the sample is suspended from a fixed point and a transverse DC magnetic field is applied up to 0.4 T. The degree of magnetoaction is quantified as the angle of deflection or rotation of the sample for a given applied field. The data is captured visually in digital images that are then processed in order to determine the quantitative deflection or rotation angle for a given applied field. Supporting magnetic, mechanical and structure (SEM) studies are utilized to investigate the origins of the differences in magnetoaction.

For the FFF architectures studied, we find that the greatest magnetoaction is found for a combination of lower infill percentages and infill oriented perpendicular to the applied magnetic field. These effects arise from both maximizing anisotropy and limiting infill crosslinking within the structure, which greatly affects mechanical stiffness and resistance to motion. Moreover, we find that the soft magnetic particulates (Fe and Fe_3O_4) give the greatest magnetoaction, but only simple, noncomplex motion; meanwhile, the hard magnetic particulate (SrFerrite) gives complex magnetoactive responses involving motion in multiple dimensions and is intricately dependent on a host of variables studied. All of these results together highlight a number of key structure and processing parameters that lead to enhanced magnetoactive performance in 3D-printed magnetic elastomer architectures.

1:45 PM SF04.07.03
Complex Magnetoactuation of 3D-Printed Hard Magnetic Elastomers—Effects of Infill Percentage and Poling Orientation William Howell, Michael Ennis, Daniel P. Fagan, Jacob Schewe, Jimmy (Dingming) Lu, Thomas Hoft and Brittany Nelson-Cheeseman; University of St. Thomas, United States

Magnetic elastomers are composite smart materials made up of a flexible polymer and magnetic particulate which mechanically articulate in response to an applied magnetic field (H). They allow for highly configurable and untethered actuators. To enhance configurability, 3D-Printing allows for great control of the object’s meso and macro structure, both in terms of shape geometry and property anisotropy. Specifically, Fused Filament Fabrication (FFF) is an additive manufacturing process by which material is extruded in lines (infill) to gradually build up an object through layer-by-layer extrusion. One of the clear advantages of FFF is that it requires no curing time after the piece has been printed. Magnetic elastomers with hard magnetic particulate, due to the presence of large remnant magnetization, have the unique advantage of performing more complex actuation, such as rolling, twisting, and folding. SrF is an excellent hard magnet candidate given its lower price and greater accessibility compared to Neodymium Iron Boride. Poling allows for consistency of the object's remnant magnetization, giving more control and magnitude to its motion. In this study, we explore how the FFF structural parameter of infill percentage, sample orientation relative to H, and poling orientation affect the magnetoactive response of printed elastomer structures made up of SrF particulate suspended within a thermoplastic urethane polymer matrix. Rectangular sample beams are 3D-printed with dimensions of 5mm x 5mm x 60mm.Prior to testing, the samples are first poled in a certain direction, and then the magnetoactive properties are measured by a custom setup where each printed sample beam is suspended vertically and optically tracked for a transverse H up to 0.4 T. In order to isolate different components of the complex movement to see how our variable change affect magnetoaction, multiple orientations relative to H are studied. Sample sets are either studied for rotational motion or deflection, and within each set the sample itself is rotated 90 degrees each new testing cycle for four cycles. A custom MATLAB program overlays the digital images for increasing H in order to quantify the magnetoactive deformation that results. The magnetoactive responses exhibited by the various sample types highlight clear design goals for tailoring large and complex magnetoactive actuation modes. In addition to the traditional transverse bending seen from typical (magnetically soft) magnetic elastomers, we also observe complex twisting and torquing of the beams in multiple dimensions based upon the printed structure and the sample orientation relative to H. These effects are greatest for the orientations and structures that maximize magnetic anisotropy and minimize the infill crosslinking. This work demonstrates the clear potential to tailor complex magnetoactive responses from FFF-printed hard magnetic elastomers, opening the door to highly complex actuators that can be readily and accessibly designed and created.

3:00 PM SF04.07.04
Soft and Switchable Pearls—Capsules that Exhibit Pearlescence on Heating Medha Rath, Taylor J. Woehl and Srinivasa R. Raghavan; University of Maryland, College Park, United States

A pearl-like luster (i.e., pearlescence) is seen in many natural materials like nacre and also in some commercial products such as paints and cosmetics. This optical phenomenon is attributed to the diffraction of light from plate-like particles in the material, with the particle size or spacing being comparable to the wavelength of light. Here, for the first time, we demonstrate the onset of pearlescence in soft capsules that contain no plate-like particles. The capsules (~ mm in size) are transparent and non-pearlescent at room temperature. The thin (~ 500 µm) outer shell of the capsules is a hydrogel of N-isopropylacylamide (NIPA), which shrinks when heated above its lower critical solution temperature (LCST) of ~ 32°C. When heated above this LCST, the transparent capsule spontaneously turns pearlescent. The effect is reversible, with the transparent state being recovered upon cooling. This is the ***first example of reversible pearlescence*** in any material. Spectral reflectance measurements show that the pearlescence of the capsules is comparable to that of real pearls. Interestingly, bulk hydrogels of NIPA do not turn pearlescent on heating ¾ they simply become turbid. Thus, pearlescence is observed only in NIPA-shelled capsules, and we show that it requires both a thin NIPA shell and a water-rich core capable of swelling. When heated above its LCST, the NIPA shell further shrinks, and we postulate that NIPA-rich domains phase-separate within this shell. The size or spacing of these domains is likely to be responsible for the pearlescence. Our work sheds fresh insight into the nature of pearlescence, on how it can be tuned, and on how it can be introduced into various soft materials.

2:30 PM BREAK

3:15 PM *SF04.07.05
Additive Manufacturing of Robotic Metamaterials Xiaoyu Zheng; University of California, Berkeley, United States

Additive manufacturing has shown the promise of freedom of designs, enabling parts customization and tailorable properties where superior structural performances can be achieved by a fraction of weight density compared to bulk material. However, it is presently difficult to combine different materials (structural, dielectric, conducting and ferroelectrics) to create a complex device with multiple functionalities that responds to multiple stimuli. Unlike biological systems where functions, including sensing, actuation, and control, are closely integrated, few materials have comparable system complexity.
In this talk, I will present a suite of new multi-material additive manufacturing processes and design methodologies to create materials with tailorable structural and functional behaviors. The structural materials consist of a network of micro-unit cells which collectively influence new mechanical behaviors (from high-strength, lightweight to toughening) not seen in their native counterpart. When combined with an electronic and functional phase, these materials turn themselves into a "robotic material" and is capable of motions with multiple degrees of freedom motions and amplification of strain in a prescribed direction in response to an electric field (and vice versa), and thus, programmed motions with self-sensing and feedback control. I will present the manufacturing and synthesis of these materials, as well as their mechanics and design methods underpinning their novel behaviors.

3:45 PM SF04.07.06
Programming Molecular Order of a Liquid Crystal Elastomer with Magnetic-Field-Assisted DLP Printing Yueping Wang[1], Jongwon An[2], Sehui Jeong[2] and Howon Lee[2]; [1]Rutgers, The State University of New Jersey, United States; [2]Seoul National University, Korea (the Republic of)

Shape memory polymers (SMPs) and hydrogels are two major materials classes of stimuli-responsive materials that have been widely used in 4D printing. As such, additively manufactured responsive architected materials are made of either SMPs or hydrogels. SMP can memorize its original printed shape and restore it when needed, but its stimuli-responsive morphing is only one-way in that mechanical processing is always required for shape programming. Stimuli-responsive hydrogels can deform reversibly depending on various environmental changes, but they suffer from extremely slow time-scale for shape change due to a quadratic scaling law for the diffusive water molecule migration process and are not suitable for applications where surrounding water is not available. Recently, liquid crystal elastomers (LCEs), combining polymeric elasticity with liquid crystalline anisotropy, have received growing attention as a new class of a 4D printing material that can overcome the limitations of SMPs and hydrogels.
LCEs can show reversible stimuli-responsive deformation driven by rearrangement of molecular orientation of liquid crystal (LC) molecules. However, alignment of LC molecules has been achieved primarily using mechanical extension or viscous shear, which significantly limits its applicability in additive manufacturing. Here, we report a DLP system capable of printing an LCE structure while selectively programming molecular orientation of LC molecules using a magnetic field. We report a LCE precursor solution that maintains a nematic phase at room temperature. Using a custom-built DLP printing system with an integrated magnetic field generator, LC molecules are aligned in the desired orientation and selectively cured by patterned digital light projection. Therefore, LC orientations can be freely encoded in a single structure. This allows for spatial patterning of LC orientations independent of the geometry of the printed structure. Considering the advantages of DLP printing over other additive manufacturing methods, this approach can offer unmatched opportunities for programming various modes of shape deformation of responsive architected materials.

4:00 PM SF04.07.07
Comparison of Ink Formulations for Direct Ink Writing and Photothermal Actuation of Liquid Crystal Elastomers Michael Ford[1], Yuchen Wang[2], Rodrigo Telles-Arriaga[3], Dominique Porcincula[1], Julie Mancini[1], Mehedi Hasan Rizvi[4], Bryan Moran[1], Joseph Tracy[4], Jennifer Lewis[3], Shu Yang[2], Elaine Lee[1] and Caitlyn C. Krikorian (Cook)[1]; [1]Lawrence Livermore National Laboratory, United States; [2]University of Pennsylvania, United States; [3]Harvard University, United States; [4]North Carolina State University, United States

Light as a stimulus for shape change may be useful for localized actuation that does not require physical contact with the shape-changing material (e.g., as wires that transmit electrical power might require). Thus, the development of liquid crystal elastomers (LCEs) with light responsivity may be important for actuation that is activated at a distance, like for search-and-rescue or medical robots/devices. In this talk, I will outline our approach to formulating an ink that would produce photoresponsive LCEs that are 3D-printable (e.g., using direct ink writing), specifically focusing on the use of gold nanorods (AuNRs) in these inks. We examined the advantages and disadvantages of various formulations by characterizing curing kinetics and molecular weight along with rheological and thermal properties of the inks. Specifically, we considered possible routes for formulating inks. The first approach followed a synthetic scheme that was previously reported for LCEs that incorporated AuNRs. Other synthetic approaches were compared and contrasted with the previously reported approach to formulate an ink that was optimized for actuation strain and compatibility with AuNRs. Finally, we added AuNRs to one of the formulations and characterized the photothermal actuation properties. These printed actuators could respond to locally to light or globally to heat, and the use of direct ink writing was leveraged to form multiresponsive architectures, making these promising functional materials for advanced applications.

SESSION SF04.08: Functional Application of Responsive Materials
Session Chairs: Xiaoyue Ni and Xiaoxing Xia
Friday Morning, April 14, 2023
Marriott Marquis, B2 Level, Golden Gate C3

9:45 AM SF04.08.01
Physical Unclonable Function of Surface Random Wrinkles with Optical Anisotropic Matter Kitae Kim, Choi Moon Young and Jun-Hee Na; Chungnam National University, Korea (the Republic of)

Periodic microstructures over a large area allow interesting functionalities such as structural color and self-cleaning surfaces and lead to a wide range of applications from adaptive bioengineering and flexible electronics to adhesives. To construct microstructures of diverse classes of materials, lithography has been widely used but often involves inherent limitations to the applicability for non-planar surfaces and the pattern resolution predefined by the stamp. Surface wrinkles can be used in various fields and it has been applied to improve the efficiency of electro-optical devices and the mobility of charge carriers in semiconductor devices. Our work shows that to generate pixelated wrinkles by controlling reactive mesogens (RMs) alignment. A custom-built optical setup employing a spatial light modulator (SLM) illuminates polarized ultraviolet light on a particular area of photo-alignment layers, such as the RMs. Wrinkles produced during the plasma-treatment polymerization of RMs can be aligned accordingly. The pixelated wrinkles can record naturally invisible images by mapping the gray level to the orientation of the wrinkles. As a result, it is shown that pixelated wrinkles enable new applications in optics such as image storage, informative labeling, anti-counterfeiting, and physical unclonable functions(PUFs).

10:00 AM SF04.08.02
A Smart Skin for Hydrogels that Enables Switchable Solute Release Sai Nikhil Subraveti[1,2] and Srinivasa R. Raghavan[1]; [1]University of Maryland, United States; [2]Princeton University, United States

Many applications of hydrogels rely on their ability to deliver encapsulated solutes such as drugs; however, small hydrophilic solutes rapidly leak out of gels by diffusion. A need exists for a way to regulate solute release out of gels - to ensure zero release until a desired time, and thereafter, for the release to be 'switched on' at a high rate. This should ideally be a repeatable switch, i.e., the gel should be cyclable repeatedly between the on and off states. Such perfect, cyclical on-off release of solutes is demonstrated for the first time through a 'smart skin' that is synthesized rapidly (in ~ 10 min) around gels. The thin (~ 50 – 100 μm) and transparent polymer skin is endowed with redox-responsive properties through the use of urethane and acrylate monomers, one of which contains a thioether group. Initially, the skin is hydrophobic and it completely prevents hydrophilic solutes from leaking out of the gel. When contacted with oxidants such as hydrogen peroxide (H_2O_2), the thioethers are converted to sulfoxides, making the skin hydrophilic and thereby 'turning on' the release of solutes. Conversely, solute release can be 'turned off' subsequently by adding a reducing agent such as Vitamin C that reverts the sulfoxides to thioethers and thus returns the skin to its hydrophobic state. The release rate in the 'on' state can be tuned via the skin thickness as well as the oxidant concentration. The ability to regulate solute delivery from gels using smart skins is likely to prove significant in areas ranging from separations to agriculture to drug delivery.

10:15 AM SF04.08.03
Microfluidic Shape-Memory Microparticles for Embolization System Jérémie Caprasse, Raphaël Riva and Christine Jerome; University of Liege, Belgium

Embolization that involves the selective occlusion of blood vessels may be used to control or prevent abnormal bleeding, close off vessels supplying blood to a tumor, eliminate abnormal connections between arteries and veins, or to treat aneurysms. It is a highly effective way to control bleeding and is much less invasive than open surgery. The selection of an embolic agent is based on many considerations, notably on the clinical indication for the procedure, on the desire to produce temporary or permanent occlusion, on the level of occlusion, on flow dynamics/collateral circulation, on the risk of complications such as necrosis or nontarget embolization, and on cost. Microparticles embolics can be made of several types of materials such as hydrogels able to swell after injection until occlusion.[1,2]

Shape-memory polymers (SMPs) are remarkable stimuli-responsive materials able to switch from one stable macroscopic shape to another one, are also of prime interest to afford well-controlled embolization systems. Among shape-memory materials, poly(ε-caprolactone) (PCL) networks are widely studied for biomedical applications since PCL is biocompatible, and biodegradable.

In our work we formulated by a microfluidic system, shape-memory microparticles composed of 4-arms PCL stars end-functionalized by coumarins[3]. The obtained highly monodispersed particles were crosslinked by on-line UV irradiation (365nm). These crosslinked particles that still exhibit crystallinity possess temperature triggered shape-memory properties by heating above the melting temperature, around 50°C, making them promising hydrophobic and biodegradable candidates for embolization aplication.

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10:30 AM SF04.08.04
Cu(I) Coordination Polymer-Based NH_3 Gas Sensor with High Response at Room Temperature TaeHun Im[1,2] and Sohee Jeong[1]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Korea University, Korea (the Republic of)

High performance in NH_3 gas sensor is highly demanded because ammonia which has highly toxic and corrosive properties causes ailments in human body under the certain concentration of NH_3. Up to date, metal oxide gas sensor (MOS) is widely used for detecting NH_3 gas; however, high operating temperatures and producing costs are considered as limitation in the effective applications.
Here, we report on a new type of NH_3 gas sensor with high response (> 800% at 100 ppm) and low detection limit (<0.25 ppm) at room temperature. The sensor is semiconducting coordination polymers (CPs) containing Cu(I) ions and thiourea derivatives, which can be produced by cost-effective solution-based method within 10 min. For improving NH_3 gas sensing performance, Ag was doped into CPs. It exhibits the excellent gas sensing capability with ~ 2000 % at 100 ppm which is the best of our knowledge. Additionally, response and recovery time decreased by 8% and 70%, respectively compared to that of parent CPs. Ag in CPs was detected by XPS measurements, which verified that Ag elements exist individually inside of CPs. To determine the origin of outstanding gas sensing properties of CPs, we performed a simulation of crystal structure based on the PXRD results. And In-situ FT-IR spectroscopy was used to identify the mechanism of NH_3 gas sensing in CPs. NH_3 gas and NH_4^+ ions acted as Lewis, Brønsted acid site, and additionally NH_3-Cu^+ peaks were observed at 1620 cm^{-1}, and it could be inferred that the high reactivity of the sensor was caused by Cu^+ acting on NH_3 detection.

10:45 AM SF04.08.05
Fabrication of Carbonized Structures with Controlled Pore Direction for Improved CO_2 Capturing Functionality Using Bio-Material Based Nanofibers TaeGeon Kim, Dmitry Sergeev and Ruth Schwaiger; Forschungszentrum Juelich, Germany

Porous architectures demonstrating high strength-to-weight ratio, large surface area and high resilience have been of recent interest for gas storage, battery electrode and fuel cell applications. Desired properties can be achieved in this class of materials by tuning the characteristics of the pores, including wall thickness, pore size and directionality of the pores, and by making use of different constituent materials. Another application of such materials is carbon dioxide capture, which can contribute to halting global warming caused by an increase in atmospheric concentration of CO_2. Early stage of CO_2 capturing research was mainly focused on materials based on chemical absorption, such as metal-organic framework (MOF) materials, which exhibit reduced cyclability due to the low physical strength and low chemical durability including their low resistance to moisture. These drawbacks can be overcome by exploiting physical absorption through surface activation of carbon-based materials. However, previous research has mainly focused on powders, which typically do not achieve high efficiency of CO_2 absorption due to the inefficient and random pathways of gas penetration.
In this work, we fabricated free-standing carbonized structures with oriented pores using nanofiber-type cellulose, chitin, and chitosan bio-materials. Using directional freeze-casting, the directional growth of ice crystals according to an applied temperature gradient functions as a template for the formation of a structure with oriented pores and bio-nanofibers walls. The porous architecture of the materials was controlled by the concentration of bio-materials in the solution. After sublimation of the ice crystals, free-standing structures were obtained with xylem-like architecture, which were then pyrolized resulting in carbonized structures with nanoscale thickness of walls containing cellulose, chitin and chitosan nanofibers. In addition, activation through potassium hydroxide (KOH) was studied for enhancing CO_2 capturing. To characterize the CO_2 capturing functionality, the surface activation of the oriented carbon structures was studied using multiple cycles of CO_2 absorption-desorption by Thermogravimetric analysis (TGA) and Raman spectroscopy. This study will elucidate the correlations between the pore architecture, which is characterized by well-oriented walls of nanoscale thickness, and its effect on the CO_2 capturing properties.

11:00 AM SF04.08.06
Molecular Approaches to the Production of Enzymatic Construction Material towards a Durable, Carbon-Negative Infrastructure Rebecca J. Gilchrist, Shuai Wang, Sara Heidarnezhad, Nima Rahbar, Suzanne Scarlata and Ronald L. Grimm; Worcester Polytechnic Institute, United States

We recently developed an Enzymatic Construction Material, ECM, that utilizes carbonic anhydrase to catalyze the conversion of carbon dioxide into carbonate. The resulting concrete-like material demonstrates high strength, crack tolerane, and self-healing properties throughout the lifetime of the carbonic anhydrase enzyme. Presently we are investigating molecular alternatives to carbonic anhydrase to improve the durability of the catalytic conversion of gas-phase carbon dioxide to crystalline carbonate species. Molecular alternatives include Zn^{2+}-based molecular catalysts that not only replicate the active site of carbonic anhydrase, but the supramolecular environment that orients the water and carbon dioxide reagents and shuttles unwanted proton products from the reaction site. We will discuss free molecular catalysts as well as surface-tethered systems that demonstrate good catalytic rates and durability at the high pH and thermal environments that exist in construction materials.

11:15 AM SF04.08.07
3D Aperiodic Cellular Structures of Polymer Materials by Rotational Layer-by-Layer Stacking for Enhancement Mechanical Properties Seo Rim Park, Seok Kim and Young Tae Cho; Changwon National University, Korea (the Republic of)

Microlattice is a two- or three-dimensional microarchitecture in which unit cells of a specific shape are regularly arranged. It has characteristics such as a high strength-to-weight ratio and shock absorption, so it can be used in various fields. However, due to the mutually exclusive relationship between strength and toughness, it is difficult to simultaneously increase the strength and toughness of microlattice. Bouligand structure is a structure in which chitin-protein fibers parallel to each other rotate at a certain angle around a vertical axis to increase strength and toughness at the same time. This maximizes the energy dissipation of the structure by crack bridging, deflection, arrest, and twisting caused by rotational stacking.
This study proposed deterministic aperiodic cellular structures with enhanced mechanical properties by bioinspired Bouligand rotational stacking of periodic lattices. The aperiodic cellular microstructure was 3D-printed with photopolymer materials and then was performed compression test to analyze mechanical properties. For proof of concept, the printed aperiodic cellular structures were designed by rotational layer-by-layer stacking of periodic hexagonal microlattices.
As a result of the compression test, linear elasticity, yielding, plateau, and densification sections appeared in order in the stress-strain graph as the compressive strain increased. Through this, it was confirmed that it had the same tendency as the microlattice stress-strain graph. However, unlike 3D aperiodic cellular structures, the monolith did not show a yielding section. This is considered to be because monoliths are bending-dominated, but 3D aperiodic cellular structures are stretch-dominated.
The in-plane strength, stiffness, and toughness of 3D aperiodic cellular structures fabricated at stacking angles of 0°, 15°, 20°, 30°, 45°, 60° and 90° were analyzed. Compared to the monolith, the strength, stiffness, and toughness of the 3D aperiodic microlattices were higher at all stacking angles, and among them. The reason for the superior mechanical properties compared to the monolith is that the strut breaks later, similar to the bouligand structure. We believe that these enhanced mechanical properties could be originated from the minimization of stress concentration due to the existence of many struts and the maximization of energy dissipation due to the dispersion of the crack initiation point.

Acknowledgment This work has supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(NRF-2022R1C1C1003966) This work has supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(MIST)(No. 2019R1A5A8083201)

11:30 AM SF04.08.08
Thermally-Responsive Softening Intravenous Needle for Enhancement of Patient Care and Healthcare Provider Safety Karen-Christian C. Agno, Keungmo Yang, Sang-Hyuk Byun, Subin Oh, Simok Lee, Heesoo Kim, Kyurae Kim, Sungwoo Cho, Won-Il Jeong and Jae-Woong Jeong; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Conventional intravenous needles are manufactured from materials with high and fixed stiffness that allows for rigid tissue insertion followed by therapeutic fluid delivery into the bloodstream. Their rigid structure not only causes chronic tissue complications among hospitalized patients receiving IV medication but also heightens the risk of needle stick injuries among healthcare providers after usage. Here, we introduce a liquid metal-based needle that can autonomously change its stiffness by body temperature (~ 37 °C) to match the softness of the delicate blood vessel after rigid tissue insertion. The needle has a rectangular hollow structure formed from U-shaped liquid metal frames which are encapsulated with silicone of high tear strength. We utilize gallium for the channel frames because of its unique phase conversion between solid (elastic modulus = 9.8 GPa) and liquid, low melting temperature (T_{melt} = 29.76 °C) below the body temperature, and biocompatibility. At room temperature (20-25 °C), the needle is rigid and straight like the commercial rigid needle, but it becomes soft and compliant after rigid tissue insertion (~ 37 °C) within 60 seconds as the encapsulated gallium frames melt, achieving three orders of magnitude of independent modulus-tuning ratio. After one usage, the softened needle becomes completely non-reusable because supercooling phenomena prevent solidification of liquified gallium. Our *in vivo* studies indicate that the softening needle has potential to reduce inflammation injury in the injection site owing to its enhanced tissue-adaptability in comparison to commercial rigid IV access device of comparable size. To further add functionality, a nanomembrane temperature sensor was integrated with the softening needle, demonstrating that the integrated system-device can monitor the on-site temperature to measure core body temperature or undesirable fluid leakage during IV administration. Overall, the gallium-based intravenous needle envisions wide-range of clinical applications, as it actively responds to the call of the World Health Organization for the improvement of patient care and safer medical practice.

SESSION SF04.03: Poster Session: Development and Design of Responsive Architected Materials
Session Chairs: Michael Frazier and Xiaoyue Ni
Tuesday Afternoon, April 11, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SF04.03.02
Self-Healing Polymer Composites with Enhanced Strength for Use in Protective Textiles Evan A. Griffiths, Blaine Barrington, Scott Coguill, Brahmananda Pramanik, Richard LaDouceur, Jessica M. Andriolo and Jack L. Skinner; Montana Technological University, United States

Self-healing materials have the potential to increase the lifetime of products exponentially through both non-reversible healing and reversible healing processes. For instance, non-reversible healing has been demonstrated with the use of micro-spheres filled with healing-compounds used to mitigate micro-crack propagation within materials like concrete or asphalt. Upon use however, micro-sphere rupture is irreversible. Reversible self-healing traditionally is manifested in polymeric or rubber materials designed to exhibit both covalent and ionic bonds within the same material. Reversible self-healing materials not only repair other products but can have extended lifetimes themselves. However, reversible self-healing materials are often mechanically weak when compared to non-reversible self-healing materials, thereby limiting applications. In this work, we aim to improve the strength of reversible self-healing materials for sustainability and to increase the extent of applicable uses of these materials. We hypothesize that through the addition of aramid nanofibers, the mechanical stability of reversable self-healing polymers can be improved.

To produce aramid-reinforced polymer composites, aramid fabric will first be dissolved in dimethyl acetamide and lithium chloride to form nanofibers. The aramid fibers will then be dispersed within a self-healing polymer matrix (previously described by Wang et al. in *J. Am. Chem. Soc.* 2019) by sonication to randomly align the fibers for enhanced shear and bulk moduli. To determine a preferable fill concentration, aramid will be distributed in a polymer matrix over a range of concentrations. Aramid-reinforced polymers will then be examined for shear strength using an ASTM D 732 punch tool, and the dynamic stress-strain of the materials will be characterized on a split-Hopkinson pressure bar and Charpy impact tester. The reinforced polymer will also be formed into dog bones using a 3D printed mold for determination of the elastic modulus through quasistatic tensile testing. In addition to these tests, ability and time required for the polymer to repair will be monitored over the range of aramid concentrations used.

The primary objective of this work is to provide self-healing textiles with enhanced strength for soldiers in the field to maintain protection following damage of protective gear or uniforms. Following determination of a preferable aramid concentration in a reinforced polymer matrix, the polymer will be electrospun into fibrous textiles for further testing including self-repair following impact, splitting or ripping due to an encounter with a sharp object. Future work hopes to follow self-healing of these reinforced textiles using lab-on-a-chip technologies and determination of how re-use impacts mechanical properties.

5:00 PM SF04.03.03
Real-Time and Label-Free Biosensing Using Moiré Pattern Generated by Bioresponsive Hydroge Semin Kim, Soeun shin, Yujin Kang and Won-Gun Koh; Yonsei University, Korea (the Republic of)

Bioresponsive hydrogels are smart materials that respond to various external stimuli and exhibit great potential as biosensors owing to their capability of real-time and label-free detection. Here, we propose a sensing platform based on bioresponsive hydrogels, employing the concept of moiré patterns. Two sets of line patterns with different pitch sizes are prepared; a hydrogel grating whose pitch size changes according to external stimuli and a reference grating with constant pitch size. The volume changes of the hydrogel caused by external stimuli changes the pitch size of the hydrogel grating, and subsequently, the pitch sizes of the moiré patterns (moiré signal), whose values can be obtained in a real-time and label-free manner through customized moiré microscopy and signal processing. After confirming that the pH-induced swelling of hydrogel could be monitored using moiré patterns, we performed moiré pattern-based detection of specific proteins using protein-responsive hydrogel that underwent shrinking via interaction with target proteins. Brain-derived neurotrophic factor and platelet-derived growth factor were selected as the model proteins, and our proposed system successfully detected both proteins at nanomolar levels. In both cases, the pitch size change of hydrogel grating was monitored much more sensitively using moiré patterns than through direct measurements. The changes in the moiré signals caused by target proteins were detected in *ex-vivo* environments using a custom-made intraocular lens incorporating the hydrogel grating, demonstrating the capability of the proposed system to detect various markers in intraocular aqueous humor, when implanted in the eye.

5:00 PM SF04.03.04
On-Demand Selective Chirality of Flower Corolla-Like Micropetal Arrays with Magnetic Twisting Actuation Jeong Eun Park[1,2], Jisoo Jeon[2], Sei Jin Park[3], Sukyoung Won[1,2], Zahyun Ku[4] and Jeong Jae Wie[1]; [1]Hanyang University, Korea (the Republic of); [2]Inha University, Korea (the Republic of); [3]Lawrence Livermore National Laboratory, United States; [4]Air Force Research Laboratory, United States

.Selective chirality has attracted interest in the field of optics to distinctively detect light with a left- or right-circularly polarized direction. Typically, artificial chiral structures are, however, stationary and cannot dynamically change the directionality of the chirality once the structures are fabricated. In this study, we present on-demand selective chirality of the micropetals with radial arrangements of several micropillars, inspired by natural flower corolla with intrinsic chirality. Individual micropetal performs the directional magneto-mechanical twisting actuations toward the linear external magnetic fields. Accordingly, the micropetal arrays appear the dynamic chiral switching from achiral to clockwise or counterclockwise directions depending on the changed direction of the external magnetic fields. Toward realizing the chirality of three-dimensional (3D) microstructure, we will discuss relationships between the chirality and symmetry properties of the magnetically twisted five- and six-micropetal arrays. Along with this, by wetting the achiral and chiral micropetal arrays with a polymeric solution, we would demonstrate 3D capillary-assembled achiral flower corolla and solute-assisted shape-immobilized chiral flower corolla.

5:00 PM SF04.03.05
Magnetoactive Properties of Biocompatible Magnetic Hydrogel Composites—Effects of Magnetic Particulate Type and Magnetic Annealing Jacob Schewe, James Michael Ennis, Jimmy (Dingming) Lu and Brittany Nelson-Cheeseman; University of St. Thomas, United States

Magnetic hydrogels are a novel composite smart material made up of a flexible, tissue-like hydrogel polymer with an incorporated magnetic particulate, producing a material capable of mechanical deformation in response to an applied magnetic field (H). Polyvinyl alcohol (PVA) ferrogels were successfully fabricated by the freezing-thawing (FT) cycle technique, employing magnetite (Fe_3O_4) and strontium ferrite ($SrFe_{12}O_{19}$) as the materials for magnetic, micron-sized, additives. Strontium ferrite was specifically chosen as a hard magnetic additive due to its availability and lower price compared to Neodymium Iron Boride additives. In this study, the differing effects of magnetically soft and hard additives on the properties of PVA ferrogels were investigated by comparing the magnetic, mechanical, and magnetoactive properties of PVA ferrogels impregnated with magnetite and strontium ferrite, respectively. The effects of magnetic annealing on ferrogels during crosslinking were investigated in this study by comparing their resulting magnetic, mechanical, and magnetoactive properties with analogous control samples. Magnetoactive properties are determined by quantifying the angle of sample deflection in an applied transverse magnetic field, via a custom digital image overlay program. To further study the effects of magnetic annealing and material type to create complex magnetoaction, multiple orientations relative to H were adopted during magnetoactive deflection testing. Mechanical properties are determined via tensile elongation testing. The distribution of the magnetic additives was investigated using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (SEM EDS). SEM EDS analysis revealed an evenly dispersed particulate throughout the hydrogel network at all loading content levels. Mechanical analysis revealed an increase in ferrogel stiffness contingent on an increase in magnetic additive content, regardless of the magnetic properties of the additive. Addition of magnetically hard additives yielded magnetically responsive ferrogels capable of complex motion and actuation. These ferrogels were characterized by a high magnetic remanence, and highly customizable magnetoaction that included a combination of deflection along a transverse magnetic field (H) and twisting around the same field. This complex responsiveness was varied by additive loading content, the presence of magnetic annealing, and sample orientation during testing. In contrast, the inclusion of a soft magnetic additive yielded highly magnetoactive ferrogels with only a single pattern of magnetoaction. These ferrogels were characterized by variable deflection along a transverse magnetic field (H) but were only characterized by their highly deflective magnetoaction, as compared to the deflection displayed by hard magnetic ferrogels yet had no capacity for complex motion. This deflective magnetoaction based upon magnetic additive loading content and presence of magnetic annealing.

5:00 PM SF04.03.06
Development of Novel Precursors for Lubricious Metal Chalcogenide Coatings Ciaran P. Llewelyn[1], Andrew Johnson[1], Joshua Smith[2] and James Parish[2]; [1]University of Bath, United Kingdom; [2]Infineum International Limited, United Kingdom

Tribology plays an integral role in the development of energy-efficient technologies at numerous levels by increasing the energy efficiency and longevity of components through minimising friction and wear. This covers a wide array of sectors including energy, health, manufacturing, and transport with over 20% of total energy consumption on earth being used to overcome these effects with the majority arising from large industrial processes involving heavy machinery.[1] The development of materials for reducing friction and wear in machine elements is an enormous challenge and one area of significant interest is the automotive sector with a particular focus on the internal combustion engine (ICE).

Currently employed additives in ICEs such as zinc dialkyldithiophosphate (ZDDP)[2,3] and molybdenum dithiocarbamate (MoDTC)[4,5] have been utilised as anti-wear and friction-reducing agents in lubricants for over 80 years. Despite their unquestionable success during this time, the resulting by-products of combustion have been known to damage catalytic convertors forming metallic ash and sulfurous/phosphorus oxide layers over the active sites of the catalyst inhibiting the performance.[2,6] This has led to several governing bodies restricting the amount of sulfur and phosphorus within engine oil.[7] This restriction has led to significant interest in alternative metal chalcogenide systems which could compete with the current additives.

This presentation reports on the design and development of adaptive, multifunctional novel precursors; which act as a delivery molecule for Mo and W chalcogenide systems combined with the ability to decompose in situ to form lubricious metal-containing thin films. These responsive thin films are predicted to offer competitive friction and wear protection whilst limiting the use of sulfur and phosphorus. New tribologically responsive precursor systems have been fully characterised by NMR, TGA and SCXRD, and the tribological performance of the precursors has been analysed using a TE-77 tribometer. The resulting scars from the friction evaluation and wear measurements have been analysed by energy-dispersive X-ray analysis. Responsive metal chalcogenide precursors can be utilised for their tribological properties and aid in minimizing wasted energy with a focus on honing effectiveness and efficiency.

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5:00 PM SF04.03.07
Multi-Functional Architected Swarms of Magnetic Microrobot Assemblies Kijun Yang[1,2], Sukyoung Won[1,2] and Jeong Jae Wie[3,4,5]; [1]The Research Institute of Industrial Science, Hanyang University, Korea (the Republic of); [2]Program in Environmental and Polymer Engineering, Inha University, Korea (the Republic of); [3]Department of Organic and Nano Engineering, Hanyang University, Korea (the Republic of); [4]Human-Tech Convergence Program, Hanyang University, Korea (the Republic of); [5]Department of Chemical Engineering, Hanyang University, Korea (the Republic of)

Magnetically responsive microrobots have attracted a significant interest as functional materials for untethered robotic systems operating by external magnetic fields. Research on the magnetic microrobots has generally been focused on the sophisticated locomotion manipulation of individual robots. However, individually moving microrobots have limitations in muti-functionality due to their light weight and tiny size. Herein, we report a programmable architected swarm of magnetic microrobots by controlling magnetic anisotropy in the microrobots. By programming magnetization profiles in magnetic microrobots, the magnetic microrobots can build a long-axial or short-axial assembly. When permanent magnets rotate underneath the magnetic microrobots, the assembled magnetic microrobots rotate with a lift angle, i.e., pivoting. Through the pivoting, the assembled magnetic microrobots can climb obstacles that are five times taller than the body length of the single microrobot. Long-axial assembly of the magnetic microrobots facilitates climbing an obstacle than the short-axial assembly counterpart. Meanwhile, by the short-axial assembly, the magnetic microrobots can effectively transport cargo through rotational force of assembled microrobots. Furthermore, we will discuss collective behaviors of the assembled magnetic microrobots toward atherosclerosis plaque rupture.

5:00 PM SF04.03.08
Effects of Particle Distribution on Maneuver of Nanocomposite-Based Helical Magnetic Microrobots Sukyoung Won[1,2], Jaeyong Lee[3], Young Joon Ko[2], Jong Hoon Jung[2], Jinkon Kim[3] and Jeong Jae Wie[1,1]; [1]Hanyang University, Korea (the Republic of); [2]Inha University, Korea (the Republic of); [3]Pohang University of Science and Technology, Korea (the Republic of)

Three-dimensionally (3D) architected magnetic microrobots can locomote remotely in terraqueous environments by external magnetic fields. To actuate magnetic microrobots, various 3D architectures have been prepared through a conventional lithography technique and a direct laser writing of polymer nanocomposites. Although magnetic nanoparticles are embedded in polymer matrices for magnetic actuation of 3D architected magnetic microrobots, correlations between dispersion of magnetic nanoparticles and robot locomotion have not yet been studied intensively. Herein, we compare solvent evaporation and rapid precipitation strategies of thermoplastic polyurethane (TPU)-magnetic nanoparticle nanocomposites to maneuver the nanocomposite-based magnetic microrobots. Depending on the strategies, magnetic nanoparticles are phase-separated or dispersed in nanoscale in the polymer nanocomposites even with identical chemical compositions and particle concentrations. The dispersion states of the magnetic nanoparticles affect torsion-induced polymer processing which is designed to prepare 3D helical architecture of microrobots from the 2D nanocomposite films. When the helical magnetic microrobots feature dense structures without micro-voids in the 3D helix, they can rotate uniformly and revolve in a regular orbit under a rapid rotation of external magnetic field. We will investigate the effects of nanoparticle dispersion not only on the locomotion of the 3D helical magnetic microrobots but also physical properties of nanocomposites.

5:00 PM SF04.03.09
Magnetically Actuated Modular and Biodegradable Hydrogel Robot Units Portia Rayner, Audrey Sedal and Jianyu Li; McGill University, Canada

Small scale soft robots have been proven to be attractive candidates for applications in dynamic and confined spaces such as inside the human body. An increasing number of stimuli-responsive hydrogels has been developed in recent years, enabling the fabrication of more sophisticated designs. These systems have typically been actuated using remotely applied external stimuli such as heat, light, electric fields, or magnetic fields. Of these options, magnetic fields are particularly appealing because the magnitude, phase, and frequency can be adjusted rapidly with a high degree of accuracy. There are few magnetically actuated hydrogels, however, that integrate sensing, computation, and actuation. This work reports a design for hydrogel building blocks that could be combined in order to produce full robot functionality. An alginate-based scaffold is used as the foundation for these units. Since alginate is a biopolymer, this could allow for biocompatible degradation of the units and subsequent recovery of the magnetic particles, enabling a system-level recycling process. Two types of magnetic particles are compared: carbonyl iron and iron oxide. The effect of the particles, individually and combined, on the mechanical and structural properties of the scaffold in addition to the actuation response of the unit is examined. Multiple unit models are created by varying the type and distribution of magnetic particles as well as the scaffold structure in order to achieve different properties, motions, and responses to magnetic fields. The surface of the units is functionalized in order to allow for assembly. Physical polymer entanglement, chemical bonding, and magnetic adhesion are compared as methods for assembly. The type, number, and relative orientation of the units within the larger structure can be altered in order to achieve different functionalities such as cargo delivery, programmed degradability, and multiple modes of actuation. This approach provides the materials foundation for more sophisticated robotic systems which have previously been difficult to achieve using hydrogels.

5:00 PM SF04.03.10
Universally Applicable Encapsulation and Functionalization Method for Preparing Functional Nanocomposites and Hybrids for Biomedical Applications Artur Feld[1,1], Agnes Weimer[1,1], Jan-Philip Merkl[1], Johannes Ostermann[1], Christian Schmidtke[1], Rieke Koll[1], Lisa Sarah Fruhner[2] and Horst Weller[1,1]; [1]University of Hamburg, Germany; [2]Forschungszentrum Jülich GmbH, Germany

By synthesizing homogenous magneto-responsive nanocomposites and functional nanohybrids, we demonstrate the universal applicability of our advanced encapsulation technique.[1-3]

Our encapsulation technique is based on the micellar encapsulation of various nanocrystals in a polyisoprene-block-poly(ethylene oxide) (PI-b-PEO) diblock copolymer shell with subsequent thiol-ene click reaction initiated cross-linking of the PI block. This leads to a robust and functionalizable polymer shell that provides maximum stability to the nanocrystal in both water and host matrix. These even offer the possibility to perform copper(I) catalyzed click reactions while keeping the fluorescence of the quantum dots. We demonstrate the robustness of the shell by synthesizing a magneto-responsive nanocomposite with homogeneously dispersed superparamagnetic iron oxide nanocrystals in a poly(ethylene oxide) matrix. We present an extensive step-by-step characterization during the different stages of preparation by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM), with both methods perfectly complementing each other.[1]

Biocompatibility and functionalizability were demonstrated by a systemic study with human alveolar epithelial cells (A549) and murine macrophage leukemia cell (RAW-264.7). Thereby, we could show that using different polymer architectures besides the variation of the polymers' molecular weight allows us to control the size of the resulting constructs and the permeability of the shell. As a general trend, it can be stated that those coatings, which were most stable against quenchers, also showed the best resistivity concerning unspecific cellular uptake.[2]

All these results underline the vast variability and controllability of the PI-b-PEO diblock copolymer system for the encapsulation and functionalization of nanoparticles for biological applications and magneto-rheological nanocomposites.

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5:00 PM SF04.03.11
Exploring the Effects of Magnetic Particle Composition on the Magnetoactive Properties of Magnetic Elastomer Filament and 3D Printed Samples Daniel P. Fagan, William Howell, Sarah Ziemann, Jimmy (Dingming) Lu, Jacob Schewe, Michael Ennis, Thomas Hoft and Brittany Nelson-Cheeseman; University of St. Thomas, United States

Magnetic elastomers are a composite smart material that contains an elastomeric matrix with magnetic particles. This results in a material that can mechanically deform when exposed to a magnetic field (H), termed magnetoaction. The focus of this research was on tuning (1) the type of magnetic particle and (2) the percent-by-volume of magnetic particles in magnetic elastomer 3D printer filament and printed samples. Different types of magnetic particles yield better deflection, some yield better twisting, and some respond at a lower magnetic field. Another factor that needed to be kept in mind was the stiffness increased as the percentage of magnetic particles by volume increased. The 3D printer filament was made by utilizing solvent casting to dissolve TPU pellets to then be able to mix in the desired mixture of magnetic particles. Either solely hard magnetic particles or a combination of hard (permanent) and soft (impermanent) magnetic particles was used in the filament's composition. Strontium ferrite (SrF) and magnetite (Fe_3O_4) were the magnetic particles used. Fe_3O was used for its high magnetic susceptibility and the SrF was used because of its hard magnetic property, which allows the printed sample to exhibit complex motion. The resulting sheets from solvent casting were cut into strips that were then put through a filament extruder. The annealed filament was put through an apparatus that applied a magnetic field as the filament was cooled to preferentially align the magnetic moments. The filament was used to 3D print samples by way of fused deposition modeling (FDM) 3D printing. The magnetoactive properties of the filament and printed samples (rectangular beams) were tested by suspending samples in a magnetic field (H) of up to 0.4T. Digital images were taken at set field intervals and then later put into a custom MATLAB program to measure the deflection angle for both the filament and printed samples and the twisting angle for just the printed samples. Complex motion was observed in the printed and filament samples as a result of the hard magnetic particles. The twisting angle was only recorded for the printed samples due to the difficult nature of measuring the angle of twist for the filament. For this research, a combined percent by volume of 20-25% of magnetic particles were used. It was observed that the magneto action decreased as the percent by volume of magnetic particles increased, and that was due to the increased stiffness of the composite from more magnetic particles. Furthermore, proper dispersion of the particles was verified using scanning electron microscopy (SEM). The combination of Fe_3O and SrF did not yield the results that were expected for magneto action. It was expected that the mixture of Fe_3O and SrF would yield a magnetic elastomer that would yield high deflection at lower fields and would also allow for twisting. However, the deflection for the mixture of two types of magnetic particles was even less than it was for only SrF (hard magnetic particle).

5:00 PM SF04.03.12
Uniform Gallium Microgranules-Based Adaptive Electronic Skin for Advanced Pressure Sensing Beyond Human Touch Perception Simok Lee[1], Sang-Hyuk Byun[1], Steve Park[1,2], Joo Yong Sim[3] and Jae-Woong Jeong[1,2]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]KAIST Institute for Health Science and Technology (KIHST), Korea (the Republic of); [3]Sookmyung Women's University, Korea (the Republic of)

Human skin exhibits excellent pressure sensing capabilities, including high sensitivity and wide detection bandwidth. Through these strengths, it can adaptively detect external mechanical forces, ranging from delicate touches to heavy loads. Electronic skin which mimics pressure sensing ability of the human skin can bring a huge impact in numerous fields, such as medical devices, robotics, prosthetics, and human-machine interfaces. However, the current technology is limited due to the trade-off between sensitivity and bandwidth, allowing only a single aspect of sensing performances – that is, either high sensitivity or large bandwidth. Furthermore, the invariant nature of the sensing properties of the electronic skin restricts their applications to the original target uses.
Herein, we introduce an adaptive electronic skin that overcomes the above limitations of existing electronic skin, showing advanced pressure sensing beyond human touch perception. The adaptive electronic skin is built with arrays of tunable pressure sensors based on gallium microgranules embedded in the elastomer matrix. Gallium microgranules undergo the phase shift between the liquid-solid phase through the temperature change, which allows the mode conversion of the pressure sensor between the high-sensitivity mode (soft mode) and the wide-bandwidth mode (rigid mode). The mode conversion allows the pressure sensor to measure pressure from a minimum of 3 Pa in the high-sensitivity mode to a maximum of 1.45 MPa in the wide-bandwidth mode. Considering that the detection range of human skin is from 100 Pa to 400 kPa, our tunable pressure sensor has 97 % higher sensitivity and 262.5 % wider detection bandwidth compared to human skin. We expanded our pressure sensors into large-area sensor arrays to develop an adaptive electronic skin and investigated its practicality in real-life applications ranging from measuring sophisticated blood pressure to measuring body weight. Successful demonstrations of this technology show the great potential of the adaptive electronic skin for robotics, bionics, and health monitoring.

5:00 PM SF04.03.13
Repurposing of Industrial Polymer Waste into Sustainable Built Environment Application and Its Characterization Hengky Chang, See Ying Isabel Ong, Kowee Stanley Luar and Jiale Chew; Nanyang Polytechnic, Singapore

This is a collaboration project between Dow Pacific (Singapore) Pte ltd and Nanyang Polytechnic. Dow is one of the largest acrylic co-polymer producers in the world for use in various coatings, adhesives, and other construction materials. As part of the polymerization process in the plant, certain quantities of polymer solids end up in wastewater tank from clean-up and other related plant processes. The polymer solids are then filtered out before the wastewater is further processed in wastewater treatment facility. Collected acrylic polymer waste was pressed to remove water to form polymer cakes with moisture of less than 10% are disposed which eventually ends up in land fill or sometimes used for waste-to-energy generation. However, in consideration for the contribution towards economic benefit and sustainability, there is a need to find alternative commercial usage to this waste polymer waste cake, such as in the built environment or construction industry, in concrete application for instance.

The utilization of a large amount of waste in concrete production is considered the best alternative for solving the issues associated with improper disposal.

Polymer waste is considered as one of such waste and could be utilized in several applications. The drawback associated with the utilization of a large amount of polymer waste is the decrease in the mechanical properties of the mortar or concrete. The purpose of this project is to study how to repurpose the acrylic polymer waste in short form Polycake waste in the construction material with the main focus on replacing sand in mortar mixture with polycake waste.

In order to achieve the above purposes, firstly it will be the processing of the chunky polycake sample through freezing drying process, it turns into a powdered form which makes it easier to be used as a premix formula in the mortar mixture. After processing the polycake into the powdered form, it is being analysed using various method. The powdered polycake waste sample was initially analysed using scanning electron microscope to observe the powdered polycake sample particle size. It is found that the size distribution of the powdered polycake is very wide and hence need to standardize the size of the polycake particle through sieving.

The powdered polycake waste sample's elemental composition was analysed using X-ray fluorescence, to analyse the chemical composition to ascertain that the chemical composition remains similar to original acrylic polymer after processing it into powder form, and to detect if there is any traces of chemical contaminant of the polycake waste.

The powdered polycake sample's moisture level is tested using thermogravimeter analyzer. This is to ensure the method used to process the powdered polycake sample has a moisture level of less than 5%. The powdered polycake sample's thermal transition would be tested using differential scanning calorimeter. This is to find out the melting point and degradation of the polycake sample.

Next stage is to blend the powdered polycake waste into the mortar mixture to see if it affects the mechanical properties such as compression and flexural strength of the mortar mixture as well as porosity test and water absorption. The flowability of the mortar mixture blended with powdered polycake waste before curing was also analysed and measured using flow table device and viscometer. This is to ensure the mortar that was blended with powdered polycake waste has the same flow property with original standard mortar. This will affect the applicability by the construction worker in applying the modified mortar. Hence, before the powdered polycake waste was added into mortar, the control mortar formulation is needed. The strongest mortar ratio by far would be cement (5): water (4.8): sand (15), which is then used as a control for the study involving powdered polycake to replace a percentage of sand in the mortar mixture starting from 5% to 25% with 5% increment interval.

SESSION SF04.09: Virtual Session: Development and Design of Responsive Architected Materials
Session Chairs: Michael Frazier and Carlos Portela
Tuesday Morning, April 25, 2023
SF04-virtual

10:30 AM SF04.09.02
Effect of Surface Organ-Silanization on SBA-15 Mesoporous Silicas in CO2 Adsorption Precesses—Design, Synthesis and Computational Studies
Eduardo Cueto Diaz[1], Fabián Suárez García[2], Santos Galvez Martinez[1], Eva Mateo Marti[1], Alberto Castro Muñiz[2], María Pilar Valles Gonzalez[3] and María Carmen Torquemada Vico[1]; [1]Instituto Nacional de Técnica Aeroespacial, Spain; [2]Instituto de Ciencia y Tecnología del Carbono, Spain; [3]Instituto Nacional de Tecnica Aeroespacial, Spain

CO$_2$ presents a very unique property among other gases as it absorbs and re-emits IR radiation becoming the most prominent physical driver of climate change together with methane. It has been stablished that the current concentration of CO$_2$ in Earth atmosphere is close to 412 parts per million (ppm), representing a 47% increase since the beginning of the Industrial Age, which may lead in the future to not only an alarming increase in Earth's temperature, but also it could provoke serious health problems if the concentrations exceed 5,000 ppm. As a result of these problems, sensing, monitoring, and ultimately capturing CO$_2$ is of great interest.
The conventional CO$_2$ sensor devices, mostly based on solid-state electrolytes and metal oxides, inevitably show huge cross-sensitivity to other gases and suffer from several other limitations, such as higher cost, heavier weight, less durability, and bigger size; thus, to enable the widespread adoption of CO$_2$ sensing materials in many aspects of modern society, two major requisites are needed, i) their inexpensive mass production and ii) ultralow power demand, as well as overcoming the previously mentioned limitations. As an alternative to these traditional sensing devices, nanomaterial-based sensing machinery are gaining widespread popularity owing to their long-term durability in harsh conditions, low-cost and reduce size properties. However, nano-sensing devices still face certain challenges to fulfill the diverse sensing demands. For example, cross-sensitivity with other gases at high temperatures is still challenging (1) and the production of uniform modified areas in the nanomaterial is problematic.
In the present work, these two major drawbacks have been partially overcome, by building CO$_2$ sensing artifacts following two premises; first, it was carried out the homogeneous surface deposition of nanoparticle (SiO$_2$) monolayers over metallic wafers(2)(3) and secondly, we have implemented a robust protocol for the organic-ligand decoration of silica-based nanomaterials displaying two different morphologies 1) nanospheres(4) and 2) interconnected rod-like.(5) The production of well-ordered and densely packed silica-nanoparticle monolayers was conducted by the chemical modification of gold wafers with 3-mercaptopropyl triethoxysilane groups, allowing the organization of 3D nanospheres in a well-ordered fashion. The total CO$_2$ adsorption capacities of silica-based nanomaterials ranges from 0.9 – 1.7 mmol * g-1 at 25°C, as a function of their morphology and their organic-ligand coating. The absorption selectivity factor (*S*) was also studied in the nanospherical SiO$_2$ nanoparticles, showing remarkable adsorption selectivities of CO$_2$ over N$_2$ >70 matching and even surpassing other solid sorbents designed for the separation of binary mixture of gases. Furthermore, it was demonstrated their high sensitivity towards CO$_2$ at low concentrations (12.4 ppm) using numerous material characterization techniques (XPS, FTIR and UV-Vis spectroscopies, SEM microscopy, etc.). Thus, we expect that the high modulability of silica-based nanomaterials, could open new routes in the development of CO$_2$ chemical sensor and capture devices, under conditions similar to the real indoor environments but also in fields that require sensing at low pressures (planetary environments, enclosed spaces, etc.).

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(4) *Nanomaterials* 2021, 11, 2893.
(5) Submitted to ACS Applied Nanomaterials.

10:45 AM SF04.09.03
Abstract Presented (ON-DEMAND ONLY) Design of Solar-Driven Self-Cleaning and Antimicrobial Magnesium Oxychloride Cement Panels Luis

F. Rodríguez Alfaro[1], Edith Luévano-Hipólito[1] and Leticia M. Torres-Martínez[2]; [1]Instituto de Ingeniería Civil, UANL, Mexico; [2]Centro de Investigación en Materiales Avanzados, CIMAV, Mexico

In recent years, the use of smart construction materials with photocatalytic activity has emerged as a new alternative technology that can help mitigate air pollution, dirtiness, and the growth of pathogenic microorganisms on building surfaces. The growing interest in this type of material and the promising results obtained in both laboratory and outdoor conditions have encouraged the design and commercialization of different types of building materials on market. Among them, photocatalyst cement as a smart building material has become one of the most popular and used to be applied outdoors as a technological strategy to reduce environmental pollution. This kind of special cement is fabricated when a nanoparticulate photocatalyst is incorporated and mixed into a cementitious matrix, causing this material acquires self-cleaning and antimicrobial activity, as well as air-purifying capacity. However, most of them have been made with ordinary Portland cement (OPC) which is known leaves severe damage to the environment during its production (4.6 billion tons of CO_2 are emitted into the atmosphere annually). For this reason, magnesium oxychloride cement (MOC) is proposed in this study as an alternative material to OPC, as it is considered a more environmentally friendly and eco-efficient material, besides having a more attractive marble-like appearance. The titanium dioxide (TiO_2) nanoparticles were used as photocatalysts to functionalize the MOC cement and to explore for the first time the self-cleaning and antimicrobial activity in this kind of cement. Different prototypes of MOC functionalized with TiO_2 were fabricated and characterized by various analytical techniques such as XRD, FTIR, SEM, EDS, UV-Vis, compressive strength, and nanoindentation tests. Preliminary results indicated that the amount of TiO_2 nanoparticles did not influence MOC samples' composition, morphology, or bandgap energy. Results showed good self-cleaning efficiencies upon 75% in the first 3 h under solar radiation and ~85% in the accelerated weathering chamber. It was noted that the manufactured MOC prototypes showed great photocatalytic stability in the accelerated weathering tests throughout the evaluation time, which suggests good durability over the operation period. On the other hand, the antimicrobial activity was performed against *E. coli* (gram-negative) under artificial visible light. The zone of inhibition (ZOI) showed diameters higher than 21 mm to *E. coli* for samples with 5% of TiO_2 or superior, revealing a high microbial inhibition of the gram-negative bacteria. These results demonstrated that the MOC cement functionalized with TiO_2 nanoparticles has the potential to be applied as self-cleaning and antimicrobial smart materials in outdoor conditions and to contribute to a sustainable environment.

SYMPOSIUM

April 10 - April 26, 2023

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* Invited Paper
\+ Distinguished Invited

SESSION SF05.01: Particle Aggregation I
Session Chairs: Qian Chen and Xin Zhang
Monday Morning, April 10, 2023
Moscone West, Level 3, Room 3012

8:00 AM SF05.01.01
Multi-Component Plasmonic Nanocrystal Gel Assemblies with Thermoreversible Links Jiho Kang, Zachary M. Sherman, Hannah S. Crory, Diana L. Conrad, Marina W. Berry, Benjamin J. Roman, Eric V. Anslyn, Thomas M. Truskett and Delia Milliron; The University of Texas at Austin, United States

Colloidal inorganic nanocrystals (NCs) can display unique properties, such as localized surface plasmon resonance (LSPR), that can be synthetically controlled by their elemental composition, size, and shape. Gelation offers an opportunity to exploit not only the distinct properties of individual NCs but their structure-dependent collective properties. With molecular linkers that can form dynamic covalent bonds, reversible NC gelation can be realized under conditions based on thermodynamic principles, opening door to responsive, tunable functional materials. Recently, we introduced thermoreversible NC gel assemblies using a metal coordination linkage, of which spectroscopic signal enabled in situ quantification of the linking and provided microscopic insights

for gelation. Plasmonic coupling between linked tin-doped indium oxide NCs led to abrupt, yet reversible, infrared absorption shifts at a chemically tunable gelation.
The characteristics of NC assemblies can be tuned in a broader range when two or more distinct components are incorporated into NC networks. Here, we demonstrate randomly-mixed multi-component NC gel assemblies using thermoresponsive metal coordination linkage. Tin-doped indium oxide NCs with different sizes, doping concentrations, and shapes are reliably intermixed in linked gel assemblies, exhibiting collective LSPR response that reflects the contributions of each component while also deviating systematically from expectations based on simple linear mixing. We extend a many-bodied, mutual polarization method to simulate the infrared response of mixed NC gel assemblies, reproducing the experimental trends with no free parameters and revealing that spectral deviations originate from cross-coupling between distinct plasmonic components. Our gelation strategy using thermoreversible metal coordination links enables the modular incorporation of NCs regardless of their doping concentration, size, and shape, giving access to continuously tunable far- and near-field optical properties that are distinct from those of the constituent building blocks or mixed close-packed structures.

8:15 AM SF05.01.02
Engineering Self-Assembly of Nanoparticles into Chiral Superlattices Using Liquid-Phase TEM Jiahui Li[1], Shan Zhou[1], Jun Lu[2], Chang Liu[1], Chang Qian[1], Nicholas A. Kotov[2] and Qian Chen[1]; [1]University of Illinois, Champaign-Urbana, United States; [2]University of Michigan, United States

Achieving chiral nanomaterials from nanoparticle self-assembly has attracted increasing attention due to their strong chiroptical activity and wide range of potential applications. Therefore, understanding the formation pathway at nanoscale is essential for precise chiral nanomaterial fabrication and engineering. Here, by using liquid-phase transmission electron microscopy (TEM) and theoretical interaction calculations based on coarse-grained models, we study the dynamics of chiral pinwheel superlattices formed by achiral tetrahedral gold nanoparticle self-assembly in solution. We show rapid nucleation and growth of low-density tetrahedral bilayer lattices from single particles. Chiral pinwheel superlattices 'compressed' from the low-density state at nanometer precision is experimentally realized by harnessing the energetics. Furthermore, diverse superstructures with variable domain sizes are achieved by engineering interparticle interactions and particle-substrate interactions simultaneously in real-time. Our study proposes a simple and versatile strategy to manufacture chiral and responsive nanomaterials based on the rich library of nanoparticles with unique optical, mechanical, and electronical properties.

8:30 AM *SF05.01.03
Colloidal Nanoparticle Assemblies—Templating Electropolymerizations, Brushes and Viruses Rigoberto C. Advincula; The University of Tennessee/Oak Ridge National Laboratory, United States

Understanding self-assembly in nanomaterials requires hierarchical levels of ordering and structuring: from molecular to macroscopic. Perfect colloidal spheres are able to pack and pattern as thin films, enabling surface assemblies amenable for templating properties that lead to function: from lithographic to non-lithographic methods. Thse layered ordered systems can result in new material stimuli-responsive properties. This talk will highlight the colloidal nanosphere lithography and non-lithographic approaches used by our group to produce systems that include: 1) conjugated polymers, 2) electropolymerized molecularly imprinted sensors, 3) electronanopatterning, 4) polymer brush lithography, and 5) patterned virus assemblies. Novel surface-sensitive spectroscopic and microscopic analytical tools are applied rationally to highlight evidence of order and function. This enables platforms for developing practical devices on electrode surfaces, e.g. sensors and battery electrodes.

9:00 AM SF05.01.04
Engineering the Assembly Pathway of DNA Origami Crystals Daniel C. Redeker[1], Jason S. Kahn[2], Brian Minevich[1], Aaron Michelson[2] and Oleg Gang[1,2]; [1]Columbia University, United States; [2]Brookhaven National Laboratory, United States

DNA-guided nanoparticle self-assembly has emerged as a promising method to form designable and ordered 3D nanomaterials. However, the isotropic nature of interactions of spherical nanoparticle makes it difficult to form designed structures. In contrast, DNA origami polyhedron frames loaded with nanoparticles can be assembled to form diverse crystal symmetries through the use of directional bonds. Specifically, the directionality of interactions is provided through origami shape and placement of addressable bonds, while the specific DNA sequences prescribe interaction addressability. Recently, an inverse design approach has been developed by our group to form a variety of arbitrary crystal structures from octahedral origami by using different addressable bonds to promote a desired crystal symmetry. However, the assembly pathway plays an important role in structure formation. We investigated how the self-assembly pathway can be controlled through modulating the relative binding energies of DNA mediated interactions. In this work, the assembly of DNA origami octahedral frames with two unique interaction types with varied relative binding energies was studied. Through a combination of small angle x-ray scattering (SAXS) and scanning electron microscopy, we demonstrate that while the local crystal structure is preserved, the long-range crystal order and morphology of the assembled crystal is strongly affected by the relative binding energies and coordination of addressable DNA interactions. We further apply these findings to tune the assembly pathway and promote the formation of a desired crystal structure and morphology.

9:15 AM SF05.01.05
Virus-Based Biomimetic Collagen Supramolecular Structure and Function Inseok Chae[1,2], Woo-Jae Chung[1,3] and Seung-Wuk Lee[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States; [3]Sungkyunkwan University, Korea (the Republic of)

Collagen is a major component of the extracellular matrix and serves as a scaffold for the growth of minerals and cells in our body. As secreted from osteoblast cells, collagen triple helices spontaneously form a supramolecular structure, mostly fibrils and interact with other constituents in connective tissues from nano- to macroscopic length scales. Various materials were reported to mimic the hierarchical structure and function of collagen; however, creating a higher-order supramolecular collagen-like structure is still challenging. Here we develop a bio-mimetic approach to create the hierarchical collagen-like structure and biological function using M13 bacteriophage (phage). Through phage display – a high-throughput screening process, we identified a new phage engineered with a collagen-like peptide that can strongly bind to bone hydroxyapatite crystals, termed as a collagen-like phage. We then exploit the collagen-like phage to develop bone-tissue like hierarchical structures and tissue functions. Using a self-templating assembly process, we show the collagen-like phage can self-assemble supramolecular structures with a smectic periodic band and quasi-hexagonal packed crystalline ordered structure. The resulting self-assembled structures can direct biomineralization and guide directional growth of cells. Our new approach to develop biomimetic materials will be broadly used for other materials to create a hierarchically organized structure and desired function.

9:30 AM *SF05.01.06
Desirable Nanomaterials through Programmable Assembly and Prescribed Transformations Oleg Gang; Columbia University/Brookhaven National Laboratory, United States

The ability to organize diverse types of functional nanocomponents into the targeted 3D architectures can enable a broad range of nanotechnological applications, from new classes of engineered biomaterials to photonic devices. However, the current top-down methods are limited in their ability to create 3D nanostructures with prescribed architectures and an integration of different types of nanocomponents, while the typical bottom-up methods do not provide a flexibility of a system design. The talk will present our progress in establishing a self-assembly platform for the fabrication of designed large-scale and finite-size nano-architectures from diverse inorganic and biomolecular nanocomponents through the DNA-programmable assembly. The recent advances in creating periodic and hierarchical organizations from inorganic nanoparticles and proteins will be presented. The formed nanostructures can be farther transformed into fully inorganic 3D replica of different materials via nano-templating. The developed assembly approaches were applied to demonstrate a fabrication of functional nanomaterials with nano-optical, electrical, mechanical, and biochemical functions. Finally, the progress for creating reconfigurable nanomaterials with well-defined switchable states will be presented.

10:00 AM BREAK

10:30 AM SF05.01.07
Graph Theoretical Engineering of Self-Assembled Biomimetic Nanocomposites Nicholas A. Kotov; University of Michigan, United States

Biomimetic nanocomposites address the critical bottlenecks of modern technologies from energy storage to wearable devices because they combine multiple application-critical properties that were not available in materials before, exemplified by hard to reach combinations of mechanical toughness, electrical conductivity, optical transparency, and biological compatibility, while being structurally versatile and resource conscious. Their design is however slow and empirical. Since Leonardo Da Vinci engineering of biomimetic materials was based on replication of the geometry of molecules, tissues, and organisms found in biology using non-biological preparatory techniques. It is possible to transition from inexact approach of good-luck-based engineering of nanocomposites to purpose-driven biomimetic materials design using graph theoretical (GT) methodology. Furthermore, GT-based engineering enables one to transition from simple nanocomposites to those with complex multiscale architecture. The organization of biomimetic materials and structures was developed to assess complexity of self-assembled nanostructured particles. It was concomitantly extended to the composites from aramid nanofibers (ANFs) and nanoparticle-based gels. It was shown that mechanical, ion- and charge transport characteristics of these materials are directly related to GT-based structural parameters. Increase of complexity can be paralleled with the increase of combinations of different properties that require multiscale hierarchical organization, which will be established analyzing load-bearing and functional nanocomposites of iconic biomimetic nanocomposites, such as nacre and cartilage. Applications of biomimetic composites for energy, biomedical, and optoelectronic applications batteries will be discussed with particular emphasis for their implementation in energy technologies.

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10:45 AM SF05.01.08
Controlling Phases of Isotropic DNA-Grafted Nanoparticle Assembly through Tuning Pair Interactions Daniel McKeen[1], Brian Minevich[1], Runfang Mao[2], Qizan Chen[3], Jeetain Mittal[3] and Oleg Gang[1,4]; [1]Columbia University, United States; [2]Lehigh University, United States; [3]Texas A&M University, United States; [4]Brookhaven National Laboratory, United States

It has been predicted theoretically that isotropic pair potentials with complex shapes can yield targeted lattice organizations, but due to limited experimental implementation methods to engineer pair potentials, realization of such predictions remains challenging. Nanoparticle-grafted DNA shells can direct self-assembly in a tailorable manner by leveraging complementary base pairing and repulsive polymeric effects, presenting a material well-suited to encoding designed pair potentials. We utilize two DNA-grafted nanoparticle types that are independently functionalized with a unique linker to tune the potential through DNA motif design; these linkers have a non-complementary spacer and a hybridization sequence for pairing with complementary motifs on the other particle. Complementary motifs drive attraction causing DNA shells to hybridize at an encoded distance prescribed by shell length and location of the complementary motif. Non-complementary motifs define particle repulsion, the range of which is prescribed by shell length alone. Computational simulations show that isotropic pair potentials are effectively approximated by the ratio of repulsion and attraction ranges. By fixing either linker length or hybridization regime location and altering the other, we experimentally explored a range of ratios. We observed, using small-angle x-ray scattering, structural evolution from body-centered cubic to simple cubic crystals to weakly ordered cubic diamond-like networks as a function of increasing ratio of repulsion to attraction ranges.

11:00 AM SF05.01.09
Biomimetic Control of Sequence-Defined Peptoids Over Ag Nanocrystal Formation and Anisotropic Self-Assembly Biao Jin[1], Emtias Chowdhury[1], Feng Yan[1], Xin Qi[2], Lili Liu[1], Jim Pfaendtner[2], James J. De Yoreo[1] and Chun-Long Chen[1]; [1]Pacific Northwest National Laboratory, United States; [2]University of Washington, United States

Controlling the stability and assembly of plasmonic nanoparticles through biomimetic strategies has significant potential for both advancing the fundamental science of biomimetic synthesis and developing functional applications. However, achieving such control remains a great challenge due to a lack of readily programable ligands and limited mechanistic understanding. Here we demonstrate that sequence-defined peptoids, which serve as capping and structure-directing agents, can drive cooperative formation and self-assembly of ~ 2-3 nm Ag nanocrystals (NCs) into nanoribbons in a template-free manner through a two-step process comprised of i) formation of Ag NCs with a ~1.8 nm thick surface-adsorbed peptoid layer, followed by ii) peptoid-driven anisotropic assembly of the Ag NCs. By examining the effects of peptoid side chain chemistry and varying reaction conditions, and comparing the results to computational simulations, we conclude that: 1) the stability of Ag NCs is attributable to the stronger interactions with peptoids than peptoid-peptoid interactions, and 2) self-assembly is initiated by the reorganization of the hydrophobic tails of peptoid ligands to achieve the typical pi-pi stacking seen in 2D sheets formed from similar peptoids in the absence of Ag NCs. The self-assembly behavior of peptoid-stabilized NCs can be rationalized based on the simulation results, which predict that attractive hydrophobic inter-peptoid interactions drive the approach of neighboring Ag NCs and the subsequent reorganization of the peptoids ligands. This work provides insight into how peptoids can be programmed to control both inorganic nanomaterials formation and self-assembly into hierarchical nanostructures, offering a new strategy for the design and synthesis of functional materials.

11:15 AM SF05.01.10
Enantioselective Polymerization on Chiral Nanoparticles Ji-Young Kim[1], Wonji Lee[2], Zhi-bei Qu[3], Chung Man Lim[1], Sangho Cha[2] and Nicholas A. Kotov[1]; [1]University of Michigan, United States; [2]Kyonggi University, Korea (the Republic of); [3]Fudan University, China

Chiral materials constructed using chiral helical polymers (CHPs) are especially interesting, which can be described as biomimetics of natural helical biomacromolecules. CHP materials can be directly constructed from chiral monomers. This approach, however, shows some disadvantages because of the limited variety and number of easily available chiral monomers. To overcome the limitations, many powerful methodologies have been established to prepare CHPs starting from achiral monomers; However, it either requires toxic transition-metal catalysts or suffers from lower regioselectivity. Here, we report helical polymerization of achiral monomers using chiral ceramic nanoparticle (NP) as asymmetric catalyst. The tungsten oxide NP with the chirality of the metal oxide core, with an average size of ca. 1.6 nm, is imparted by aspartic acid ligands via bio-to-nano chirality transfer. The prepared chiral tungsten oxide NPs initiate the stereoregular polymerization of various monomers while their chiral surface provides the chiral bias, resulting the helical conformation of polymers. Depending on handedness of NP used, the resulted NP-polymer composites showed the mirrored spectra for their optical and vibrational circular dichroism. The density functional theory (DFT) calculation also supports that the rotational direction of resulted helical polymer were determined by the handedness of NPs used as the absorption energy of the chiral dimer showed specific enantiopreference on the NP surface. Since the NP played role as not only initiator but also cross-linker of the polymer matrix, the resulted composite structure has more uniformity of NP distribution, enhancing mechanical properties compared to one of simple mixing composite. More importantly, the NP-initiated composites show facinating enantioselective mechanical properties; The stiffness and hardness of composite with complex chirality driven by mixture of L- and D- NPs are up to one order of magnitude higher than the one of composite with homo chirality prepared by pure L- or D- NPs. The reported NP-initiated chiral NP-polymer composites can be used for various applications that needs soft composite with unique chiroptical and strong mechanical properties.

11:30 AM SF05.01.11
Controlling Macroscale Morphology in DNA-Based Assembly Using Acoustic Energy Zohar A. Arnon[1], Silvia Piperno[2], Ornit Nagler Avramovitz[2], Ewelina Randall[1], Hagay Shpaisman[2] and Oleg Gang[1]; [1]Columbia University, United States; [2]Bar-Ilan University, Israel

One of the main challenges of developing bottom-up designed materials is the issue of scaling their formation and shaping them into a desired morphology. A high degree of nanoscale control hinders the ability to form nanomaterials with predefined macroscale morphology. DNA nanotechnology allows accurate spatial control at the nanoscale which enables fabrication of intricate organizations; yet, structural arrangement at the macroscales remains a challenge. We developed an assembly approach driven by acoustic waves in order to control the morphology of DNA-assembled materials at the scales from tens of microns to millimeters, thus complementing a nanoscale assembly regime offered by DNA-guided methods. Specifically, we explored the use of standing surface acoustic waves (SSAW) to direct assembly and control morphology of DNA origami based crystal lattices. By controlling both acoustic forces and temperature, we investigated the assembly process at different scales by a combination of optical microscopy, small-angle x-ray scattering and electron microscopy techniques. We further studied the annealing, crystal fusion and disassembly under different SSAW conditions. The developed approach allows to form macroscale nanomaterials with prescribed morphology, as defined by the acoustic field, while their nanoscale organization is programmed by DNA. The presented approach is further enhanced by microfluidics through a combination of a flow and SSAW for achieving morphology control. Once the morphology is realized, cross-linking of the formed structure is induced, resulting in fixation of the formed macroscale morphology with DNA-prescribed nanoscale structure.

11:45 AM SF05.01.12
Encoding Lattice Symmetry of Nanoparticle Self-Assembly through Programmable Valences Honghu Zhang[1,1], Sha Sun[1,2], Shih-Ting Wang[1], Dmytro Nykypanchuk[1], Yugang Zhang[1], Alexei Tkachenko[1] and Oleg Gang[1,3,3]; [1]Brookhaven National Laboratory, United States; [2]Xi'an Jiaotong University, China; [3]Columbia University, United States

In atomic and molecular systems, directional interactions, as defined by a valence, guide formation of complexly organized lattice structures. Translating the idea of valence-driven interactions to nanoparticle systems would open great opportunity of controlling material fabrications through self-assembly. However, understanding the relationships between directional interactions and the resultant phases and packing structures remains a nontrivial fundamental problem. Here, we present a study of binary self-assembly system built from nano-objects with directional interactions, valence-programmable DNA mesh balls, and with isotropic interactions, inorganic nanoparticles. Our study reveals that controllable phase behaviors can be achieved by tailoring interactions through valence modes and size ratios between DNA mesh balls and nanoparticles. By prescribing 8 different valence modes for mesh balls, we have observed assembly of 2D and 3D crystalline phases with distinct crystallographic symmetries, as uncovered by *in situ* small-angle X-ray scattering. We have established a theoretical framework based on thermodynamics and geometric constrains that explains the discovered self-assembly behavior for the presented binary system with directional and isotropic interactions. Our combined experimental and theoretical work provides a roadmap for rational design of complex self-assembled structures through bonds engineering.

SESSION SF05.02: Aggregation-Induced Emission (AIE) and Molecule Self-Assembly I
Session Chairs: Sijie Chen and Ben Zhong Tang
Monday Afternoon, April 10, 2023
Moscone West, Level 3, Room 3012

1:30 PM *SF05.02.01
Accelerating Biomedical Research through Materials Innovation Bin Liu[1,1,2]; [1]National University of Singapore, Singapore; [2]International Campus of Tianjin University, China

The recent years have witnessed the fast grow of fluorogens with aggregation-induced emission characteristics (AIEgens) in biomedical research. The weak emission of AIEgens as molecular species and their bright luminescence as nanoscopic aggregates distinguish them from conventional organic luminophores and inorganic nanoparticles, making them wonderful candidates for many high-tech applications. In this talk, we summarize our recent AIE work in the development of new fluorescent bioprobes for biosensing and imaging. The simple design and fluorescence turn-on feature of the molecular AIE bioprobes offer direct visualization of specific analytes and biological processes in aqueous media with higher sensitivity and better accuracy than traditional fluorescence turn-off probes. The AIE dot probes with different formulations and surface functionalities show advanced features over quantum dots and small molecule dyes in noninvasive cancer cell detection, long term cell tracing, and vascular imaging. In addition, our recent discovery that AIEgens with high brightness and efficient reactive oxygen species generation in aggregate state further expanded their applications to image-guided cancer surgery and therapy. Recently, we combined accurate prediction of material performance via first-principle calculations and Bayesian optimization-based active learning to realize a self-improving discovery system for high-performance photosensitizers, which can significantly accelerate the materials innovation for biomedical research.

2:00 PM SF05.02.02
Clickable Hydrogels of Cholesteryl Hyaluronic Acid with Tunable Amphiphilicity and Physical Crosslinking for Drug Delivery and Tissue Engineering Shing-Yun Chang and Jie Song; University of Massachusetts Chan Medical School, United States

Synthesis of amphiphilic biopolymers has recently attracted attentions due to their potential for delivering a broad range of biotherapeutics including cells and hydrophobic drugs, as well as dynamic biophysical properties enabled by the conformational changes driven by hydrophobic-hydrophobic interactions. Hyaluronic acid (HA), as one of the major extracellular matrix components in native tissues, plays size-dependent, multifaceted roles in defining a wide range of biological activities. Although HA has long been exploited for regenerative medicine applications due to its excellent cyto- and bio-compatibility, its capacity as a versatile drug delivery carrier remains fully explored.

In this study, HA was chemically modified with cholesterol, a critical hydrophobic cell membrane component known for excellent cell permeability, via copper-free, strain-promoted azide-alkyne cycloaddition (SPAAC) "Click" chemistry. Specifically, azide and dibenzocyclooctyne (DBCO) were first conjugated to HA and cholesterol, respectively, as biorthogonal functional groups. The degree of azidation was restricted to <10% by design to retain core properties of HA. A range of cholesteryl HA was prepared by stoichiometric SPAAC, which exhibited cholesterol content-dependent morphologies. We found that, the cholesteryl HA with higher cholesterol contents spontaneously formed nanoparticles (NP) in aqueous media, with their negative surface charges supporting a cholesteryl core-HA shell configuration. Hydrophoblic drug loading capacity of the NP was visualized by fluorescent hydrophobic dyes. The cholesteryl HA with low cholesterol contents remained as extended polymers where their associated cholesterol units helped form hydrophobic domains within the 3D amphiphilic HA network. Acting as physical crosslinkers, the very low amount of robust cholesterol-cholesterol interactions was enough to significantly enhance the viscosity of HA. For skeletal tissue regeneration applications, the potential of the resulting amphiphilic polymers for sustained drug/biologics release and potential as cellular niches are being examined.

2:15 PM SF05.02.03

Structural Characterization of 5-fluorouracil in the Self-Assembly of the Pluronic Biomedical Hydrogels for Prolonged Drug Release Tz-Feng Lin, Xin-Yu Zeng, Pei-Jung Shih and Wei-Chieh Wang; Feng Chia University, Taiwan

Chemotherapy is the medical treatment for human cancer through intravenous injection or oral administration. However, high dosage of chemotherapeutic drugs was required to de delivered to the malignant tumor. In recent years, the use of polymer composites for local and sustained drug release has become leading research to carry chemotherapeutic drugs without concentrated dosage. Pluronic biomedical hydrogels (PBHs) was proposed to be deployed on the tumor site for precision medicine as a targeted delivery for clinical and practical applications. PBHs also served as a microenvironment and a drug delivery system offering many attractive benefits such as intrinsic biocompatibility, ease of preparation, scalable production. Binary blending of biocompatible Pluronic® F127 and Pluronic® L121 is the main ingredient in the PBHs. Based on the same formulation, the addition sequence of fluorouracil (5-FU) was deployed in three ways when it was individually incorporated with F127-(5-FU), L121-(5-FU), as well as the binary mixing F127-L121-(5-FU).

Small angle X-ray scattering (SAXS) and 19F-{1H} heteronuclear Overhauser enhancement spectroscopy (HOESY) was used to discover the self-assembled structures of the PBHs. According to the SAXS results, structural changes of the micelle and the lamellar affected the distribution of 5-FU. F127-L121-(5-FU) has the fastest drug release rate owing to the undulated amphiphilic boundary. In contrast, L121-(5-FU) has a prolonged drug release rate at 67% for one month of the continuous drug release experiment because the flat lamellar amphiphilic boundary which slows the migration of 5-FU from the hydrophobic core.

Further, HOESY was used to study the micellular environment of the F-containing chemotherapeutic drug 5-FU in PBHs. Results show that the diffusion of the 5-FU medicine in the Pluronic micelles will move across the interface between the hydrophilic corona and the hydrophobic core with respect to elevated temperatures. At 25 °C, the drug loading location of the 5-FU medicine is dominated by PEO segments. As the temperature increases from 25 to 45 °C, the 5-FU medicine migrates aggressively to the hydrophobic core inside the micelles. The 5-FU medicine was embedded into the PPO segment of Pluronic® polymers above 37 °C as a stable micellization. The precise 5-FU loading in the hydrophobic area gives rise to prolonged and sustained drug release in rountine clinical practice. Thus, the drug loading location and drug–carrier interactions can be designed to deliver drugs at predetermined release rates. The chemotherapeutic drugs of 5-fluorouracil (5-FU) were released from PBHs nearly one month without continuous supplementary.

Also, the inhibition of multidrug resistance was developed in this study. The effective ingredient of L121 inhibited multidrug resistance in human pancreatic cancer and caused the malfunction of the ATP binding cassette subfamily C (ABCC) transporter as evidenced by the flow cytometer studies. PBHs effectively suppresses the function of ABCC transporter up to 25 days. 5-FU can accumulate in the cancer cells of AsPC-1 and PANC-1 at a designated effective concentration. This synergy effect of the continuous drug release of 5-FU and intrinsic cytotoxic effects of L121 could inhibited the function of a multi-drug resistance regarding ABCC transporter. Then, a surgical dressing was prepared by 3D bio-printing technology with PBHs cross-linked by sodium alginate. Results show that the surgical dressing of 24 layers with 10 mm x 10 mm would continuously release 5-FU in effective anticancer concentration for six days. The flexibility of the PBHs makes tailored drug delivery system possible and improve the life quality of patients. Sustained and prolonged drug release and 3D printable surgical dressing was completed.

2:30 PM *SF05.02.04

Assembling Bright Fluorescent Polymeric Nanoparticles for Biosensing and Bioimaging Andrey Klymchenko; University of Strasbourg, France

Dye-loaded fluorescent polymeric nanoparticles (NPs) appear as an attractive alternative to inorganic NPs, such as quantum dots (QDots).[1] Primary requirement for fluorescent NPs in biological applications are their controlled small size and brightness. To obtain small NPs, we introduced a concept of charge-controlled nanoprecipitation of hydrophobic polymers in aqueous media.[2] We found that charged groups in hydrophobic polymers, such as poly(methyl methacrylate), favor formation of NPs with controlled small size down to 7 nm.[3] On the other hand, to ensure high brightness of polymeric NPs, aggregation-caused quenching (ACQ) of dyes should be prevented. To this end, we proposed ionic dye insulation by bulky hydrophobic counterions,[4] which serve as spacers between dyes to block ACQ and favor dye encapsulation inside NPs.[5] As a result, we obtained NPs that are ~100-fold brighter than QDots of similar size.[6] Assembling dyes inside polymeric NPs resulted in giant light-harvesting nanoantenna, where ~10000 encapsulated dyes undergo efficient Förster resonance energy transfer (FRET) to a single acceptor, providing >1000-fold signal amplification (antenna effect).[7] The light-harvesting concept was applied to amplify phosphorescence of porphyrins for ratiometric sensing of oxygen with minimal phototoxicity.[8] Functionalization of these nanoatennas with nucleic acids yielded ultrabright FRET-based nanoprobes for amplified detection of oligonucleotides with single-molecule sensitivity,[9] and compatibility with detection by RGB camera of a smartphone.[10] When applied to cells, the small size of NPs was found essential for their free diffusion in cytosol[3] and for their intracellular delivery by electroporation.[11] Moreover, ultrasmall DNA-NPs enabled RNA detection inside cells by fluorescence in situ hybridization. At the animal level, the high brightness of NPs enabled unprecedented single-particle tracking in the mice brain and visualization of crossing the blood-brain barrier.[12] The developed small dye-loaded polymeric NPs open the route to ultrabright tools for sensing and tracking of biomolecules in biology and medicine.

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3:00 PM BREAK

3:30 PM *SF05.02.05
Logical Design for Functional NIR Materials Based on AIE-Active Element-Blocks Kazuo Tanaka; Kyoto University, Japan

Near infrared (NIR)-emissive films have attracted tremendous attention as a versatile platform for realizing future optical technology, such as sensors and organic NIR-luminescent electronic devices. However, due to aggregation-caused quenching (ACQ) caused by non-specific intermolecular interactions in condensed state, it is still difficult to obtain intense solid-state emission from film materials. In particular, since conventional NIR-luminescent dyes have expanded π-conjugated system which are essential for inducing NIR emission, critical intermolecular interactions followed by ACQ are induced in NIR-luminescent dyes. Therefore, it is still challenging to develop organic materials with solid-state luminescent properties in the NIR region. We recently established to narrow energy gaps between frontier molecular orbitals (FMOs) without expanding π-conjugated system. By replacing the skeletal carbon, where only the lowest unoccupied molecular orbital (LUMO) is localized, to nitrogen (aza-substitution), it is possible to selectively lower the energy level of LUMO. Finally, we obtained deep-red and/or NIR-luminescent dyes through the aza-substitution without expanding π-conjugated system. Based on this protocol, we obtained deep red-luminescent AIEgens. In this presentation, the basic concept for obtaining NIR emission with the aza-substitution at the isolated LUMO is initially illustrated. Several examples on the deep-red or NIR-emissive AIEgens are demonstrated based on the aza-substitution at the isolated LUMO position. Finally, we will mention NIR-luminescent materials with solid-state luminescent properties.

4:00 PM SF05.02.06
Self-Assembled Monolayers Functionalized Surfaces for VOC's Detection Mandeep Singh[1,2], Navpreet Kaur[2] and Elisabetta Comini[2]; [1]Politecnico di Milano, Italy; [2]University of Brescia, Italy

Self-assembled monolayer (SAM) functionalized surfaces represent an excellent tool for the performance enhancement and selective detection of different chemical analytes such as biomolecules and gases etc. as they offer unique surface-specific interactions.The ability of SAM to generate different functional groups on a single surface can also be used to immobilize variety of biomolecules. The typical structure of SAM contains head and end groups connected via a backbone (aromatic oligomer or aliphatic chain). The head group is attached to the surface via strong bonds (e.g silanes attachment to oxides surface takes place via formation of siloxane bonds). While, the end groups play an extremely important role as they define the surface functionality and can be used for further functionalization and to detect different analytes via molecular interactions with analytes.
Herein, we are presenting novel SAMs functionalized p-type (NiO) and n-type (ZnO) metal oxides nanowires (NWs) for VOC's detection. In particular, the VLS-grown ZnO and NiO NWs were functionalized with mono and mixed self-assembly of organosilanes ((3-aminopropyl) trimethoxysilane (APTES), 3-glycidoxypropyltrimethoxysilane (GOPS), and tetraethyl orthosilicate (TEOS))) to generate different functional groups. Specifically, via functionalization with mono APTES, GOPS and TEOS monolayers, —NH_2, —epoxy and —CH_3 terminated NWs surfaces were generated. On the other hand, in the case of mixed-SAMs (APTES and TEOS), mixed —NH_2 and —CH_3 terminated ZnO NWs surface was generated. The NWs morphology was assessed using scanning electron microscopy, while the surface chemical properties of SAMs functionalized surfaces were examined via X-Ray photoelectron spectroscopy (XPS). Finally, the set of conductometric sensing devices of these functionalized surfaces were prepared and tested for different gas analytes to explore their sensitivity and selectivity.
Both mono (APTES and TEOS) and mixed-SAMs functionalized ZnO NWs showed highly selective behavior toward acetone due to two phenomena. The first one is the modulation of surface electron density caused by SAMs (affecting the electron depletion layer (EDL) of ZnO NWs). Secondly, the molecular interaction between acetone carbonyl groups (C=O) and terminal groups of both SAMs causes their selective behavior. We also observed that mixed-SAMs are a superior strategy for sensing performance enhancement not only from bare ZnO NWs but also from mono SAM provided suitable mixing ratios were selected.
In the case of p-type NiO NWs, we have used these unique properties of SAM to enhance their sensing performance which remains a huge challenge due to their poor electrical properties. In particular, NiO NWs were functionalized with GOPS to modulate the majority carrier concentration near the surface or in hole accumulation layer (HAL). We have observed that the negatively charged terminal-epoxy groups of GOPS enhance the accumulation of holes near the surface that in-turn increase the electron transfer from reducing gases to NWs. As a result, SAM-functionalized sensors showed 9-times higher response as compared to bare NiO NWs at 200 °C. Interestingly, bare NiO NWs able to achieve comparable response values at 500 °C. Hence, the SAM approach not only improves the performance of NiO NWs sensor but also helps to significantly lower the sensor working temperature.
In conclusion, we showed that the SAM functionalization strategy has the greatest potential to develop future high-performance chemical sensor devices not only for acetone but also for other important analytes such as environmental pollutants.

4:15 PM SF05.02.07
Nanomechanical Behaviour of Self-Assembled Metal-Organic Framework Monoliths and Luminescent Composites Michele Tricarico and Jin-Chong Tan; University of Oxford, United Kingdom

Metal-organic frameworks (MOFs) are multifunctional organic-inorganic porous hybrid materials. They consist of metal ions or clusters coordinated to organic ligands that self-assembly into repeating lattice structures, which results in an extraordinary large internal surface area, up to 7800 m^2/g (*i.e.,* the surface area of a gram of this material is larger than the area of a football pitch). Moreover, MOFs offer unique structural diversity compared to other porous materials, for tuning the framework topology, porosity, and functionality to yield numerous potential applications such as gas capture, catalysis, photonic sensors, microelectronics, and lighting.
The majority of MOFs are synthesized as polydisperse microcrystalline powders that present intrinsic limitations, which inevitably reduce the range of practical applications. The synthesis of MOFs in a monolithic morphology is considered a promising way to achieve the transition of this class of materials from academia to industrial applications. The sol-gel process has been identified as a cheap and simple technique to produce a wide range of MOF monoliths. However, the mechanisms involved in this process are not yet clear, since the formation of gel and subsequent drying depend on several parameters. Shedding light on how nanoparticles aggregate to form a monolithic structure and how this affect the mechanical properties is therefore crucial for the transition of MOFs monoliths to industry.
The presentation will be divided in three case studies:
1) The morphology of the single nanoparticles – the building blocks of the monolithic structure – and their nanoscale aggregation for the zeolitic imidazolate frameworks (ZIFs) ZIF-8 and ZIF-71 was studied by means of atomic force microscopy (AFM), X-ray diffraction (XRD) and nanoscale

Fourier transform infrared spectroscopy (nanoFTIR). The mechanical behaviour of the monoliths was studied by means of instrumented nanoindentation. Moreover, for the first time, tip force microscopy (TFM), an extension of AFM, was used to reveal the nanostructure of the ZIF monoliths. We employed finite element (FE) simulations of the nanoindentation tests to establish a suitable constitutive model and determine an improved estimate of the yield stress (σ_Y) of ZIF monoliths. The combination of all the above-mentioned techniques allowed us to identify the deformation mechanisms taking place in this type of materials: grain boundaries sliding (GBS) is dominating at low stresses, then a partial failure of the framework occurs, leading to densification in the contact region. Local nanoFTIR spectra of residual indents confirm the breakage of chemical bonds under a mechanical stress. We also reported the fracture toughness of the monoliths to be appreciably higher than recently reported MOF glasses. This enhanced toughness could be attributed to the fine-grained nanostructures that facilitate grain boundary sliding. [1]
2) The fracture behaviour of four prototypical MOF sol-gel monoliths, namely ZIF-8, HKUST-1, MIL-68 and MOF-808 was analysed. We studied the initiation and crack propagation of cracks by nanoindentation and nanoscratch tests. We observed that shear faults inside the contact area represent the main failure mechanism of MOF monoliths and are the source of radial cracks. MIL-68 and MOF-808 showed a remarkably high resistance to cracking, which can be ascribed to a combination of both the framework structure (within the nanograins) and their consolidated nanostructure. [2]
3) Three novel composites, composed of luminescent dies (fluorescein, rhodamine B and coumarin) embedded in a MOF monolith matrix (namely, UiO-66), were successfully synthetised. We explored the effect of dies encapsulation on the mechanical and luminescent properties.
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SESSION SF05.03: Aggregation-Induced Emission (AIE) and Polymer Self-Assembly II
Session Chairs: Sijie Chen and Shuai Zhang
Tuesday Morning, April 11, 2023
Marriott Marquis, B2 Level, Golden Gate B

10:30 AM *SF05.03.02
Constructing Reactivity-Based Fluorogenic Probes for Monitoring Protein Unfolding and Aggregation in Cells Yuning Hong; La Trobe University, Australia

Understanding how cells maintain the functional proteome and respond to stress conditions is critical for deciphering molecular pathogenesis and developing treatments for conditions such as neurodegenerative diseases. Efforts towards finer quantification of cellular proteostasis machinery efficiency, phase transitions and local environment changes remain a priority but still challenging. Herein, we present our recent progress in developing fluorescence-based strategy and methodology for the study of proteostasis. To measure the level of proteostasis efficiency, our approach is to directly measure unfolded protein load in cells, as the decline of proteostasis capacity results in the accumulation of unfolded proteins. To achieve this goal, we designed and synthesized a series of cysteine reactive fluorogenic probes which can react with unfolded proteins with exposed cysteines and exhibit fluorescence turn-on effect. Strikingly, these probes selectively display strong fluorescence with unfolded proteins but only weak fluorescence with proteins bearing surface-exposed cysteine in their folded structure and no fluorescence with small molecule biothiols. We then apply our method to measure proteostasis collapse in cells treated with pharmacological stressors, expressed with mutant proteins in Huntington's disease models, or infected with virus. By combining with advanced fluorescence techniques, we also resolve the changes of subcellular polarity, viscosity and macromolecular crowding in cells under different stress treatment. Our approach will provide a robust strategy for understanding protein unfolding and stress responses, as well as facilitating biomarker discovery for clinical diagnosis and therapeutics development.

SESSION SF05.04: Particle Aggregation II
Session Chairs: Oleg Gang and Shuai Zhang
Tuesday Afternoon, April 11, 2023
Marriott Marquis, B2 Level, Golden Gate B

1:30 PM *SF05.04.01
Designing 3D Optical Metamaterials from Colloidal Nanocrystal Assemblies Cherie R. Kagan; University of Pennsylvania, United States

Colloidal noble metal nanocrystals (NCs) have metal cores and organic or inorganic ligand shells and are known for their size- and shape-dependent localized surface plasmon resonances. Here, we will describe the use of these NCs as building blocks of assemblies with designer optical properties for 3D metamaterials. Chemical exchange of the long ligands used in NC synthesis with more compact ligand chemistries reduces the interparticle distance (*d*) and increases interparticle coupling. This ligand-controlled coupling allows us to tune through a dielectric-to-metal phase transition, seen by a 10^{10} range in DC conductivity and a dielectric permittivity ranging from everywhere positive to everywhere negative across the whole range of optical frequencies. By exploiting the different chemical and physical properties of NC assemblies from bulk thin films, we construct NC/bulk bilayer heterostructures, that upon ligand exchange fold into 3D structures providing a simple route to 3D metamaterials. We exploit these folded, bilayer heterostructures to demonstrate chiral structures that form broadband circular polarizers. We expand on these ideas to include other NC compositions and their use to create stimuli-responsive 3D optical metamaterials.

2:00 PM SF05.04.02
Design, Collapse and Mixing of Nanoreactors for *In Situ* TEM Imaging of Confined Reactions in Liquids Emory Chan and Sardar Alam; Lawrence Berkeley National Laboratory, United States

Nanocapsules are hollow nanoscale shells that have applications in drug delivery, batteries, self-healing materials, and as model systems for naturally occurring shell geometries. In many applications, nanocapsules are designed to release their cargo as they buckle and collapse, but the details of this transient buckling process have not been directly observed. Here we use *in situ* liquid phase transmission electron microscopy to record the mixing of lipid nanocapsules and the electron-irradiation-induced buckling in spherical polymer capsules. We observe in real time the release of aqueous cargo from these nanocapsules and their buckling into morphologies with single or multiple indentations. The *in situ* buckling of nanoscale capsules is compared to *ex situ* measurements of collapsed and micrometer-sized capsules and to Monte Carlo (MC) simulations. The shape and dynamics of the collapsing nanocapsules are consistent with MC simulations. Our experiments suggest design rules for nanocapsules with desired buckling response based on parameters such as capsule radius, wall thickness, and collapse rate.

2:15 PM SF05.04.03
***In Situ* Imaging of Active Assemblies of Nanoparticles Driven by Electric Field** Chang Liu, Zuochen Wang, Chang Qian and Qian Chen; University of Illinois at Urbana-Champaign, United States

Application of electric field to colloidal suspension has been shown as an efficient strategy to create dynamic materials otherwise impossible. Although numerous efforts have been devoted to the understanding and optical microscopy imaging of micron-sized colloids driven by external electric field, how nanoparticles (NPs) interact with electrodes and behave under various flow effects induced by electric field remain underexplored due to the experimental challenge to image them in-situ and the theoretical challenge to consider multiscale effects due to the small size of NPs. Here we will present our recent work on using patterned microelectrodes in a liquid-phase transmission electron microscopy chamber, to apply electric field to a NP suspension and to induce active assemblies. These assemblies are extensively dynamic and exhibit ensemble crawling motions along field gradient. Simulation of velocity flow field and electric field strength further shows how different field-induced hydrodynamic effects concur to control the active assembly. Our study can bridge the fields of active matter and colloidal NPs towards making active nanorobots and dynamic non-equilibrium assemblies.

2:30 PM *SF05.04.04
Liquid-Phase TEM Imaging of NP Self-Assembly and Protein Fluctuation Qian Chen; University of Illinois at Urbana-Champaign, United States

We will present our group's recent progresses on establishing and utilizing electron microscopy to image, understand, and manipulate colloidal and biological systems, in space and time at a nanometer resolution. This involves systems that underpin the fundamentals of structure-functional relationship for a wide range of phenomena and applications. In this talk, we will discuss in detail three types of such systems, including metallic nanoparticles assembling into Moire superlattices as promising optical and mechanical metamaterials, membrane protein lipid assemblies' structure fluctuations and fingering dynamics, and electrochemical energy materials' strain propagation with nano-sizing effects. We will show how we build upon liquid-phase transmission electron microscopy and four-dimensional scanning transmission electron microscopy, and couple them with machine learning and molecular dynamics simulations. This coupling enables us to study the dynamic, squishy, multifunctional soft and biological systems in liquid and at operation, and to study the charge-lattice interactions in an ordered materials' phase transformation.

3:00 PM BREAK

3:30 PM *SF05.04.05
Interfacial Structure, Interparticle Forces and Assembly Dynamics During Crystallization by Particle Attachment James J. De Yoreo[1,2]; [1]Pacific Northwest National Laboratory, United States; [2]University of Washington, United States

Crystallization by particle attachment (CPA) to form hierarchical structures is a common phenomenon and a promising approach to synthesizing functional materials. CPA exhibits diverse styles ranging from oriented attachment (OA), by which individual nanocrystals of the same phase attach with crystallographic coalignment, to mis-oriented aggregation of nanocrystals with disparate phases followed by coarsening to single-phase, ordered structures. CPA leads to remarkable morphological outcomes, including formation of tetrapods, chains and sheets, highly branched nanowires, and self-similar 3D mesocrystals. Moreover, CPA has now been widely observed in semiconductors, metals, silicates, oxides, fluorides, carbonates, organic compounds, peptides, and proteins. While descriptions of CPA must share a commonality with continuum-based DLVO-type theories for simple isotropic colloids, nanocrystals present additional complexities, including face-specificity of dielectric properties, inherent diopolar interactions, structured nanoscale interfaces, solvent-responses at a length scale comparable to particle size, and the impact of organic ligands often used to stabilize nanoparticles on the interparticle potentials. Macromolecular systems add another level of complexity due to their electrostatic patchiness and specific interactions via side chain chemistry. To understand the relationship between interfacial structure, interparticle forces and assembly dynamics, as well as the role of organic ligands and the properties of macromolecules, we are investigating CPA in a range of systems, including noble metals, metal oxides, peptides, and proteins, using a combination of in situ TEM, in situ AFM, and molecular modeling. In this talk I will focus on, 1) the effects of organic ligands in both driving CPA and creating unique crystal morphologies, and 2) the distinct behavior exhibited by proteins, due to their uniform, but anisotropic, dimensions and charge distributions. The results shed light on the mechanisms by which CPA progresses, the interaction potentials that drive the process, and the role of interfacial structure in defining those potentials.

4:00 PM SF05.04.06
Building 3D Circular Nanotubes Using *In Situ* Monitored Self-Assembly Process Zihao Lin, Chunhui Dai and Jeong-Hyun Cho; University of Minnesota, Twin Cities, United States

Tubes with a circular cross-section can be noticed everywhere in daily life, from large ventilation pipes to a human's small capillaries. Circular cross-sections also play an important role in fluidic channels, as it can eliminate the corner flow effect, undermine nonuniform pressure build up, and minimize shear stress in the channel. Moreover, it can largely simplify the fluidic theory model built for corners and improve its accuracy. However, in nanofluidics, fabrication of circular nanotubes (10-1000 nm) remains challenging, especially the curved one remains unsolved. In this work, both straight and curved circular nanotubes are fabricated via electron beam induced in-situ monitored self-assembly. This in-situ monitored ability provides real time images with a nanoscale resolution, leading to extreme fabrication precision for the realization of three-dimensional (3D) nanostructures (circular nanotubes). Two-dimensional (2D) nanopatterns defined on a planar substrate are firstly defined by electron beam lithography, followed by a deposition process and Si etching underneath. An electron beam is used to transform each 2D pattern into segmented 3D cylinder structures. Gaps on the top and between each cylinder are sealed by atomic layer deposition and the diameter of the tube can be precisely controlled from hundreds of nm down to ~10 nm with the resolution of 0.1 nm. To verify its capability for fluidic transportation, through the nanotubes with radius of ~100 nm, liquid flow/evaporation was in-situ monitored using a darkfield microscope via optical scattering effect. From the observations of fluidic flow in the curved circular nanocylinders, the dynamic behavior of the fluid was characterized, and novel counter-intuitive physical effect was discovered: nano pumping through evaporation in a nanocylinder.

4:15 PM SF05.04.07
Connecting Energetics to Dynamics in Particle Aggregation Revealed by Real-Time Observations Lili Liu, Elias Nakouzi, Maria Sushko, Gregory K. Schenter, Christopher Mundy, William Smith, Ben Legg, Xin Zhang, Carolyn Pearce, Jaehun Chun and James J. De Yoreo; Pacific Northwest National Laboratory, United States

Although the physical insights into oriented aggregation of mineral nanoparticles have been recently gained a lot from real-time observations, the impact of many fundamental solution parameters such as particle shape, solution structural and pH, on governing aggregation behavior and dynamic is largely unexplored. Using zinc oxide (ZnO) nanoparticle and boehmite(γ-AlOOH) nanoplatelets as two different anisotropic systems, we combine in situ liquid phase TEM (LPTEM) observations of single particle and ensemble assembly dynamics with simulations of interparticle forces and responses to relate experimentally derived interparticle potentials to the underlying interactions. We also establish the relationships between solution chemistry, forces and response dynamics to address the challenging of the crystal structure in directing the oriented aggregation behavior. Our findings on nanocrystal aggregation and interactions provide insights toward the predictive understanding of nanoparticle growth, assembly, and aggregation, which are of great importance in the strategic development of nanomaterials and nature environments.

4:30 PM SF05.04.08
Formation Mechanism of Flower-like Polyacrylonitrile Particles Huaxin Gong[1], Jan Ilavsky[2], Ivan Kuzmenko[2], Shucheng Chen[1], Hongping Yan[1], Christopher B. Cooper[1], Gan Chen[1], Yuelang Chen[1], Jerika A. Chiong[1], Yuanwen Jiang[1], Jiancheng Lai[1], Yu Zheng[1], Kevin Stone[3], Luke Huelsenbeck[4], Gaurav Giri[4], Jeffrey Tok[1] and Zhenan Bao[1]; [1]Stanford University, United States; [2]Argonne National Laboratory, United States; [3]SLAC National Accelerator Laboratory, United States; [4]University of Virginia, United States

Flower-like polyacrylonitrile (PAN) particles have shown promising performance for numerous applications, including sensors, catalysis, and energy storage. However, the detailed formation process of these unique structures during polymerization has not been investigated. Here, we elucidate the formation process of flower-like PAN particles through a series of in situ and ex situ experiments such as in situ USAXS. We have the following key findings. First, lamellar petals within the flower-like particles were predominantly orthorhombic PAN crystals. Second, branching of the lamellae during the particle formation arose from PAN's fast nucleation and growth on pre-existing PAN crystals, which was driven by the poor solubility of PAN in the reaction solvent. Third, the particles were formed to maintain a constant center-to-center distance during the reaction. The separation distance was attributed to strong electrostatic repulsion, which resulted in the final particles' spherical shape and uniform size. Lastly, we employed the understanding of the formation mechanism to tune the PAN particles' morphology using several experimental parameters including incorporating comonomers, changing temperature, adding nucleation seeds, and adjusting the monomer concentration. These findings provide important insights into the bottom-up design of advanced nanostructured PAN-based materials and controlled polymer nanostructure self-assemblies.

4:45 PM SF05.04.09
Supramolecular Polymerization of Photopolymer Enables Tough 3D Soft Objects Hae Seung Lee[1], Jiyun Kim[1], Hyunchang Park[2] and Jiheong Kang[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Stanford University, United States

Light-based 3D printing remains to be the only technique able to build free-form 3D architectures in high resolution. By crosslinking photocurable monomers or macromonomers using UV light, layers of rigid polymer networks are formed to construct a 3D structure. Ever since its development, light-based 3D printing has continued improving printing speed and resolution through optimization of printing systems such as use of dead layers[1], flowing liquid interface[2] and two-photon polymerization[3]. Despite the advance in printability, the lack of photopolymers to print stretchable and durable elastomers has restricted further application of 3D printing to stretchable devices such as bio-implantable devices, E-skin, and soft robots.
Here I present the supramolecular approach to toughen 3D printed elastomers. Our designed photopolymer includes supramolecularly polymerizable 'sticker' in their backbone, which spontaneously polymerize to form a preliminary network even before printing. Due to this supramolecular network, the printed elastomer network shows superior stretchability, compressive strength, toughness, fracture toughness, and fatigue threshold in one system. The key of this result reveals to be suppressing network defect formation. Even though defects are well known to weaken the mechanical properties of polymer networks, conventional photopolymers were not able to avoid defects due to the rapid process of 3D printing. In my presentation, I will discuss details of the design strategy and its toughening mechanism.

References
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SESSION SF05.05: Particle Aggregation III
Session Chairs: Shuai Zhang and Xin Zhang
Wednesday Morning, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate B

8:00 AM SF05.05.02
Tuning Polymerization-Induced Self-Assembly in Polymer Thermosets to Optimize Their Physical Properties Brad H. Jones[1], Samuel C. Leguizamon[1], Sangwoo Lee[2] and Jessica Kopatz[1]; [1]Sandia National Labs, United States; [2]Rensselaer Polytechnic Institute, United States

Polymer thermosets are frequently modified via polymerization-induced self-assembly (PISA), wherein the addition of secondary or higher order components that phase separate during the polymerization is intended to improve a specific property. Generally speaking, it is challenging to control the characteristic self-assembled length scale in such materials beyond a limited range. This presentation will describe an approach to PISA in step-growth polymer networks that enables the length scale to be tuned over a broad range, from nanoscale to macroscale. The key element of this approach is a balance of multiple reactive species that simultaneously favor and disfavor phase separation. We demonstrate how ensuing, systematic variation of the length scale leads to exquisite control over the curing behavior and glass transition of the resultant materials. We further discuss application of this approach in the optimization of physical properties, including for rubber-modified epoxies where toughness is critically impacted by rubber particle size, as well as for the development of materials with improved damping performance. Our results and insights may help guide the future design of polymer thermosets with precisely tailored microstructures and unique combinations of physical properties.

8:15 AM *SF05.05.03
Near Surface Solution Structure Controls the Oriented Attachment of Metal Nanoparticles—Reactive Molecular Dynamics Kristen A. Fichthorn; The Pennsylvania State University, United States

Oriented attachment (OA) of nanoparticles has been recognized as a common mechanism for crystal growth, affecting the micro- and macroscale morphologies over a large variety of materials. However, the role of environmental constraints such as pH, temperature, and ionic concentration in controlling the pathways and kinetics of OA remains unaddressed, which makes it difficult to control and exploit OA syntheses to create unique materials. Experimental studies with *in situ* liquid-cell and *ex situ* transmission electron microscopy indicated that the solution pH affects the OA of Pt nanoparticles.

With pH varying from ~3 -1.5, the attachment facet of Pt nanospheres switches from {001} to {111}. The initial {001} attachment of ~2-5 nm nanoparticles leads to the formation of nanocubes (~50-200 nm), and the subsequent {111} attachment results in the extrusion of Pt nanorods from the surface of the nanocubes. Using molecular dynamics simulations based on a ReaxFF reactive force field fit to results from quantum density-functional theory, we simulated the approach of two Pt nanocrystals in HCl solution under conditions of relatively low and high pH. Our studies confirm the experimental findings and reveal the key role of solution environment in controlling OA.

8:45 AM SF05.05.04
Exploiting Interfacial Assemblies of Nanoparticle Surfactants to Design Reconfigurable Materials and Devices Brett A. Helms; Lawrence Berkeley National Lab, United States

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The interface between two or more immiscible liquids provides an opportunity to structure the liquids into complex shapes through the interfacial assembly and jamming of nanoparticle surfactant films, whereby nanoparticles (including colloidal nanocrystals) dispersed in one of the liquids bind to the end groups of polymeric surfactants concd. at the interface. When the interface is perturbed, additional nanoparticle-surfactants spontaneously form, lowering the interfacial free energy in the system. As the system evolves in time, so as to minimize the interfacial area between the fluids, the nanoparticle-surfactants jam and the structures of the liquids becomes shape-persistent. I will describe our recent efforts in printing and patterning such structured liqs. with functional nanoparticle surfactants to fabricate, in turn, a variety of useful energy devices, including microreactors, all-liquid electronics, magnetics, and electrochemical cells. The potential to couple chemical and energetic processes across the liquid-liqiod interface, and mediated by the nanoparticle-surfactant film, is distinct from related fluidic architectures and devices in lithographically patterned solid media, and more reminiscent of biological systems that dynamically reconfigure, adapt, and respond to local physiochemical cues and thereby derive new functional properties.

9:00 AM SF05.05.05
Assembly of Prescribed 3D Nanoparticle Organizations Using Inverse Design of Programmable DNA Bonds Brian Minevich[1], Jason Kahn[2], Guolong Zhu[1], Aaron Michelson[2,1], Hamed Emany[1], Kim Kisslinger[2], Shuting Xiang[1], Sanat Kumar[1] and Oleg Gang[1,1,2]; [1]Columbia University, United States; [2]Brookhaven National Laboratory, United States

The ability to fabricate functional materials and devices by-design at small scales has led to tremendous technological progress over the last decades, primarily through lithographic and additive manufacturing technologies. However, there remains a need for a platform approach for the fabrication of materials with ordered three-dimensional (3D) nanoscale matter with emergent functions, by-design. Here, we will demonstrate the concept and experimental realization of the encoded assembly of nanoparticles into prescribed, hierarchically ordered 3D organizations using DNA programmable bonds. These directional bonds are encoded onto 3D nanoscale DNA origami frames or “voxels”. Our information-constrained, inverse design approach allows for encoding of targeted 3D hierarchical architectures with programmable bonds through identification of repeating mesoscale motifs and their elemental blocks, nanoscale “voxels”, that can also carry a wide variety of encoded nano-cargo. As examples of this approach, we assemble spatially ordered, low-dimensional arrays with coupled plasmonic and photonic scales, a nanoscale analog of face-perovskite lattice, and a hierarchically organized lattice of spiral motifs, each with domain sizes on the order of several microns. Detailed X-ray scattering and electron microcopy studies confirm the correspondence between the designed and realized architectures. We also demonstrate that dynamic DNA nanotechnology elements can be integrated into the bonds to selectively control bond activity and determine the structure of the resultant assembly. This design strategy was shown to selectively regulate the assembly of multiple crystal symmetries from the same pool of “voxels” depending on the particular DNA signal given to the system.

9:15 AM *SF05.05.06
Facet-Dependent Dispersion and Aggregation Behavior of Aqueous Hematite Nanoparticles Jianbin Zhou, Duo Song, Sebastian T. Mergelsberg, Yining Wang, Narendra Adhikari, Nabajit Lahiri, Yatong Zhao, Ping Chen, Zheming Wang, Xin Zhang and Kevin Rosso; Pacific Northwest National Laboratory, United States

The aggregation state of nanoparticles in solution plays a commanding role over their function. In technological applications, particularly in aqueous media, particle dispersion often requires additive sorbents to impart a net repulsive interaction. However, facet engineering of nanocrystals holds promise for achieving clean monodisperse suspensions simply based on facet-specific interaction with solvent molecules. Here, we systematically studied the dispersion/aggregation behavior of three sets of hematite (Fe_2O_3) nanoparticles in various aqueous solutions using ex situ electron microscopy and in situ small angle X-ray scattering (SAXS). Comparison of particles dominated by (104), (001), and (116) facets revealed a unique tendency of (104) hematite nanoparticles to maintain a monodisperse state across a wide range of pH, electrolyte type and concentration, temperature, and aging time. Density functional theory (DFT) calculations reveal how this behavior arises from a relatively inert, densely hydrogen-bonded first water layer unique to the (104) facet that favors interparticle dispersion by saturating interaction sites on the surface. Our finding validates the notion that nanoparticle dispersion can be controlled through expression of specific facets for specific solvents, and thus may help in the development of various nanoparticle applications that rely on their interfacial area to be highly accessible in robustly stable suspensions.

9:45 AM BREAK

10:15 AM *SF05.05.07
Hierarchically Structured Porphyrin Nanoparticle Photosensitizers Hongyou Fan; Sandia National Laboratories, United States

Design and engineering of the size, shape, and chemistry of photoactive building blocks enable the fabrication of functional nanoparticles for applications in light harvesting, photocatalytic synthesis, water splitting, phototherapy, and photodegradation. Here, we report the synthesis of such nanoparticles through a surfactant-assisted interfacial self-assembly process using optically active porphyrin as a functional building block. The self-assembly process relies on specific interactions such as π–π stacking and ligand coordination between individual porphyrin building blocks. Depending on the kinetic conditions, resulting structures exhibit well-defined one- to three-dimensional morphologies such as nanowires, nanooctahedra, and hierarchically ordered internal architectures. At the molecular level, porphyrins with well-defined size and chemistry possess unique optical and photocatalytic properties for potential synthesis of metallic structures. On the nanoscale, controlled assembly of macrocyclic monomers leads to formation of ordered nanostructures with precisely defined size, shape, and spatial monomer arrangement so as to facilitate intermolecular mass and energy transfer or delocalization for photocatalysis. Due to the hierarchical ordering of the porphyrins, the nanoparticles exhibit collective optical properties resulted from coupling of molecular porphyrins and photocatalytic activities such as photodegradation of methyl orange (MO) pollutants and hydrogen production. The capability of exerting rational control over dimension and morphology provides new opportunities for applications in sensing, nanoelectronics, and photocatalysis.

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DE-NA0003525.

10:45 AM SF05.05.08

Crystallization of Polymer-Grafted Nanoparticles (PGNPs) Induced by Polymer Additives and Kinetic Pathways of PGNP Interfacial Assembly

Yiwen Qian[1,2], Peter Ercius[2], Yi Liu[2] and Ting Xu[1,2]; [1]University of California, Berkeley, United States; [2]Lawrence Berkeley National Laboratory, United States

Growing nanoparticle (NP) crystals has been pursued extensively using ligand chemistries such as DNA and supramolecules, controlled evaporation and patterned surfaces. In this talk, I will introduce a precipitation-induced NP crystallization process where a trace amount of polymeric impurities (<0.1 wt.%) leads to reproducible, rapid growth of high quality 3-D NP crystals in solution and on patterned substrates with high yield. The polymers preferentially precipitate on the PGNP polymeric surfaces inducing the formation of small PGNP clusters, which subsequently act as nuclei to initiate PGNP crystal growth in dilute solution. Formation of 3-D PGNP crystals can be tuned by varying polymeric additives loading, solvent evaporation rate and NP size. This study elucidates how to balance cohesive energy density and PGNP diffusivity in the self-assembly to favor nuclei formation energetically and kinetic growth in dilute solutions.

Further structural diversity is achieved by enabling co-crystallization of two types of PGNPs into binary crystals. Kinetic process of binary PGNP assembly at liquid-air interface is captured by *in-situ* X-ray scattering combined with *ex-situ* TEM characterization, featuring a polymer-like autophobic dewetting process to lower surface energy. Nanoscale microphase separation within binary PGNP mixtures is followed by surface-induced particle reorganization. Metastable structures form through stacking of PGNP layers and short-range diffusion, which can further form “frustrated” lattices. Alternatively, equilibrium crystals nucleate and grow through lattice distortion depending on the compatibility of the preferred local order and global crystalline order. This study helps illustrate the process of how different interactions interplay and influence the final structures and provide guidelines for hierarchical functional materials fabrication.

11:00 AM SF05.05.09

Preparing Chiral Hydrogel by Using Coordination-Assembly Complex of Cobalt Oxide Nanoparticles for Chiromechanical Response Chung Man Lim, Francesco Serafin, Xiaoming Mao and Nicholas A. Kotov; University of Michigan, United States

Nanomaterials are considered as an important class that has found interest in various fields including electrical, optical, catalytical, and biomedical applications. In nanoscale, chemical, biological, and physical properties are all different from the properties of each atom or molecule of bulk materials. Meanwhile, gels also make up a crucial class of materials on account of their large free space between the networks and highly adjustable mechanical properties. Many hydrogel systems have been researched utilizing covalent cross-linking processes, including radical polymerization initiated by temperature, UV, and pH. It is important to understand the physical behavior of these gels, as they are being continuously introduced into various fields like electrical, pharmaceutical, and biomedical applications.

On the basis of previous research about nanoparticles, gels, and chirality, we envisioned that a coordination-assembly complex might be able to couple with nanoparticles to form a chiral gel. The advantage of this method is that it does not require the use of a specific device or conditions. Mechanical properties such as storage and loss modulus showed chirality-response with critical frequency. The aim of this research is to demonstrate unique features of the coordination system of cobalt oxide nanoparticles with cadmium salts to produce a structure that responds to the chirality.

11:15 AM SF05.05.10

Self-Assembly of 3D DNA-Nanoparticle Superlattices on Patterned Surfaces Feiyue Teng[1], Honghu Zhang[1,1], Dmytro Nykypanchuk[1] and Oleg Gang[1,2,2]; [1]Brookhaven National Laboratory, United States; [2]Columbia University, United States

DNA-programmable assembly is a powerful approach to organize nanoscale objects into well-defined 2D and 3D lattices and translate the advances of nanoscale building blocks into mesoscale architectures. However, to integrate the lattices into devices and other material systems, the methods for their precise placements on planar substrates, as well as assembly at the pre-determined surface locations are required. We developed an approach to direct the growth of 3D DNA-nanoparticle lattices at the desired surface locations over macroscopic areas using microscale lithographic patterns. We investigated the factors affecting the growth of 3D superlattices on these patterned substrates and established a robust pattern-guided assembly method. We applied small angle x-ray scattering (SAXS), optical microscopy, scanning electron microscopy (SEM) to reveal the assembly processes and the structure of the resulting lattices. The established approach provides a new material fabrication platform that combines nanoscale control of 3D lattices, as provided by DNA-programmable assembly, with mesoscale and macroscale control of self-assembled materials, as enabled by patterning. The developed method also allows for a systematic investigation of the nucleation and growth of DNA-guided assemblies at the interfaces. The established approach opens a possibility for integration of 3D nanoparticle lattices into devices for precisely positioning assemblies on substrates.

11:30 AM SF05.05.11

Ethanol-induced Condensation and Decondensation in DNA-Linked Nanoparticles—A Nucleosome-Like Model for the Condensed State Qinsi Xiong, One-Sun Lee, Chad Mirkin and George C. Schatz; Northwestern University, United States

Inspired by the conventional EtOH precipitation strategy, ethanol condensation has been applied as a routine method to dynamically tune “bond” lengths (i.e., the distances between adjacent nanoparticles that are linked by DNA) and the thermal stabilities of colloidal crystals engineered with DNA. However, the underlying mechanism of how the DNA bond changes in this class of colloidal crystals in response to ethanol remains unclear. Here, we conducted a series of all-atom molecular dynamic (MD) simulations to explore the free energy landscape toward DNA condensation and decondensation. Our simulations confirm that DNA condensation is energetically much more favorable under 80% ethanol conditions than in pure water, as a result of ethanol’s role in enhancing electrostatic interactions between charged species. Moreover, the condensed DNA adopts B-form in pure water and A-form in 80% ethanol, which indicates the higher-order transition does not affect DNA’s conformational preferences. We further propose a nucleosome-like supercoiled model for the DNA condensed state, and we showed that the DNA end-to-end distance matches the experimentally measured DNA bond length of about 3 nm in the fully condensed state for DNA where the measured length is 16 nm in water. Overall, this study provides an atomistic understanding of the mechanism underlying ethanol-induced condensation and water-induced decondensation, whereas our proposed nucleosome-like model allows the design of new strategies for interpreting experimental studies of DNA condensation.

SESSION SF05.06: Self-Assembly I

Session Chairs: Biao Jin and Lili Liu

Wednesday Afternoon, April 12, 2023
Marriott Marquis, B2 Level, Golden Gate B

1:30 PM SF05.06.01
A Study on Elastic Behavior of Liquid Crystal Phase of DNA Polymers Evaporating on Geometric Template Soon Mo Park, Hyoungsoo Kim and Dong Ki Yoon; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Evaporation process is a complex dynamical system in which fluid flow, known as 'Coffee ring effect', continues to occur and influenced by many factors such as the types of solute, wettability with the substrate, and the evaporation rate. Understanding the phenomenon is positively necessary for providing insights associated with fundamental science and engineering application.
For the improvement, we delved into evaporation process, deposition mechanism and liquid crystal (LC) phase expression of DNA solution on flat substrate and micro-post template and controlled the orientation and morphology of DNA molecules using solution coating method. One of the biopolymers, DNA has recently emerged as a building block because it is abundant in nature, can be functionalized by electrostatic interaction and shows liquid crystal phase depending on the concentration. Their bulk elastic properties are quite different from other materials due to concentration-dependent LC phase. Additionally, predesigned substrates can be applied for confinement and deformation of triple-phase contact line. Then, unique and complex structure can be formed spontaneously due to the interaction between the elastic properties of DNA and confinement effect of the substrate.
Here, we conducted the evaporation-induced experiments on geometrical template and controlled novel and sophisticated DNA microstructures. The pattern of the DNA can be modulated by shear direction and template spacing. This will help to understand the self-assembly of DNA molecules in confinement effect and can provide applications to bio-template for polymers, liquid crystals or other nanoparticles.

1:45 PM SF05.06.02
Three-Dimensional Hierarchically Porous MoS2 Foam as High-Rate and Stable Lithium-Ion Battery Anode Xuan Wei[1,2]; [1]King Abdullah University of Science and Technology, Saudi Arabia; [2]Li Auto, China

Architected materials that actively respond to external stimuli hold tantalizing prospects for applications in energy storage, wearable electronics, and bioengineering. Molybdenum disulfide, an excellent two-dimensional building block, is a promising candidate for lithium-ion battery anode. However, the stacked and brittle two-dimensional layered structure limits its rate capability and electrochemical stability. Here we report the dewetting-induced manufacturing of two-dimensional molybdenum disulfide nanosheets into a three-dimensional foam with a structural hierarchy across seven orders of magnitude. Our molybdenum disulfide foam provides an interpenetrating network for efficient charge transport, rapid ion diffusion, and mechanically resilient and chemically stable support for electrochemical reactions. These features induce a pseudocapacitive energy storage mechanism involving molybdenum redox reactions, confirmed by in-situ X-ray absorption near edge structure. The MoS_2 Foam electrode exhibits extremely high reversible capacities of 1575, 1550, 1515, 1431, 1268 and 1111 mA h g^{-1} at current densities of 0.2, 0.5, 1.0, 2.0, 5.0, 10 A g^{-1}. Furthermore, MoS_2 Foam remains electronically functional and shows the specific capacity of 1000 mA h g^{-1} and 700 mA h g^{-1} even when measured at high current densities of 5 A g^{-1} and 10 A g^{-1} after 1,000 cycles. The extraordinary electrochemical performance of molybdenum disulfide foam outperforms most reported molybdenum disulfide-based lithium-ion battery anodes and state-of-the-art materials. This work opens promising inroads for various applications where special properties arise from hierarchical architecture.

2:00 PM SF05.06.03
A Scalable and Straightforward Approach to the Self-Assembly of Mesoporous Metal Oxide Thin Films David W. Collinson, Thomas W. Colburn and Reinhold H. Dauskardt; Stanford University, United States

Evaporation induced self-assembly (EISA) has been widely applied as an approach to prepare mesoporous ceramics and carbanecous materials. Typically, sol-gel oxide precursors in combination with soft templating agents such as the Pluronic® tri-block co-polymers self-assemble to produce thin films with highly ordered, accessible porosity with pore diameters on the order of 5-10 nm. Depending on the deposition conditions and precursor composition, a wide range of structured mesoporous oxide thin films can be achieved with potential applications in energy, sensors and catalysis.
However, the EISA and mesostructuration process is very sensitive to atmospheric conditions and humidity. The formation of the oxide network also requires extended delicate aging and sintering steps to produce high quality thin films. As a result, producing self-assembled oxide thin films in this manner incurs significant energy and time costs that prevents scalable manufacturing of the mesoporous thin films. The limiting factor preventing the scalable manufacture is not the self-assembly process, which can occur quickly under appropriate deposition conditions; instead it is the time required to condense the sol-gel oxide network and prevent collapse of the film structure. To achieve appropriate condensation and high quality films, extended processing times up to 2 days and elevated sintering temperatures up to 400 ^{o}C are required.
To overcome the limitations of the sol-gel chemistry, we utilize solution combustion synthesis to produce large area mesoporous thin films rapidly with significantly reduced processing temperatures and time. Carboxylic acid species act both as chelating agents and as fuel sources in conjunction with metal nitrate salts to generate a stable oxide network at low processing temperatures and short processing times. In addition, the complexation of the carboxylic acids with metal salts prevents hydrolysis and condensation until the moment the combustion reaction is initiated simplifying the conditions required for self-assembly. Upon initiation, the combustion reaction allows for rapid and efficient oxide network formation before the Pluronic® burns out, preventing loss of the desired self-assembled mesostructure. Further, our chosen chemistry also lends itself to rapid deposition approaches such as spray coating for scalable manufacturing. A suitable choice of metal salt and carboxylic acid can potentially allow for the production of a range of functional mesoporous metal oxide thin films. Finally, we also demonstrate how the self-assembled matrices can then be filled with polymers to produce nanocomposites with potential applications as dielectric layers and barrier coatings.

2:15 PM SF05.06.04
Tailoring Mass and Light Transport in Nanoparticle-Based Aerogels for Gas-Phase Photocatalysis Fabian Matter and Markus Niederberger; ETH Zürich, Switzerland

Aerogels are among the most fascinating human-made materials due to their numerous extraordinary properties. These extremely lightweight materials not only have a very intriguing appearance but also are made up of a finely branched three-dimensional network that offers very high porosity and extraordinary surface area. Due to their structural characteristics, aerogels offer great potential for diverse applications such as detection and sensing, filtration, and catalysis. Aerogels have been fabricated for decades using conventional sol-gel chemistry, a process that, however, is limited in design flexibility. More recently, an alternative method for aerogel fabrication has emerged that uses pre-synthesized building blocks to create such highly porous three-dimensional assemblies.[1] Since the properties of the nanoscale building blocks are typically preserved during the assembly process, the final aerogel can be precisely tailored to a specific application not only in terms of composition, but also in terms of crystallinity, size, shape, and surface chemistry of the underlying aerogel framework.

By using highly crystalline titanium dioxide nanoparticles, for example, transparent monolithic aerogels can be prepared that have a surface area of up to 500 m^2/g and a porosity of up to 99 %. The photoactive backbone can be further decorated with selected co-catalyst nanoparticles to enhance the photocatalytic performance. The potential of particle-based aerogels has been demonstrated in numerous studies, centimeter-sized titania-metal aerogels, for example, have been explored in the photocatalytic conversion of gaseous carbon dioxide [2] and also show excellent activity in hydrogen production from organic feedstocks. [3,4]

In the last decade, the focus has been centered on exploiting new building blocks and tuning their composition to improve light utilization or enhance catalytic activity. [5] In contrast, little attention has been paid to modification at the structural level. This is partly because the internal structure of aerogels is morphologically complex and difficult to characterize, but also because the parameters controlling particle assembly are not yet fully understood.

In this talk, titania-based aerogels will be used as an example to show how structural modifications of particle-based aerogels can be realized in order to tune two essential properties for gas-phase photocatalysis: gas permeability and light transmission. [6] Furthermore, it will be shown how measurements of gas permeability can not only serve as a tool to determine fundamental properties of mass transfer through such particle-based assemblies, but in conjunction with optical measurements, gas sorption analysis, and microscopy techniques can also provide valuable insights into the formation mechanism of this fascinating class of materials.

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2:30 PM SF05.06.06
Programmable Assembly of Semiconductor Mesostructures via Inorganic Phototropism Azhar I. Carim and Nathan S. Lewis; California Institute of Technology, United States

Plants exhibit a phototropic response and direct the addition of new biomass to optimize collection of solar insolation. Analogous inorganic phototropism growth enables the programmable assembly of complex 3D nanoarchitectures with instruction by an incoherent, unstructured, mW cm^{-2} intensity light beam. Inorganic phototropism has been demonstrated via the light-mediated electrochemical assembly of semiconductor deposits from solution-phase precursor ions. No structured light field (no photomask), no lithographic processes and no templating agents (ligands, surfactants, etc.) are utilized. Nevertheless, ordered nanoscale features are conformally assembled over full macroscale (cm^2) areas with feature heights on the order of several um with growth times < 5 min. In-plane anisotropy is a function of the input polarization. Isotropic morphologies consisting of ordered arrays of nanoscale holes were generated using unpolarized illumination whereas linearly polarized light resulted in anisotropic lamellar structures with in-plane orientations set by the polarization direction. The structure pitch was dependent on the spectral distribution of the input light with shorter wavelengths effecting higher feature densities. The out-of-plane growth direction is related to the propagation direction of the input light, mirroring the way in which palm trees develop an observable tilt toward the average position of the solar azimuth. Time-varying optical inputs enable programming of 3D intricacy by evolving the in-plane structure along the out-of-plane dimension, e.g. an abrupt reduction in the input wavelength results in a concomitant increase in the interfacial density resulting in tuning fork structures similar to how blue light effects branching in many shade-intolerant plants. Additional morphological control has also been effected by using multiple simultaneous illumination inputs. Modeling of the growth using a combination of full-wave electromagnetic simulations of light absorption and scattering coupled with Monte Carlo simulations of mass addition successfully reproduced the experimentally observed morphologies and indicated that assembly was directed by evolution of the growth front to maximize anisotropic light collection. The assembly was observed to be a highly emergent phenomenon involving optical communication between neighboring features including cooperative scattering and synergistic absorption and thus is similar to the manner in which neighboring plants exchange information and avoid competition for light resources.

3:15 PM SF05.06.07
Electrostatic Self-Assembly of Magnetic and Plasmonic Nanoparticles on Gold Nanorods Mehedi Hasan Rizvi[1], Ruosong Wang[2], Jonas Schubert[2], Andreas Fery[2,3] and Joseph Tracy[1]; [1]North Carolina State University, United States; [2]Leibniz Institute for Polymer Research Dresden, Germany; [3]Technische Universität Dresden, Germany

Overcoating gold nanorods (GNRs) with plasmonic or magnetic satellite nanoparticles (NPs) can modify the longitudinal and transverse surface plasmon resonances (LSPR and TSPR) through coupling with the satellite NPs. We report use of electrostatic interactions to reversibly assemble different types and amounts of satellite NPs on GNR cores, which allows coupling with and manipulation of the LSPR and TSPR of the GNR core. Cationic Fe_3O_4 NPs and spherical gold NPs (GNPs) functionalized with polyethylenimine (PEI) assemble on the surface of anionic GNRs functionalized with bovine serum albumin (BSA). The distinct extinction spectra of Fe_3O_4 NPs and GNRs make possible quantification of the loading of satellite NPs from optical extinction spectra. pH is a useful lever for controlling assembly and disassembly processes because the electrostatic properties of PEI- and BSA-functionalized NPs strongly depend on pH. Stable assemblies are obtained at pH between the isoelectric points (pH_I) of BSA (pH_I ~5) and PEI (pH_I ~11), because the core and satellite NPs have opposite charges within this window. At lower or higher pH, the core and satellite NPs have like charges, which inhibits assembly. Moreover, disassembly is possible by adjusting the pH to values outside of this range.

3:00 PM BREAK

3:30 PM SF05.06.08
Nanostructure Polymorphism Induced By Rotational Freedom of Self-Assembling Amphiphiles Yukio Cho[1], Yu-Jin Choi[1,2] and Julia Ortony[1]; [1]Massachusetts Institute of Technology, United States; [2]University of California, Santa Barbara, United States

Amphiphiles with strong intermolecular interactions that self-assemble in water have drawn attention due to their high stability and tunability for a range of applications. These strongly interacting amphiphiles tend to be planar and have a high propensity for hydrogen bonding and π-π stacking, thus the morphological design spaces of the corresponding self-assembled nanostructures are constrained. We hypothesized that a broad range of self-assembled morphologies can be achieved by introducing conformational freedom within each amphiphile. In this study, we incorporate a diacetylene domain into the aramid amphiphile (AA) platform, which yields a rotational axis of aramid amphiphile perpendicular to the planes of hydrogen bonding and π-π stacking. We observe polymorphism in AA assemblies with helical, twisted, short planar, or long planar nanoribbons, by varying the concentration and annealing temperature. We demonstrate that polymorphism in AA assemblies originates from changes in molecular packing induced by rotational constraints. This study of self-assembly in AAs serves as a model study for understanding the relationship between rotational freedom and molecular packing within a nanostructure.

3:45 PM SF05.06.09
Structural Diversity in Dimension-Controlled Assemblies of Tetrahedral Gold Nanocrystals Yi Wang[1], Jun Chen[1], Yaxu Zhong[1], Soojin Jeong[1], Ruipeng Li[2] and Xingchen Ye[1]; [1]Indiana University Bloomington, United States; [2]Brookhaven National Laboratory, United States

Polyhedron packings have fascinated humans for centuries and continue to inspire scientists of modern disciplines. Despite extensive computer simulations and a handful of experimental investigations, understanding of the phase behaviors of synthetic tetrahedra has remained fragmentary largely due to the lack of tetrahedral building blocks with tunable size and versatile surface chemistry. Here, we report the remarkable richness of and complexity in dimension-controlled assemblies of gold nanotetrahedra. By tailoring nanocrystal interactions from long-range repulsive to hard-particle-like or to systems with short-ranged directional attractions through control of surface ligands and assembly conditions, more than a dozen of two-dimensional and three-dimensional superstructures including the cubic diamond and hexagonal diamond polymorphs are selectively assembled. We further demonstrate multiply twinned icosahedral supracrystals by drying aqueous gold nanotetrahedra on a hydrophobic substrate. This study expands the toolbox of the superstructure by design using tetrahedral building blocks and could spur future computational and experimental work on self-assembly and phase behavior of anisotropic colloidal particles with tunable interactions.

4:00 PM SF05.06.10
Porous Self-Assembly in Binary Mixtures of Lobed Colloidal Particles Brunno Carvalho Rocha and Harish Vashisth; University of New Hampshire, United States

The self-assembly of colloidal particles is emerging as a promising approach for designing novel advanced materials. During self-assembly, particles spontaneously reorganize to form macrostructures with desired properties for applications in diverse fields, including in tissue engineering, catalysis, and photonics. The addition of attractive hard lobes to the surfaces of the colloidal particles can provide directionality for the interparticle interactions and create more excluded volume around each particle, leading to the formation of porous morphologies. In this work, we performed Langevin Molecular Dynamics simulations of binary mixtures of lobed colloidal particles, where the self-assembly process is mediated by short-range interactions between the lobes of the particles. We investigated the formation of porous macrostructures in mixtures of particles with varying number/size of their lobes across a range of temperatures. Among the self-assembled morphologies, we primarily identified the formation of three-dimensional aggregates, spherical aggregates, and crystalline structures. We observed that the formation of crystalline structures is progressively preferred as the number of lobes in the particles increases, and that the crystalline character of these structures leads to more homogeneous pore sizes, in contrast to random and spherical aggregates that have more heterogeneous pore sizes. We also observed that the larger lobes allowed the self-assembly of the lobed particles at higher temperatures when compared to the smaller lobes. The evolving understanding of how to optimize the bottom-up design of lobed colloidal particles gained by leveraging simulation techniques can serve as a guide for further improving the manufacturing of advanced materials.

4:15 PM SF05.06.11
Light Induced Surface Tension Gradients for Hierarchical Assembly of Particles from Liquid Metals Jiayun Liang and Zakaria Al Balushi; University of California, Berkeley, United States

Achieving control over the motion of dissolved particles in liquid metals is of importance for the meticulous realization of hierarchical particle assemblies in a variety of nanofabrication processes. Brownian forces can impede the motion of such particles, impacting the degree of perfection that can be realized in assembled structures. Here we show that light induced Marangoni flow in liquid metals (i.e., liquid-gallium) with Laguerre-gaussian (LGpl) lasers as heating sources, is an effective approach to overcome Brownian forces on particles, giving rise to predictable assemblies with high degree of order. We show that by carefully engineering surface tension gradients in liquid-gallium using non-gaussian LGpl lasers, the Marangoni and convective flow that develops in the fluid drives the trajectory of randomly dispersed particles to assemble into 100-μm wide ring-shaped particle assemblies. Careful control over the parameters of the LGpl laser (i.e., laser mode, spot size, and intensity of the electric field) can tune the temperature and fluid dynamics of the liquid-gallium as well as the balance of forces on the particle. This in turn can tune the structure of the ring-shaped particle assembly with a high degree of fidelity. The use of light to control the motion of particles in liquid metals represents a tunable and rapidly reconfigurable approach to spatially design surface tension gradients in fluids for more complex assembly of particles and small-scale solutes. This work can be extended to a variety of liquid-metals, complementary to what has been realized in particle assembly out of ferrofluids using magnetic fields.

4:30 PM SF05.06.12
Using CO_2 to Modulate Self-Assembly—Viscosity Increase or Decrease in Surfactant Fluids Induced by CO_2 Mahima Srivastava; University of Maryland, United States

The self-assembly of surfactants in water can be tuned by a number of stimuli, including temperature, pH, and light. In particular, self-assembly into wormlike micelles (WLMs) has been shown to be sensitive to the above stimuli. WLMs are long, polymer-like chains that entange into transient networks. Thus, when WLMs are formed, the solution becomes highly viscoelastic. Conversely, if WLMs are converted into spherical structures (micelles or vesicles), the viscoelasticity is lost and the viscosity of the solution will drop to that of water.

Here, we focus on modulating the self-assembly of WLMs using carbon dioxide (CO_2). CO_2 is of concern due to its role in the atmosphere as a greenhouse gas (thus impacting global warming and climate change). Approaches for CO_2 sequestration often introduce gaseous CO_2 into a solution containing an amine such as diethanolamine (DEA), but such amines are a rather toxic molecules. We are interested in absorbing CO_2 in a fluid that is completely safe and biocompatible. Moreover, could CO_2 absorption transform the viscosity of the fluid?

In this regard, we have devised a fluid containing an anionic fatty acid and a nontoxic amine-bearing molecule. Both the constituents of our fluid are biocompatible and in fact, they are found in the body. We will show that the viscosity of the fluid can be switched from low to high (or high to low) by contact with CO_2. The low-viscosity state corresponds to spherical micelles (or vesicles) whereas the high-viscosity state corresponds to WLMs. By bubbling CO_2 into a fluid of given composition, we can rapidly (within seconds) drive a transition from one type of self-assembly to another. We are interested in exploiting such rapid transitions, not only for CO_2 sequestration but also for certain biomedical applications.

SESSION SF05.07: Poster Session I: Building Advanced Materials via Aggregation and Self-Assembly
Session Chairs: Sijie Chen, Shuai Zhang and Xin Zhang
Wednesday Afternoon, April 12, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SF05.07.01

Selective Localization of Nanofiller on Interface of Polymer Composites via Surface Energy Modification to Improve Compatibility of Polymer Blends Kibeom Nam, Dong Yun Lee and Kwang Woo Jeon; Kyungpook National University, Korea (the Republic of)

Dispersed nanofillers in immiscible polymer blends prevent phase separation and voids formations being localized at the interface of the blends. The nanofillers can improve mechanical properties, however, the aggregation and agglomeration during the mixing process, such as melt blending and extrusion methods. Insufficient dispersion of nanofillers in polymer blend limits the application of blends works as a defect. Therefore, we present the effects of the surface energy of nanofillers on its dispersion and selective localization in the Poly(lactic acid) (PLA)/poly(butylene adipate-co-terephthalate) (PBAT) nanocomposite. Here in, the modified cellulose nanofiber (m-CNF) and modified silica nanofillers (m-SiO2) were used to prevent self-aggregation via hydrogen bonding reducing the surface energy of them. Then, by controlling the blending time, we confirmed that the localization of modified nanofillers in the nanocomposite. As a result, the modified nanoparticles, located at the PLA/PBAT interface, changed the morphology of the PLA/PBAT nanocomposites, thereby significantly improving the tensile strength and elongation at break by approximately 7% and 16%, respectively. Furthermore, the thermal and mechanical properties of composite were comprehensively enhanced regarding the PBAT mixing sequence and selective localization of the nanofiller. It was found that the selective localization of the nanofillers can be utilized to tune the mechanical properties of the PLA/PBAT nanocomposites with respect to their corresponding morphologies. The selective localization of silica nanoparticles in the PLA/PBAT nanocomposite is described in detail, and the melt blending method is presented for achieving the selective localization in an industrial scale to develop eco-friendly packaging films.

5:00 PM SF05.07.02

Synthesis of Eco-Friendly Polymeric Biosurfactants with Excellent Environmental Compatibility and Characterization of Their Interfacial Properties for Cosmetic and Household Products KiHo Park, JeongMin Lee and JongChoo Lim; Dongguk University, Korea (the Republic of)

Tightening environmental regulations and increasing awareness for the need to protect the ecosystem have effectively resulted in an increasing interest in biosurfactants as possible alternatives to chemical surfactants. They have advantages over their chemical counterparts in specificity, relative ease of preparation, mildness, and effectiveness even at extreme temperature or pH. Biosurfactants also have the merit of diversity, environment friendly nature such as low toxicity and excellent biodegradability, possibility of large-scale production, selectivity, performance under extreme conditions, and potential applications in environmental protection. Due to their unique functional properties, biosurfactants can be used as emulsifiers as well as demulsifiers, wetting agents, foaming agents, spreading agents, environmental cleanup of pollutants, functional food ingredients and detergents. In this study, 3 types of polymeric phospholipid biosurfactants were prepared using 3 different raw materials such as linoleic acid, rapeseed oil and coconut oil respectively and the structure of the resulting products was elucidated by FT-IR, 1H NMR, and 13C NMR spectroscopies. Biodegradability, acute oral toxicity (LD50), acute dermal irritation and acute eye irritation tests revealed that the newly synthesized polymeric biosurfactants possess excellent mildness and superior environmental compatibility as well as superior interfacial properties, indicating the potential applicability in cosmetic product formulations. The patch test has been performed with 0.1 mL of 0.5 wt% surfactant solution and the result has shown that the newly prepared polymeric biosurfactants indicated no allergic inflammation on a skin during 48 hrs. The prescription test in shampoo formulation prepared with the newly synthesized biosurfactants indicated excellent sensory feeling and foam ability compared with conventional hydrocarbon and silicon surfactants. In particular, LDP-PW(A) can be considered as a strong candidate for the potential applicability in cosmetic product formulations since the newly synthesized LDP-PW(A) polymeric biosurfactant is highly surface active, mild, nontoxic, non-irritating and readily biodegradable.

Acknowledgements
This work was supported by Material Parts Technology Development Program (20011027, Development of fluorine based surfactant manufacturing technology for semiconductor and display process) and by Program (P133500002, Development of eco-friendly anionic surfactant that can be applied to household kitchens, personal cares, and cosmetics by using bio-natural raw materials for carbon neutralization), funded by the Ministry of Trade, Industry & Energy, Korea.

5:00 PM SF05.07.03

Mesogen–Containing Multi–Block Poly(ester–carbonate)s Bearing Ether Side Groups and Their Nanostructures Yuya Watanabe, Riki Kato, Kazuki Fukushima and Takashi Kato; The University of Tokyo, Japan

Aromatic condensation polymers such as poly(ethylene terephthalate) and poly(bisphenol-A carbonate) are used in the form of fibers, films, and bottles due to their mechanical and thermal stabilities. Highly aromatic polyesters are known as thermotropic main-chain liquid-crystalline polymers (LCPs), exhibiting high mechanical and thermal properties, chemical stabilities, and processability. The molecular assembly and alignment of rigid moieties, called mesogen, enable the excellent performance of the LCPs .

Aliphatic condensation polymers represented by poly(L-lactic acid) and poly(trimethylene carbonate) (PTMC) are recognized as biodegradable polymers, which can be degraded in compost and aqueous environments including body and marine with the aid of enzymes and microorganisms. These polymers have been used in medical devices such as sutures and drug delivery carriers. Side-chain functionalized analogs of these polymers have been developed to induce additional complex biological functions for applications in the fields of nanomedicine and regenerative medicine. PTMC analogs have drawn attention as the functionalized biodegradable polymers because of the variety of installable functionalities and facile accessibility in the monomer synthesis. However, the PTMC analogs with bio-related functional side chains are often flexible and have low glass transition. A PTMC analog bearing an ether side chain previously developed exhibited a high level of cell attachment and biocompatibility as well as enzymatic degradability. This polymer was a liquid material with a glass transition temperature (T_g) around –20 °C, and thus limiting its use. In the present study, we have introduced an aromatic ester triad mesogen into the backbone of the ether-functionalized PTMC analog to impart the mechanical stabilities, while maintaining the biological functions and biodegradability.

Our macromolecular design includes multi-block structures where oligocarbonate sequences with ether side chains are connected by the aromatic ester triad mesogens. The mesogen–containing multi–block condensation polymers (**P1**) were synthesized via two-step polymerization. In the first step, mesogen-containing oligocarbonates (**P2**) were obtained by ring-opening polymerization of a cyclic carbonate with an ether group, using a bis(hydroxy)-functionalized aromatic mesogen as an initiator. The mesogenic diols showed liquid-crystalline properties. The lengths of the oligocarbonates were controlled by the ratio of the cyclic monomer and the mesogen. The peripheral hydroxy groups of **P2** were then used for chain extension with adipoyl chloride to give **P1** with weight-average molecular weights over 1.0×10^5. Unlike **P2** and the original ether-functionalized PTMC analogs, **P1** exhibited elastomeric properties. Differential scanning calorimetry of **P1** only showed glass transition, indicating that they were amorphous. Polarized optical microscopy of **P1** subjected to shear suggested nanosegregation and alignment of the aromatic mesogens. Furthermore, atomic force microscopy (AFM) of **P1** revealed that **P1** formed nanosegregated structures composed of high modulus domains with approximately 10 nm in diameter, surrounded by soft matrices. Nanomechanical evaluations of the polymer surface of **P1** using the AFM technique indicated that the surface modulus of **P1** was 4-5 times higher than that of the non-mesogen-containing counterparts.

In summary, we successfully synthesized mesogen–containing aromatic/aliphatic poly(ester–carbonate)s bearing ether groups at the side chains (**P1**). The two-step polymerization using ring-opening polymerization and subsequent polycondensation gave **P1** with regulated multi-block structures. Incorporation of the aromatic ester triad mesogens into the main chain of the bio-related side-chain functionalized aliphatic polycarbonates plays an effective role in the enhancement of their mechanical properties.

5:00 PM SF05.07.04
Development of 2D and 1D ZnO Materials via Self-Assembly of Liquid-Crystalline Zinc Hydroxide Carbonate Takahiro Mikami[1], Riki Kato[1], Nobuyoshi Miyamoto[2] and Takashi Kato[1]; [1]The University of Tokyo, Japan; [2]Fukuoka Institute of Technology, Japan

Liquid crystals are soft materials that exhibit liquid-like fluidity and solid-like ordered structure. Various functional materials based on assembled structures of liquid crystals have been reported. The most common liquid crystals are molecular-based liquid crystals. Inorganic colloidal particles with anisotropic shapes such as rods and disks also form liquid-crystalline (LC) phases. Inspired by the formation process of biominerals such as seashells, bones, and teeth, we developed "biomineral-inspired colloidal liquid crystals". These are organic/inorganic hybrid nanoparticles with rod and disk shapes. The organic components of the colloidal liquid crystals are acidic polymers that interact with inorganic cation species, and the inorganic components are calcium carbonate or calcium phosphate. Most of the biominerals are hybrids of calcium salts and biomacromolecules, while some ants and scorpion hybridize heavy metal elements such as zinc and manganese with biomacromolecules as their stings and fangs. Inspired by these biological materials, we aim to synthesize zinc-based colloidal liquid crystals. Herein, we report the synthesis of new colloidal liquid crystals based on zinc hydroxide carbonate (ZHC) nanoplates. Oriented zinc oxide (ZnO) materials obtained through self-assembly of ZHC nanoplates and subsequent thermal treatment are also described.
The nanoplates of ZHC crystals were obtained by mixing aqueous $Zn(NO_3)_2$ and $(NH_4)_2CO_3$ solutions in the presence of poly(acrylic acid) (PAA) as an additive. The hybridization of PAA with ZHC crystals was supported by Fourier transform infrared (FTIR) spectras. The structures of the mesogenic ZHC nanoplates were clarified by transmission electron microscope (TEM) and X-ray diffraction (XRD) measurements. The TEM images showed that the nanoplates had polycrystalline structures. The cross-sectional TEM images and XRD patterns suggested a layered structure with stacked 2-nm thick ZHC nanosheets. A concentrated colloidal dispersion of ZHC showed a LC texture under polarizing optical microscope (POM). In small-angle X-ray scattering (SAXS) measurements, the LC phase showed anisotropic scattering, which suggests the presence of ordered structure in the colloidal dispersion. We assume that nanoplates of ZHC formed discotic nematic liquid crystals in their dispersions.
We have achieved the development of 2D and 1D ZnO materials by simple methods utilizing the ZHC liquid crystals. The ZHC liquid crystals were macroscopically oriented by external stimuli. Transparent ZHC self-standing thin films were obtained by sandwiching the ZHC liquid crystals between fluorinated polymer sheets and drying them at ambient conditions. The POM images and XRD analysis showed that the ZHC nanoplates were oriented and stacked along the interface of the thin-film surface during drying process. The ZHC thin films were converted to self-standing ZnO thin films by annealing. The annealed samples maintained thin-film morphologies. Out-of-plane and in-plane XRD patterns suggested the *c* axis of ZnO crystals was oriented perpendicular to the thin-film surface. A nanoporous structure due to the water evaporation and the decomposition of PAA was observed by scanning electron microscope (SEM). 1D ZnO fibrous materials were synthesized by thermal treatment of ZHC fibers prepared through injecting the liquid crystals into acetone solvent. The POM images of ZHC fibers revealed the formation of macroscopically anisotropic structures. These results suggested that the ZHC-nanoplates planes were aligned parallel to the injecting direction due to the shear stress and rapid diffusion of water into acetone. The SEM observation showed the ZnO fibers had nanoporous structures as ZnO thin films. As these 2D and 1D ZnO materials have oriented, nanoporous, and polycrystalline structures, they are expected to be used for varistors and catalyst materials.

5:00 PM SF05.07.05
Solvothermal Growth of Moiré Superlattices in Antimony Telluride Spiral-Type Nanoplates Robert Link, Gabriel Marcus and David Carroll; Wake Forest University, United States

Moiré superlattices (MSLs) of van der Waals (vdW) materials have been found to host emergent quantum phenomena associated with high electron correlations, and while the study of MSLs has surged in recent years, the difficulty of fabricating these structures remains high. In the present research, a one-pot, colloidal solution-liquid-solid (SLS) synthesis procedure for antimony telluride (Sb_2Te_3) spiral-type nanoplates (STNPs) is adapted to create several distinct nanostructures. In particular, Sb_2Te_3 MSLs are synthesized with observed twist angles up to 0.52°. Emphasis is given to modifications of the typical reaction procedure that lead to visible and controllable changes in the resulting nanostructures, observed primarily using Transmission Electron Microscopy (TEM). The simple and scalable synthesis methods put forward in this research hope to facilitate future investigation into the electronic properties of Sb_2Te_3 MSLs.

5:00 PM SF05.07.06
Facile Synthesis of Cu-Based Metal-Organic Framework/Chitosan Composite Granules as Adsorbents Jinsoo Kim[1], Van Nhieu Le[2] and Thach N. Tu[1]; [1]Kyung Hee University, Korea (the Republic of); [2]Industrial University of Ho Chi Minh City, Viet Nam

The *in situ* synthesis of metal–organic framework crystals incorporated into natural polymers is an efficient approach to manufacturing adsorbents of large size, which is convenient in terms of adsorbent handling, operating, and transportation for practical adsorption processes. Herein, CuBTC/CS (BTC = 1,3,5-benzenetricarboxylate; CS = chitosan) composite granules were successfully prepared by dispersing Cu^{2+} ions into the CS matrix before generating Cu^{2+}/CS composite beads, which subsequently grew into CuBTC crystals incorporated in the CS network. To evaluate their quality, the characteristics of the prepared composites were systematically analyzed, which were observed to be controlled by the amount of Cu^{2+} ions present in the reaction system. The highest quality material was utilized as an adsorbent for toluene uptake, which was estimated via breakthrough data. The adsorptive interaction was investigated by determining the heat of adsorption, whilst the kinetic behavior of the adsorption process was described by pseudo-first-order and pseudo-second-order models. Additionally, the mechanism of diffusion of toluene molecules into the granular adsorbent was examined in detail. Finally, to predict the adsorption behavior via the mathematical models of Yan and Thomas, the experimental breakthrough data were utilized. The herein-developed route allows granular adsorbents to be manufactured in large quantities and used in the practical volatile organic compound adsorption.

5:00 PM SF05.07.07
Fluorophore Self-Assembly in Liquid Crystals Abstract Mina Mandic[1,2], Kayla Winters[2], Charlotte Slaughter[2], Sophie Ettinger[2], Peter Collings[1] and Arjun Yodh[2]; [1]Swarthmore College, United States; [2]University of Pennsylvania, United States

Liquid crystals (LCs) are a state of matter, characterized by an order called the nematic phase. While past work has investigated how 5CB LC drop configuration transforms under an electric field, 5CB behavior in magnetic (B) fields is yet to be studied. This project uses the fluorophore BODIPY-C5 to visualize the transition of radial 5CB drops in response to B fields. With zero B field, radial drops with 5CB molecules arrange from the center to the edges. As the B field increases, the 5CB molecules rearrange to be aligned with the direction of the field. Similarly, drop defects (regions in which 5CB molecules do not have uniform direction) change configuration, starting as a point defect in the zero B field configuration and converts to a ring defect with an increasing B field. Fluorophores are added to topological defects formed by planar rubbing of PVA-coated substrates to stretch polymers and induce 5CB alignment. Fluorescence microscopy is used to take images of drops and quantify the intensity distribution. Preliminary results show that at zero B field, the intensity is lowest at the center of the radial drops containing the point defect. Future work will use confocal microscopy to analyze layers of drops and quantify intensity change over an increasing B field.

5:00 PM SF05.07.08
Flash Nanoprecipitation Synthesized Polymer Nanocapsules Yuri Chung and Edward Van Keuren; Georgetown University, United States

With advances in the development of nanoparticles, interest in multicomponent materials has grown. For example, nanocapsules, comprised of a solid shell and liquid core, have found applications in a number of technologies. One method of synthesizing nanocapsules is flash nanoprecipitation, in which a solution of a polymer and a small molecular organic liquid is injected into a rapidly stirring miscible non-solvent. As the two solvents mix, droplets of the polymer solution develop into nanocapsules; the polymer diffuses more slowly than the smaller molecules of the organic compound, forming a shell around it. An initial model of polystyrene-shelled nanocapsules with n-hexadecane liquid cores has been proven successful. The process may also be used to create nanocapsules using a variety of combinations of polymers, solvents, and organic compounds for different applications, primarily in biomedical imaging and drug delivery applications.

5:00 PM SF05.07.09
Biomimetically Engineered Amyloid-Shelled Gold Nanocomplexes for Discovering α-synuclein oligomer-Degrading Drugs Hyo Gi Jung, Jae Won Jang and Yonghwan Kim; Korea University, Korea (the Republic of)

The assembly of α-synuclein (αS) oligomers is recognized as the main pathological driver of synucleinopathies. While the elimination of toxic αS oligomers shows promise for the treatment of Parkinson's disease (PD), the discovery of αS oligomer degradation drugs has been hindered by the lack of proper drug screening tools. Here, we report a drug screening platform for monitoring the efficacy of αS-oligomer-degrading drugs using amyloid-shelled gold nanocomplexes (ASGNs). We fabricate ASGNs in the presence of dopamine, mimicking the *in vivo* generation process of pathological αS oligomers. To test our platform, the first of its kind for PD drugs, we use αS-degrading proteases and various small molecular substances that have shown efficacy in PD treatment. We demonstrate that the ASGN-based in vitro platform has strong potential to discover effective αS-oligomer-targeting drugs, and thus it may reduce the attrition problem in drug discovery for PD treatment.

5:00 PM SF05.07.10
Aqueous Synthesis of DNA-Nanoparticle Cluster Composites Using Various Types of Metal Ions and DNA Structures Jeesu Moon and Jae-Seung Lee; Korea University, Korea (the Republic of)

Nanoparticle clusters (NPCs) are of great interest in the field of nanotechnology owing to their distinctive properties compared to those of the single nanoparticles. To date, there have been extensive efforts to synthesize NPCs based on diverse molecular interactions. Despite the recent emergence as a new pathway to synthesize functional nanomaterials, metal ion (M^{n+})-induced DNA condensation has rarely been investigated as a tool for the synthesis of NPCs. In this presentation, we demonstrate a noble method for the synthesis of NPCs based on M^{n+}-induced condensation of linear and spherical DNA using thirty different M^{n+}s. Two types of the M^{n+}s are selected as representatives for further thermodynamic and kinetic investigation of their effects on the cluster structures of the NPCs. As a model system of clusterization, gold nanoparticles (AuNPs) are employed to elucidate the synthesis mechanism based on their advantageous properties such as intense localized surface plasmon resonance and a large atomic number of Au, ideal for optical and electron microscopic analysis. Furthermore, our approach has also been successful for the synthesis of other types of NPCs using the similar approach, proposing its effectiveness as a versatile strategy for the synthesis of NPCs.

5:00 PM SF05.07.11
Self-Assembly of Ultrahigh Porous Aramid/Poly(ether imide) Nanofibrillar Separators for Lithium-Metal Batteries Lee Donggeun and Bongjun Yeom; Hanyang University, Korea (the Republic of)

Nanoporous separators have been utilized to reduce the growth of Li dendrites for Li-metal batteries via delocalized distributions of Li ionic flux over the Li metal anode surfaces. However, the levels of the battery performances still require improvements for commercialization. Herein, we report the preparation of ultrahigh porous nanofibrillar separators with self-assembled aramid nanofibers (ANFs) with poly(ether imide) (PEI). 3-D nanoporous structures with high porosity of 95% are achieved via reprotonation-assisted self-assembly for the ANF/PEI nanofibrillar network structures. Such high porosity in the fibrillary nanostructures enables to increase ionic conductivity > 3 mS/cm. In addition, the ANF/PEI nanofibrillar separators show high Li-ion transference numbers > 0.8 that can be attributed to preferential adsorption of lithium salt on the nanofibrils and high Li ionic mobility. Combination of high Li-ion transports and delocalization of Li ionic flux via 3-D nanoporous structures enables to suppress the formation of Li dendrites on the Li-metal anodes. Li/Li symmetric cell and full-cell test results show highly stable cycle performances. Self-assembly assisted formation of the nanofibrillar network structures can be one of promising routes for the fabrications of advanced separators for energy storage devices.

5:00 PM SF05.07.13
Strain-Induced Anisotropic Alignments of Bacterial Nanocellulose Ionogels and Their Dynamic Mechanical Properties and Ionic Conductive Behaviors Wonseok Choi, Amith Abraham, Byongin Sang and Bongjun Yeom; Hanyang University, Korea (the Republic of)

Ionogels have attracted great attentions for various electrochemical applications due to their high physical and electrochemical properties. However, for practical usages, their mechanical properties and ionic conductivities still require improvements. Herein, we report anisotropically aligned bacterial nanocellulose (BC) ionogels and their dynamic mechanical properties and ionic conductive behaviors. Wet-stretching in water allows the BC nanofibers to be well-oriented throughout the films. After drying in the stretched state, the aligned BC films are obtained and the ionogels are prepared with swelling with ionic liquid of 1-ethyl-3-methylimidazolium. The aligned BC ionogels present superb mechanical properties of modulus about 5 GPa and ultimate strength of 300 MPa in the static tensile tests, majorly attributed to strengthening via anisotropic alignments of the nanofibers and molecular interactions between hydroxyl groups of glucose units. Additionally, the ionic conductivities of the ionogels are in the range of 0.12-0.45 mS cm^{-1}, even with such high values of the mechanical properties. It is possibly originated from the formation of Helmholtz-like electric double layers around the BC nanofibers that enables the fast ion transport of non-bound ions through the ionic channels. As a result, the combination of dynamic mechanical properties and ionic conductivities shows about 8.1 of E′σ values that surpass limit line value of E′σ = 5. These values were difficult to be achieved by previous ionogel materials. This approach provides the pathways to overcome the conflicts between mechanical properties and ionic conductivities for the ionogels and relevant systems.

5:00 PM SF05.07.14
Enhancing C_{2+} Products Selectivity in CO_2 Electroreduction via Metal-Organic Framework Driven Copper Nanoaggregates Sungjoo Kim[1], Dongwoo Shin[2] and Hyunjoon Song[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)

Due to the energy and climate issues in contemporary society, there has been an attempt to apply electrochemical CO_2 reduction reaction (eCO_2RR) into real world for converting CO_2 into value-added chemicals. Especially, copper is widely investigated for generating C_{2+} products from eCO_2RR, because of its moderate binding energy against CO* intermediate. One of the approaches for preparing copper electrocatalysts is to use metal-organic frameworks (MOFs) as precursor materials. These MOF-driven catalysts are advantageous in that their synthetic protocols are simple and possess numerous open active sites. Herein, we designed a synthetic route for nanocrystalline copper MOFs by nucleation and growth control. Then, copper oxide nanoaggregates were obtained by calcining copper MOF nanoparticles at specific temperature. The MOF driven copper oxide nanoaggregates showed improved catalytic activity on eCO_2RR, with Faradaic efficiencies of 63 and 81% at −1.01 V vs. reversible hydrogen electrode (RHE) upon ethylene and C_{2+} products, respectively. In addition, the catalysts exhibited prolonged stability up to 10 h in neutral condition. The partial current density of C_{2+} products was also able to be boosted to −255 mA cm^{-2} in alkaline flow cell configuration. Detailed analyses on the activated nanoaggregates revealed that smaller sized MOF crystals enabled the entire particles to receive thermal flux evenly at lower temperature, resulting in highly developed grain boundaries without agglomeration, which is one of the critical factors for C_{2+} products selectivity and durability in eCO_2RR catalysts.

5:00 PM SF05.07.16

Remote-Controllable Molecular Knob with Photochromic Chiral Dopant for Optically Tunable Devices DongMin Yu, Eunji Jang, Subin Kim, Woojin Kim, Junhwa Jang and Kwang-Un Jeong; Jeonbuk National University, Korea (the Republic of)

To fabricate the optically tunable device, photo-responsive chiral dopant (AZ_4ICD) was newly designed and successfully synthesized. AZ_4ICD is composed of photo-responsive azobenzene moiety and chiral isosorbide central core. Therefore, AZ_4ICD can be used as a remote-controllable molecular knob for the control of molecular orientation in the helical mesophases. First, the phase structures are investigated by using thermal, microscopic, and scattering analyses. Based on the experimental results, AZ_4ICD exhibits one liquid crystalline phase (SmA*) at high temperatures and two crystalline phases ($SmCr_1$ & $SmCr_2$) at lower temperatures. To find out detail molecular structures and symmetries in the ordered phases, 2D WAXD patterns are obtained at different temperatures. From the analysis of 2D WAXD patterns, the two AZ_4ICD molecules are self-assembled to the anticlinically tilted crystalline structure in $SmCr_1$ and $SmCr_2$ phases. In SmA* phase, anticlinically tilted bilayer structure transforms to the simple layered structure. Due to the photo-responsiveness of azobenzene mesogen, a photo-reversible molecular conformational change can be induced by UV and visible light. Upon irradiating UV light, the uniaxially oriented SmA* phase is transformed into an isotropic phase by *trans*-to-*cis* isomerization of AZ_4ICD. The isotropic phase is returned to the SmA* phase in the absence of UV irradiation, and this process can be accelerated by irradiation of visible light. AZ_4ICD dopant exhibits good compatibility with the nematic LC host (E7) due to the mesogenic properties of azobenzene and its side chain. To fabricate a chiral nematic (N*) thin film, the mixture composed of chiral dopant R811, AZ_4ICD, and E7 was injected into the sandwich cell. The chirality is inversely proportional to the *trans*-to-*cis* photoisomerization of AZ_4ICD, indicating the helical pitch is controlled by the UV and visible light irradiation. Another chiral mesophase that normally formed between N* and Iso phase is called by blue LC phase (BP). As the content of AZ_4ICD in the BP mixture increases, the temperature range of BP is expanded. To further investigate the photoisomerization behavior of AZ_4ICD in a 3D helical superstructure, a BP film was also prepared. Under irradiation with UV, the double twisted cylindrical alignment of BP building block is broken by the metastable *cis*-AZ_4ICD molecules. Such N* and BP films can induce the reversible phase transformation and change of reflected color without any degradation. The AZ_4ICD LC films with remote-controllable molecular knob can provide a lot of opportunities in the various applications. This work was supported by the BK21 FOUR, Mid-Career Researcher Program (2021R1A2C2009423) and Basic Research Laboratory Program (2020R1A4A1018259).

5:00 PM SF05.07.17

Norbornene-Based Dendronized Polymer with Azobenzene for Remote-Controllable Switches Mintaek Oh, Youngjae Wi, Jaeseok Hyeong, DongMin Yu, Sanghee Kim and Kwang-Un Jeong; Jeonbuk National University, Korea (the Republic of)

For the fabrication of remote-controllable switches, we newly designed and successfully synthesized norbornene-based macromonomers. The macromonomer consists of hydrophilic linkers, photochromic azobenzene mesogens, and hydrophobic alkyl chains. Hydrophilic ethylene oxide linker and hydrophobic alkyl chain were introduced to form an ordered structure by π- π interaction. Azobenzene mesogens were introduced to fabricate photoresponsive actuators. The azobenzene-based dendronized polymer (AZ-P) were polymerized by ring-opening metathesis polymerization (ROMP) to prepare high molecular weight and low polydispersity index (PDI). The high molecular weight (Mn = 173 kDa) with low polydispersity (PDI = 1.05) was confirmed by size exclusion chromatography (SEC) trace of the polymer. The photochemical properties were investigated by ultraviolet and visible light spectroscopy (UV-Vis). The initial π-π* absorption represented *trans*-rich state of azobenzene. When exposed to 365 nm UV light and 450 nm Visible light, reversible photoisomerization was confirmed through an increased π-π* and n-π* absorption peaks, respectively. We analyzed thermal phase behaviors of the AZ-P and three different phases (SmF, SmC and SmA) were identified through differential scanning calorimetry (DSC) thermograms and polarized optical microscopy (POM) images of the finally synthesized azobenzene-based polynorbornene. Uniaxially oriented AZ-P films were prepared by mechanical shearing process. The ordered packing structures were investigated through small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) at different temperatures. 1D SAXS and WAXD patterns indicated that the order is lowered as the temperature decreased, and the side chains are packed closely in the layers. The detailed molecular packing structures were investigated through two-dimensional wide-angle X-ray diffraction (2D WAXD), resulting that the backbones were arranged perpendicular to the film normal (FN) and the side chains were oriented parallel to FN, tilted as the temperature decreased. Irradiation of UV and visible light to the AZ-P film resulted in *trans*-to-*cis* isomerization indicating photodynamic reversible behaviors. When UV light was exposed to the film, it becomes a *cis*-rich state by *trans*-to-*cis* isomerization in the light source direction and actuated by anisotropic volume contraction. In order to impart electrical conductivity, silver layer was coated on the AZ-P film and an electrical circuit was formed to fabricate wireless switches by light. When a film was exposed to UV light, it was bent by photo-induced actuation and the electric circuit switched with the light-emitting diode (LED) color changes. Upon irradiation of visible light, the film returned to its original shape and switched to the initial electric circuit and LED color. As a result, the AZ-P film has shown that it can be used as remote-controllable switches, and the photoresponsive azobenzene denpol will be practical in remote-controllable devices. This work was supported by the BK21 FOUR, Mid-Career Researcher Program (2021R1A2C2009423) and Basic Research Laboratory Program (2020R1A4A1018259).

5:00 PM SF05.07.18

Uniaxial Alignment of Discotic Liquid Crystal for Heat Dissipating Materials with High Thermal Conductivity Youngjae Wi, DongMin Yu, Jaeseok Hyeong, Eunji Jang, Sanghee Kim and Kwang-Un Jeong; Jeonbuk National University, Korea (the Republic of)

For the development thermal management system in the electronic, display, and automobile industries, high heat transfer property is required. In this research, triphenylene-based liquid crystal reactive discogen (LCRD) monomers containing the vinyl and thiol functional groups were newly synthesized for the heat transfer materials with enhanced thermal conductivity. The LCRD mixtures exhibits columnar liquid crystal phase by self-assembly of doscogen, and those phases were fixed by photopolymerization. Based on POM and DSC, the phase of mixture was measured according to temperature and composition of vinyl monomers. The mixture had various phase under each condition. The 50vinyl-50thiol mixture (1:1 molar ratio) at 80 °C show the isotropic structure and tilled hexagonal columnar structure coexist. Under this condition, the LCRDs were polymer-stabilized by irradiating 365 nm UV light for 1 h. After polymerization, the network morphology of the fabricated LCRD films was identified. Through POM, it was confirmed that the dark area and the birefringent area coexist in the film. This means that the isotropic domains are percolated the liquid crystal matrix. In-plane thermal conductivity of the LCDR films produced by curing at different temperatures was measured and compared at room temperature by the transient plane source technique. The LCDR film in which the isotropic structure and hexagonal columnar structure coexist show thermal conductivity up to 1.09 W/mK. This value is higher than conventional heat dissipating organic materials, high density polyethylene, calamitic liquid crystal organic materials. The high thermal conductivity of the LCRD film due to the ordered structure by self-assembly and the hexagonal lattice structure of triphenylene core. The alignment of the columnar structure in the film was controlled by magnetic field for higher thermal conductivity than the previously prepared film. The LCRD films were fabricated using a static magnetic field and a rotating magnetic field, respectively. The columnar axes oriented using a static magnetic field were perpendicular to the direction of magnetic field but not aligned in the one direction. To solve this problem, a rotating magnetic field was used. It was realized through 2D WAXD that the columnar axes of LCRDs were aligned perpendicular to the direction of magnetic field and one direction. The uniaxially oriented LCRD film exhibits enhanced thermal conductivity normal to the columnar axis. The oriented film along the transverse direction of the film plane shows higher thermal conductivity than the aligned film along the longitudinal direction of the film plane and the film without magnetic and field up to 3.00 W/mK. High thermal conducting properties as well as excellent mechanical and chemical stabilities of LCRD films make them possible to be effectively available for heat management organic materials. This work was mainly supported by BK21 FOUR program, Mid-Career Researcher Program (2021R1A2C2009423) and Basic Research Laboratory Program (2020R1A4A1018259).

5:00 PM SF05.07.19
Optically Controllable Secret Ink Based on Kinetics of Supramolecular Structure Junhwa Jang, Jaeseok Hyeong, Subin Kim, Woojin Kim, Kwang-Un Jeong and Sanghee Kim; Jeonbuk National University, Korea (the Republic of)

Simultaneous manipulation of both fluorescence and transparency of organic fluorescent materials is one of the biggest challenges in various fields such as security inks, memory devices, organic light-emitting displays, and biomedical imaging. Conventionally, the development of materials with transparency and fluorescence has been made by mixing nano-sized fluorescent particles with transparent amorphous polymers. However, this production process has limitations such as the heterogeneous dispersion of fluorescent particles and the low fluorescence intensity from the low fluorescent substance loading. To solve this problem, we newly designed and synthesized a monopyrene-based dendron (abbreviated as MD) molecule that has both transparency and fluorescence. MD is a molecule in which three alkyl chain groups are linked by amide bonds to monopyrene. Because of the strict distinction between the solvophilic alkyl dendrons and the solvophobic pyrene groups, we predicted that MD molecules would assemble a hierarchical superstructure at the molecular level. To confirm our hypothesis, we conducted morphological analysis via both scanning calorimetry (DSC) and cross-polarized optical microscope (POM). Interestingly, it was confirmed that when there was insufficient time for molecular assembly a metastable crystalline phase (C_{ms}) appeared, and when there was sufficient time a stable crystalline phase (C_s) appeared. In addition, if the quenching process is performed with little time for assembling molecules, an optically transparent crystalline phase (C_t) is obtained. Surprisingly, the supramolecular structure of C_t was equal to C_{ms}. To confirm the molecular packing of the polymorphic MD superstructure in more detail, the molecular packing structures of C_s and C_{ms} were investigated with wide angle X-ray diffraction (WAXD) and transmission electron microscope (TEM). As a result, when the assembly time of molecules in a thermodynamic equilibrium state is sufficiently provided, stable C_s is a fully packed layered structure where a dimeric building block is assembled. In the opposite case, metastable C_{ms} is a layered structure where the head-to-head dimers are alternatively interdigitated. Furthermore, the optical properties of MD had a significant change due to the polymorphic superstructure induced by the balance between intermolecular interactions and nanophase separation. These optical properties were identified by transmittance and photoluminescence (PL) measurement. In addition, to control organic materials with transparency and fluorescence, the optical properties of MD were evaluated under various external stimuli such as solvent fuming, and thermal annealing. The transparent fluorescent superstructure of MD under UV and visible light was constructed by the quenching process. Because the supramolecular structure was changed by the fuming and annealing processes, the MD materials became opaque, and the fluorescence wavelength shifted. Based on the previous results, it was found that the transparency and fluorescence of MD were controlled by molecular packing kinetics as well as external stimuli. Our research highlights that the optically controllable smart materials were available as secret ink. The letter was written in an isotropic state using secret ink and quenched. Encrypted letters were not visible in daylight but, were easily observed under UV light. However, Secret letters could be observed with the naked eye through fuming and annealing processes. Also, the decrypted letters can be converted back into the initial state by manipulating the molecular packing structure of a fluorescent molecule via kinetic control. This work was supported by the BK21 FOUR, Mid-Career Researcher Program (2021R1A2C2009423), and Basic Research Laboratory Program (2020R1A4A1018259).

5:00 PM SF05.07.20
Planarity Control of Porphyrin Based Supramolecules for Enhanced Thermal Conductivity Jaeseok Hyeong, DongMin Yu, Eunji Jang, Subin Kim, Woojin Kim and Kwang-Un Jeong; Jeonbuk National University, Korea (the Republic of)

As heat management becomes more important in the electronics industry, many researchers have tried to improve the low thermal conductivity of organic materials used in flexible and miniaturized devices. In this regard, many researches have enhanced thermal conductivity of soft materials through utilizing the mesogen with the extended π-conjugated length or increasing crystallinity. However, there are not enough studies on enhancing and adjusting the thermal conductivity of polymers by deep understanding the correlation between the supramolecular packing structure and thermal properties. For this kind of study, porphyrin-based reactive metallomesogens (PBRM-n; n= -2H, -Ni, -Cu, - Zn) were newly designed and synthesized. Porphyrin core is purposely selected due to the extended π-conjugated aromatic chemical structure and easy metal-substitution. Its substitution with different metals changes the molecular planarity, which can induce the different molecular packing structure and thermal conductivity. Based on thermal and scattering analyses, it is realized that PBRM-2H exhibits discotic columnar hexagonal structure that is tilted and obliquely stacked without π-π stacking. PBRM-Ni has discotic columnar hexagonal structure without π-π stacking. On the other hand, PBRM-Cu, and Zn exhibit columnar rectangular structure with π-π stacking. When we confirm the energy-minimized core geometry of PBRM-n compounds in the isolated gas phase by using molecular simulation and the measured macroscopic property, the tilted angle from molecular horizontal plane depending on the substituted metal atoms is 5.4°, 17°, 8.8°, 3° (PBRM-2H, -Ni, -Cu, and Zn, respectively). It indicates that PBRM-Zn has relatively small distortion because Zn atom matches well in the hole of the porphyrin core. Therefore, PBRM-Zn could have dense molecular packing structure and higher crystallinity than other species. PBRM-2H has relatively high planarity in the isolated gas phase, but it has a mesomorphic structure due to its large in-plane distortion in the solid state, resulting in relatively loose molecular packing and low crystallinity. PBRM-n films were prepared by irradiating UV light at 50 °C for 2 hours and then their thermal conductivity and several stabilities were evaluated. The fabricated PBRM-n films have no micro voids in the cross-section and endure scratch up to 2H (hardness). In addition, PBRM-n films show good chemical stability in various organic solvents and are thermally stable up to 350 °C due to polymer network structure. The thermal conductivity of PBRM-n films is measured to be 0.88, 1.02, 0.97, and 1.2 $Wm^{-1}K^{-1}$ (PBRM-2H, -Ni, -Cu, and -Zn, respectively). It is realized that the PBRM-Zn film has the highest thermal conductivity (1.2 $Wm^{-1}K^{-1}$) due to the flattest porphyrin core and high crystallinity. As a result, this study proves the importance of understanding the correlation between chemical structure, chemical conformation, supramolecular packing and thermal conductivity when we develop advanced thermal interface materials. This work was supported by the BK21 FOUR, Mid-Career Researcher Program (2021R1A2C2009423) and Basic Research Laboratory Program (2020R1A4A1018259).

5:00 PM SF05.07.21
The Development of Smart Window Stabilized by Polymer Walls and Liquid Crystal Physical Gels Eunji Jang, Subin Kim, Woojin Kim, Junhwa

Jang, Mintaek Oh and Kwang-Un Jeong; Jeonbuk National University, Korea (the Republic of)

Liquid crystal (LC) smart windows are attractive technology because they can protect privacy as well as control indoor environments by switchable electro-optical properties. However, conventional LC smart windows require a high driving voltage and nematic LC (NLC) in LC smart windows can leak when severe mechanical stimuli are applied. Therefore, we newly developed a dual stabilization (DS) process to fabricate mechanically stabilized LC smart windows which operate at a lower voltage than conventional LC smart windows.
The DS cell was fabricated with two components. The first one is composed of NLC (5CB) and macrogelator with photoisomerizable azobenzene moiety (BTAG) for the formation of liquid crystal physical gel (LCPG). The other component is composed of photopolymerizable low molecular weight monomers (LMWM) for the construction of partition walls. The DS process is performed by irradiating UV light under a photomask. Upon irradiating UV light on the DS cell, LMWMs in the UV light-exposed region are polymerized. Because of the concentration gradient, LMWMs move from the UV light-protected region to the UV light-exposed region resulting in the construction of partition walls. At the same time, BTAG molecules in the UV light-exposed region are photoisomerized from *trans*-isomers to *cis*-isomers resulting that the 3D network structures which are formed by intermolecular hydrogen bonding between BTAG are collapsed. The *cis*-isomers move to the UV light-protected region by the concentration gradient of the macrogelator, resulting in the formation of physical 3D networks.
The electro-optical properties of the DS cell were investigated for smart window application. The DS cell is opaque due to the mismatch of the refractive index between the randomly dispersed NLC domains. Under the electric field, the NLC molecules are homeotropically aligned because the 5CB has a positive dielectric anisotropy. Thus, the mismatch of the refractive index is disappeared, and the DS cell turns transparent. When the electric field is removed, the NLC molecules are randomly dispersed in the LCPG domain again, and the DS cell returns to the opaque state. According to the voltage-dependent transmittance curves, the driving voltage of the DS cell is lower than the conventional smart windows.
To demonstrate this phenomenon, the DS cell was observed by polarized optical microscopy (POM) equipped with a quarter-wave plate. Unlike the randomly dispersed NLC molecules, the NLC molecules near the partition wall are homogeneously aligned. Hence, the NLCs in the LCPG domain can be easily reoriented at low voltage.
To confirm the mechanical stability, we fabricated a flexible DS smart window with the partition wall in the ITO-coated polyethylene terephthalate (PET) films. Because the partition wall improves the adhesion between the flexible films as well as serves as spacers, the flexible DS smart window is mechanically stable even if external stimuli such as pressing, cutting, and bending are applied. In conclusion, the dual stabilized LC smart window by the partition wall not only operates under a low voltage but also has excellent mechanical stability. This work was supported by the BK21 FOUR, Basic Research Laboratory Program (2020R1A4A1018259), and Mid-Career Researcher Program (2021R1A2C2009423).

5:00 PM SF05.07.22
Controlling the Orientation of Liquid Crystal for Thermal Managing Materials Subin Kim, Woojin Kim, Junhwa Jang, Mintaek Oh, Youngjae Wi and Kwang-Un Jeong; Jeonbuk National University, Korea (the Republic of)

With the integration and miniaturization of electronics, the demand for thermal managing materials (TMM) that effectively dissipate the problematic heat has continuously increased. Much research has been conducted for composite materials consisting of high thermal conductive additives. But the limitation of processability with using large amounts of fillers makes it difficult to develop the advanced TMMs due to the intrinsic low thermal conductivity of organic polymer matrix. Therefore, improving the thermal conductivity of organic polymers can be an effective strategy for developing thermal conducting materials with a small amount of filler. In this study, a liquid crystal monomer (LCM) was newly synthesized for the fabrication of thermal conducting polymer (TCP) films which can be applied to the advanced TMMs. Based on thermal and structural analyses, it was realized that the synthesized LCM exhibited a smectic A mesophase. By using temperature-dependent properties of LCM, TCP films were fabricated at both liquid crystal and isotropic phases using photopolymerization process. Due to the mesogenic core of LCM which has a highly ordered lattice structure providing high phonon transfer pathway, photopolymerized TCP films show outstanding thermal conductivity over 1 W/mK regardless of the molecular self-assembly structure. Moreover, the heat transfer performance of TCP films can be further enhanced in a certain direction by controlling the orientation of LCM molecules in liquid crystal network. The uniaxially oriented TCP film can be fabricated by polymerizing under the magnetic field at Liquid crystal state. Due to the high intermolecular interaction of the LCM which forms the liquid crystalline domain at liquid crystal state, the magnetic coupling energy can overcome the thermal motion that disordering the molecular alignment. The uniaxially oriented TCP film exhibited outstanding thermal conducting property which was estimated to be 2.5 W/mK along the liquid crystal director. To compare the thermal conductivity of the polymeric films according to the molecular orientation, the TCP films were monitored using an infrared (IR) camera. Thermal imaging demonstrated that polymeric films with highly ordered lattice structure show improved heat-conducting performance. In addition, the anisotropic liquid crystal network in magnetically aligned TCP film can remarkably dissipate heat along the long axis of the mesogenic core. Therefore, TCP films with high thermal conducting properties can be applied as advanced thermal management materials. This work was supported by the BK21 FOUR, Mid-Career Researcher Program (2021R1A2C2009423) and Basic Research Laboratory Program (2020R1A4A1018259).

5:00 PM SF05.07.23
Multichromatic Polarizer Using Redox Responsiveness Woojin Kim, Junhwa Jang, Mintaek Oh, Youngjae Wi, Sanghee Kim and Kwang-Un Jeong; Jeonbuk National University, Korea (the Republic of)

For developing multichromatic thin films, perylenediimide-methacrylic anhydride (PMA) was newly designed and synthesized. Conjugation system of PMA core can be reversibly changed by redox responsiveness because the imide groups can stabilize the radical anions. This reversible change of conjugation system causes the shift of the absorption wavelength band of PMA core. Then, the PMA solution’s color changes from red to dark purple because the reduced PMA mostly absorbs all the wavelength of visible light. When the reduced PMA solution is exposed to oxygen or polarized on anode, the solution’s color returns to red because the oxidized PMA specifically absorbs absorption band at $\lambda = 500$ nm. Another characteristic of PMA core is suitable for anisotropic optical properties because of its high dichroic ratio. But, in generally, perylendiimide-based molecules have low solubility in both polar and nonpolar solvents due to strong intermolecular π-π interaction. In addition, stability of organic molecules is essential in various circumstance for application feasibility. So, Introduced ionic groups and polymerizable groups at perylenediimide core improve the solubility for process and impart the stability through polymerization. Based on the results of X-ray diffraction and polarized optical microscopy, it was confirmed that the PMA molecule exhibits a lyotropic chromonic liquid crystal (LCLC) phase which is composed of both attractive force (π-π interaction and lateral correlation between perylenediimide core) and repulsive force (between ammonium bromide). To fabricate the multichromatic PMA polarizer, PMA solution was coated on transparent substrate by mechanical shearing and then photopolymerized. The polymerized PMA polarizer exhibits excellent mechanical strength and chemical resistance in both acidic and basic solution than unpolymerized state. Spectroscopic and optical properties of fabricated PMA polarizer was confirmed by ultraviolet-visible spectroscopy and polarized optical microscopy. The results of ultraviolet-visible spectroscopy show that when the polarization direction and shear direction are parallel state, the transmittance is higher than when they are perpendicular state. PMA polarizer shows the characteristic of E-type polarizer which absorbs only the ordinary wave at $\lambda = 500$ nm and transmits the extraordinary wave. Thus, the polarized optical microscopy images show the color of the transmitted light presents red image when the polarization direction is perpendicular to shear direction. On the other hand, colorless and transparent state present when the polarization direction is parallel to shear direction. These characteristics show the manufactured PMA polarizer can be applied to sign encryption as well as multichromatic smart window. This work was supported by the BK21 FOUR, Mid-Career Researcher Program (2021R1A2C2009423) and Basic Research Laboratory Program (2020R1A4A1018259).

5:00 PM SF05.07.24
Non-Covalent Reconfigurable Microgel Colloidosomes with a Well-Defined Bilayer Shell Xin Guan and To Ngai; The Chinese University of Hong Kong, Hong Kong

Microgels have been successfully used to stabilize emulsion droplets. Compared to conventional rigid particles, the use of microgels as stabilizers offers several distinct advantages: (1) being soft and porous, they become deformed and flattened at the oil-water interface. The deformability of the particles makes it possible to achieve larger interfacial loading, which in turn alters the interfacial tension and the rheological properties of the interface; (2) being responsive, microgels allow one to prepare emulsions that can be triggered by environmental stimuli, which is especially desirable in industrial and emerging applications.

Whilst soft microgels have been demonstrated as being extremely interesting stabilizers for emulsions, previous studies mainly focused on the preparation of oil-in-water (O/W) emulsions due to their intrinsic hydrophilicity and thus initially dispersed in water. Very few studies have reported on the preparation of water-in-oil (W/O) emulsions using microgels as the sole emulsifier. In addition, there have been no attempts to control over microgel-assembled structure at the interface, thus limiting our ability to exploit particle monolayers or bilayers more broadly in advanced materials applications. On the other hand, the rheological properties of colloidal bilayers from soft particles self-assembled at interfaces to resulting emulsion characteristics, have not been explored yet.

In this work, we show that by introducing octanol into poly(*N*-isopropylacrylamide-*co*-methacrylic acid) (PNIPAM-*co*-MAA) microgels, octanol-swollen microgels can rapidly diffuse from the initially dispersed oil phase onto the water droplet surface. This facilitates the formation of microgel-laden interfacial layers with strong elastic responses and also generates stable inverse W/O Pickering emulsions. More importantly, these emulsions can be used as templates to produce microgel colloidosomes, herein termed 'microgelsomes', with shells that can be fine-tuned from a particle monolayer to a well-defined bilayer consisting of self-assembled binary microgels with opposite charges via non-covalent interaction. The microgelsomes can then be used to encapsulate and/or anchor nanoparticles, proteins, vitamin C, bio-based nanocrystals or enzymes. Moreover, the programmed release of these substances can be achieved by using ethanol as a trigger to mediate the shell permeability. Thus, these reconfigurable microgelsomes with a microgel-bilayer shell can respond to external stimuli and demonstrate tailored properties, which offers novel insights into microgels and promise wider application of Pickering emulsions stabilized by soft colloids.

5:00 PM SF05.07.25
A New Methodology for the Reproducible Elaboration of SiO_2-Based Colloid Crystals as a Template for Inverse Opals Structures Federico Fookes[1,2], Luis Polo-Parada[1] and Maria M. Fidalgo de Cortalezzi[1]; [1]University of Missouri-Columbia, United States; [2]INTEC-CONICET, Argentina

Photonic crystals (PCs) are nanomaterials with photonic properties made up of periodically modulated dielectric materials that reflect light between a wavelength range located in the photonic band gap. Colloidal PCs (C-PC) made from monodisperse nanoparticles have been employed in coatings, films for surface-enhanced Raman scattering, chromatographic columns packing, and reflectometric interference spectroscopy. Additionally, C-PC have been studied as sacrifice templates to create inverse opals (IO) employing inorganic, organic, metallic, and ceramic materials, which are exact inverse replicas of C-PC structures and therefore maintain their optical properties. Several manufacture techniques have been applied for the fabrication of C-PC that involve the self-assembly of monodisperse colloidal particles by spin and spray coating, interfacial assembly and inkjet printing, sedimentation, or vertical deposition. In practice, due to its simplicity, C-PC crystals based on convective particle aggregation are elaborated either by the method of convective assembly by solvent volatilization or vertical lifting deposition. Although capable of producing good quality crystals, these methods have low uniformity between deposits in terms of thickness, and reflectance spectrum characteristics, most likely due to slight variations in temperature, humidity, arrangement geometry and particle suspension properties that influence the outcome.
In this work, a robust protocol for the elaboration of photonic crystals based on SiO_2 particles (SP) deposition using vertical lifting method was studied. A wide range of lifting speed and particles suspensions concentration were investigated by evaluating C-PC reflectance spectrum key parameters such as maximum reflectance (% R max), wavelength at % R max, and reflectance peak full width at half maximum (FWHM). The experimental conditions that led to the best performance were selected and employed for reproducibility tests.
Thinner and higher reflectance peaks were obtained with a decrease in the lifting speed and an increase in the SP concentrations up to certain values. Seven batches of 12 C-PC employing a SP 3 % suspension and a lifting speed of 0.28 μm/s were prepared to test the reproducibility of this method. Every C-PC fabricated in this assay have a wavelength peak in a range between 528 and 538 nm and a FWHM lower than 90 nm. IO polymeric films with a highly porous and interconnected morphology were obtained using the developed C-PC as a template. In the current work, we found the optimized conditions that allows to fabricate reproducible colloidal crystals that could be prepared in a large scale and a short period of time employing a simple device. These findings provide a step forward to scale-up to the fabrication of C-PC, 3D microporous structures, and IOs as those employed for the elaboration of photonic polymeric sensors.

SESSION SF05.08: Self-Assembly II
Session Chair: Shuai Zhang
Thursday Morning, April 13, 2023
Marriott Marquis, B2 Level, Golden Gate B

8:00 AM SF05.08.01
The Influence of Molecular Design on Structure-Property Relationships of a Supramolecular Polymer Prodrug Nivedina Sarma, Kelsey DeFrates, Ahmad Omar and Phillip B. Messersmith; University of California, Berkeley, United States

Supramolecular self-assemblies of hydrophilic macromolecules functionalized with hydro-phobic, structure-directing components have long been used for drug delivery. In these systems, loading of poorly soluble compounds is typically achieved through physical encapsulation during or after formation of the supramolecular assembly, resulting in low encapsulation efficiencies and limited control over release kinetics, which are predominately governed by diffusion and carrier degradation. To overcome these limitations, amphiphilic prodrugs that leverage a hydrophobic drug as both the therapeutic and structure-directing component can be used to create supramolecular materials with higher loading and controlled-release kinetics using biodegradable or enzymatically cleavable linkers. Here, we report the design, synthesis, and characterization of a library of supra-molecular polymer prodrugs based on poly(ethylene glycol) (PEG) and the proregenerative drug 1,4-dihydrophenonthrolin-4-one-3-carboxylic acid (DPCA). Structure–property relationships were elucidated through experimental characterization of prodrug behavior in both the wet and dry states using scattering techniques and electron microscopy andcorroborated by coarse-grained modeling. Molecular architecture and the hydrophobic-to-hydrophilic ratio of PEG–DPCA conjugates strongly influenced their physical state inwater, ranging from fully soluble to supramolecular spherical assemblies and nanofibers. Molecular design and supramolecular structure, in turn, were shown to dramatically alter hydrolytic and enzymatic release and cellular transport of DPCA. In addition to potentially expanding therapeutic options for DPCA through control of supramolecular assemblies, the design principles elaborated here may inform the development of other supramolecular prodrugs based on hydrophobic small-molecule compounds.

8:15 AM SF05.08.02
Probing Self-Assembly Pathways in Solvent Vapor Annealed Block Copolymer/Homopolymer Blends Gregory S. Doerk[1], Ashish Kulkarni[1], Susrut Akkineni[2,3], James J. De Yoreo[2,3], Ruipeng Li[1], Semih Cetindag[1], Beatrice Bellini[4,1], Sanat Kumar[4] and Jasmine Willard[5]; [1]Brookhaven National Laboratory, United States; [2]University of Washington, United States; [3]Pacific Northwest National Laboratory, United States; [4]Columbia University, United States; [5]Alfred University, United States

The self-assembly of block copolymer (BCP) thin films into ordered nanopatterns by microphase separation can be used to create designer functional materials, from optical metasurfaces to ultrafiltration membranes. The sluggish kinetics of macromolecular assembly, however, impedes its real-world implementation as a practical manufacturing method. Solvent vapor annealing and blending BCPs with low molecular weight homopolymer (HP) plasticizers synergistically speed up self-assembly, while solvent-HP interactions alter the free energy landscape in unexpected ways. Using *in situ* characterization during solvent vapor annealing of BCP/HP blends by grazing incidence small-angle X-ray scattering (GISAXS), we have shown that interactions of very short (~3 kg/mol) polystyrene (PS) and poly(methyl methacrylate) (PMMA) HPs with weakly selective tetrahydrofuran solvent vapors can promote the formation of highly-ordered metastable morphologies in an ultrahigh molecular weight (> 1000 kg/mol) PS-block-PMMA BCP [1]. On the other hand, solvent vapor annealing using acetone, a PMMA-selective solvent, results in assembled morphologies that align more closely with expectations based on the overall volume fraction of PS and PMMA. We hypothesize that the blended HP, untethered to domain interfaces, effectively enhances BCP dilution or segregation depending on the solvent selectivity. These metastable nanopatterns are readily transferred into other materials such as silicon, which we use in combination with a novel irradiation-controlled thermal reflow technique to fabricate structural color patterns [2]. Finally, we introduce a prototype spraying instrument designed to enable dynamic control over solvent-polymer interactions for directing self-assembly along specific pathways.

[1] G. S. Doerk *et al.*, Macromolecules **53**, 1098 (2020).
[2] A. A. Kulkarni and G. S. Doerk, ACS Appl. Mater. Interfaces **14**, 27466 (2022).

8:30 AM *SF05.08.03
Self-Assembling Polymer-Directed Hierarchical Porous Structures for Low Carbon Solutions Kwan W. Tan; Nanyang Technological University, Singapore

Hierarchically porous structured materials with multifunctional properties and higher order dimensional complexities are highly desirable for many applications. In this talk I will describe our recent synthesis approaches of directed–self-assembly with block copolymers to generate well-organized porous hierarchically ordered structures of amorphous polymers/carbon, polycrystalline ceramics as well as single-crystal semiconductors. New understanding and control in the formation pathways of self-assembled materials via rapid nonequilibrium synthesis routes will be discussed. Such advanced functional self-assembly-derived materials are of fundamental and technological relevance for emerging low-carbon technologies, e.g., solid-state carbon dioxide adsorbents, separation, energy conversion and storage.

9:00 AM SF05.08.04
Control of Macroscopic Polymer Mechanics through Supramolecular Nanostructure Hyunchang Park[1,2] and Jiheong Kang[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Stanford University, United States

Nature utilizes supramolecular architectures to sustain life. One significant role thereof is to resist external stimuli including mechanical stress and damage. The programmed assembly of biopolymers into the supramolecular structures enables precise control of macroscopic properties and leads to superior functions including mechanical toughening and self-healing. Such supramolecular structures are constructed by the elaborate arrangement of chemically imprinted non-covalent bonds in biopolymers. In the case of synthetic polymeric materials, however, it is challenging to implement stable supramolecular structures in the condensed polymeric matrix where molecular motion is highly restricted. In this study, we have proposed a new strategy to incorporate well-defined supramolecular nanofibers into the polymer matrix and clearly demonstrated the effect of the fibers on the macroscopic mechanical and dynamic properties. We employed flexible PDMS (polydimethylsiloxane)-based polymers with periodically positioned urea functional groups and different structural flexibility around the urea motifs. With low flexibility, the consecutive hydrogen bonding between urea motifs is less feasible due to the limited chance of physical contacts. In contrast, strong consecutive hydrogen bonding can be achieved by high structural flexibility, which enables the growth of stable, robust, and well-defined supramolecular fibers even in highly entangled polymer matrix. The formation of supramolecular fibers in the polymer with high structural flexibility was confirmed by AFM imaging, X-ray scattering, and UV-vis spectroscopic studies. This polymer having rich supramolecular fibers shows higher elastic modulus, compressive strength, and more solid-like behavior compared to the polymer without supramolecular structure, despite the subtle differences in the chemical structure and molecular weight. More intriguingly, we found that selective and orthogonal self-healing takes place when the fibers are embedded in the polymer matrix, which means the fibers recognize each other. To the best of our knowledge, this is the first example of macroscopic self-sorting in self-healing process. We anticipate that our design strategy modulating the structural flexibility around dynamic bonding will provide new insights into the development of versatile, multi-functional supramolecular polymeric materials.

9:15 AM SF05.08.05
Multifunctional Structural Carbon Fiber Composites Using Macropore-Infused Nanocomposite Emulsion Thermosets (MINETs) Yogin Patel, Rituparna Mohanty, Charm Nicholas and Jonathan P. Singer; Rutgers, The State University of New Jersey, United States

Acknowledgement: ONR N00014-21-1-2605
Macropore-infused nanocomposite emulsion thermosets (MINET) are a new class of nanocomposites made from epoxy, nanoparticles, a liquid porogen, and a small quantity of surfactant. These ingredients form an intermediate between a conventional surfactant and a Pickering emulsion to create a bicontinuous network of oil and epoxy composite throughout the processing. After a room temperature cure and usage of different functional nanoparticles, selected based on the performance requirements of a given application, it is possible to design a composite with a range of functionalities, including flexibility, inertness, and electrical/thermal conductivity. By further extraction of the oil phase through rinsing, MINETs can be converted into porous (30~60% open volume) structures without considerable volume shrinkage (~1~5%). The pore size (between 100~10,000 nm) and chemical functionality of the pores is tunable by the constituent nanoparticles, allowing for, for example, hydrophilic or hydrophobic pore surfaces or the incorporation of antimicrobial particles. Simultaneously, the matrix resin can change mechanical properties and use of silicone nanoparticles as a filler can establish flexible behavior. These novel thermosets molded into centimeter to micrometer scale structures that possess interconnected pore networks through the entire

component.
Here, we explore the integration of MINETs into carbon fiber composite (CFC) structures. CFCs are widely used in aerial vehicles due to their low density and high strength. We have developed carbon fiber composites with MINET as a replacement for the resin matrix. Multiple functionalities can be introduced on the same part due to the viscosity of MINET materials and through use of a common resin backbone, which allows the spatial selection of particulate function. Using these MINET materials in combination with CFCs will allow for the selection of desired multifunctionality. Each target functionality requires co-optimization of the mechanical properties of the resulting composite along with the target additional functionality. This process necessitates new fundamental understanding of each component of the MINET blend along with their interaction with each other and with the CFC. As one example, MINETs created with graphene particles can possess electrical conductivities of up to ~10 S/m, which is promising for RF shielding and energy storage applications; however, the co-optimization of processability requires that the samples also have favorable viscosity for molding with carbon fiber, leading to usable conductivities of ~1 S/m. The net outcome of this combination of materials will be a new platform for incorporating multifunctionality in future aerospace structures.

9:30 AM SF05.08.06
Frontal Polymerization-Triggered Simultaneous Ring-Opening Metathesis Polymerization and Cross Metathesis Affords Anisotropic Macroporous Dicyclopentadiene Cellulose Nanocrystal Foam Jinsu Park[1] and Seung-Yeop Kwak[1,2,3]; [1]Seoul National University, Korea (the Republic of); [2]Research Institute of Advanced Materials (RIAM), Seoul National University, Korea (the Republic of); [3]Institute of Engineering Research, Seoul National University, Korea (the Republic of)

Multifunctionality and effectiveness of macroporous solid foams in extreme environments have captivated the attention of both academia and industries. The most recent rapid, energy-efficient strategy to manufacture solid foams with directionality is the frontal polymerization (FP) of dicyclopentadiene (DCPD). However, there still remains the need for a time efficient one-pot approach to induce anisotropic macroporosity in DCPD foams. Here we show a rapid production of cellular solids by frontally polymerizing a mixture of DCPD monomer and allyl-functionalized cellulose nanocrystals (ACs). Our results demonstrate a clear correlation between increasing % allylation and AC wt%, and the formed pore architectures. Especially, we show enhanced front velocity ($\mathbf{v}_f$) and reduced reaction initiation time (t_{init}) by introducing an optimal amount of 2 wt% AC. Conclusively, the small- and wide-angle X-ray scattering (SAXS, WAXS) analyses reveal that the incorporation of 2 wt% AC affects the crystal structure of FP-mediated DCPD/AC foams and enhances their oxidation resistance.

9:45 AM BREAK

10:15 AM SF05.08.07
Block Copolymer Self-Assembly-Directed Chiral Metal Oxide Nanostructures with Visible-NIR Chiroptical Activities and Magneto-Chiral Effects Minju Kim[1], Jiweon Kim[1], Hyunjeong Lee[1], Hyeohn Kim[2], Ki Tae Nam[2] and Dong Ha Kim[1]; [1]Ewha Womans University, Korea (the Republic of); [2]Seoul National University, Korea (the Republic of)

Chiral metal oxide nanostructures have intrigued tremendous attention in nanotechnological applications owing to their remarkable chiroptical and magnetic properties. However, current synthetic methods rely on the use of amino acids as chiral inducers, limiting a large-scale production and a precise control over the synthesis. Here, a general approach to fabricate chiral metal oxide nanostructures with wide spectral responses and tunable magneto-chiral effects is devised, using block copolymer (BCP) inverse micelle templates with supramolecular chirality generated through the complexation with *R/S*-mandelic acid (MA). Diverse chiral metal oxide nanostructures are prepared by the selective occupation of precursors within micellar cores followed by the oxidation process, exhibiting intense chiroptical properties with a g-factor up to 7.0×10^{-3} in the visible-NIR range for the Cr_2O_3 nanoparticle multilayer sample. The BCP inverse micelle is found to inhibit the racemization of MA, allowing MA to act as a chiral dopant that imparts chirality to nanostructures via hierarchical chirality transfer. Notably, for paramagnetic nanostructures, magneto-chiroptical modulation is realized by regulating the direction of the external magnetic field. This BCP-driven approach can be extended to the mass production of chiral nanostructures with tunable architectures and optical activities, which may open up a new horizon for the development of chiroptical functional materials.

10:30 AM SF05.08.08
Selective Chain Mobility Control of a Self-Assembled Gradient Block Copolymer Yemin Park, Seung Won Song and Yeon Sik Jung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Ultra-high-resolution patterns have become necessary for the development of semiconductor integrated circuits, and extreme ultraviolet lithography (EUVL) is a leading candidate for the mass production of sub-10nm patterns. However, EUVL has stochastic issues that lead to the formation of defects such as bridges, broken lines, and missing holes. As a solution, directed self-assembly (DSA) of block copolymers (BCPs) can be utilized for the formation of a defect-free encapsulation layer on EUV pattern masks.
To achieve sub-10 nm patterns, BCPs with high Flory-Huggins parameters (χ) are generally required for high quality pattern resolution. However, although high-χ BCPs can be obtained, it is challenging to obtain aligned patterns due to their slow self-assembly kinetics. As an alternative, gradient BCPs are advantageous for high resolution patterns due their rapid self-assembly kinetics. A gradient block consists of gradual composition change from the block junction region to the tail, which creates enough surface energy difference between the polymer blocks to energetically drive perpendicular lamellar formation. Yet, although EUV-scale patterns can be achieved with gradient BCPs, the χ values are not sufficiently high for low roughness. Therefore, a new method for the treatment of patterned BCPs is required for the improvement of pattern quality.
Here, we suggest a simple and novel treatment method that selectively increases the mobility of block junction polymers of gradient BCPs using a pinpoint solvent vapor treatment system. For demonstration, we newly synthesized a styrene (S)/2,3,4,5,6-pentafluorostyrene (PFS) gradient with an Si-containing 4-(tert-butyldimethylsiloxy)-styrene (4BDSS) copolymer block (P(S-g-PFS)-b-P4BDSS) via reversible addition-fragmentation chain-transfer polymerization. PPFS and P4BDSS form the block junctions, and the key to the pinpoint solvent vapor treatment system is to selectively provide solvent vapor-induced mobility to PPFS chains in metaphase after annealing. Solvents with high swelling ratios and solubility parameters similar to those of the polymers were chosen for solely targeting PPFS. When the solvents plasticize the target polymers, it leads to the reduction of the effective glass transition temperature of PPFS whereas P4BDSS remains unaffected. While it is challenging to synthesize BCPs with high χ values, this simple pinpoint solvent vapor treatment system provides a universal method for increasing the morphology quality of various self-assembled BCP patterns. Ultimately, the pinpoint treatment method resolves the stochastic issues of EUV-scale BCP patterns, on which an encapsulation process is performed for EUV-mask formation.

10:45 AM SF05.08.09
Self-Regulation and Long-Range Coordination in Nanocomposite Blend Self-Assembly Emma Vargo and Ting Xu; UC Berkeley, United States

Blends of nanoparticles, polymers, and small molecules can self-assemble into optical, magnetic, and electronic devices with structure-dependent properties. Across this range of applications, a nanocomposite blend's performance is a function of both its microscopically-averaged structure and its individual nanoscopic defects. Previously, top-down approaches have been employed to control nanocomposite structures and defect densities, including lithographically-patterned templates, external fields, and/or lengthy annealing processes. The strength and beauty of self-assembly, however, comes from its bottom-up nature. We hypothesized that nanocomposite systems could achieve precise structures and extremely low defect densities through self-regulation alone. Guided by this principle, we successfully fabricated nanocomposite multilayer films with large periodicities (172 nm) and the lowest defect densities reported to date (< 0.06 stacking defects / μm^2). To produce each film, a solution of diblock copolymers, organic small molecules, and nanoparticles was drop-casted and left to dry. Successful self-assembly was achieved across a range of substrates (silicon, glass, polyester), thicknesses (1 µm films to bulk solids), and drying times (30 minutes to multiple days). The films' excellent order does not come from optimized processing conditions, but from self-regulation across increasing distances during the assembly process. Systematic neutron and x-ray scattering experiments suggest that self-assembly occurs in two stages. First, chain entanglement drives the growth of high-aspect-ratio sheets from the polymer, nanoparticle, and small molecule building blocks. After the sheets form, they proceed to self-assemble as colloidal platelets, neatly stacking to maximize entropy. The self-regulation demonstrated by the nanocomposite spans six orders of magnitude in size, from the molecular building blocks to the millimeter-sized grains of nearly-perfect layers. The combination of low defect densities and large microdomains make the nanocomposite an efficient dielectric coating material. The nanocomposite blend can be redissolved and recast without loss of structure, providing a readily-recycled alternative to existing laminated composites. Overall, this work demonstrates how microscopic and macroscopic features contribute to the performance of a technologically-useful nanocomposite, and proposes self-regulation as a means of achieving order at—and beyond—the nanoscale.

11:00 AM SF05.08.10
Helicity Control in a Chiral Twist-Bend Nematic Phase of an Achiral Conjugated Polymer Using Cosolvency Effect Zhuang Xu and Ying Diao; University of Illinois at Urbana-Champaign, United States

The chiral twist-bend nematic (N_{tb}) phase composed of heliconical structures formed by an ensemble of achiral bent-core-like mesogens is the newest nematic phase, having only been identified experimentally in 2011. To date, there are still many unknowns regarding the nature of its phase behavior and material universality. For example, such a phase has rarely been reported in a lyotropic or polymeric system. Herein, we show the formation of N_{tb} phase of an isoindigo-bithiophene-based conjugated polymer in the mixture of two seemingly poor yet selective solvents, which is governed by the balancing of the polymer backbone and side chain interactions. More importantly, by varying solvent mixing ratio, we show a fine control of liquid crystalline phase behaviors, including the aspect ratio of nematic tactoids and their critical size for homogeneous-to-bipolar transition in the coexistence region of the isotropic + nematic phase, and the helical pitch at multi-length scales in the N_{tb} phase. The underlying mechanism involves the rigidity modulation of the polymer fibers serving as building blocks for the liquid crystalline phases. This study opens up perspectives on assemblies of achiral polymeric materials into chiral N_{tb} phase with controllable helicity and phase behavior.

11:15 AM SF05.08.11
Self-Assembly Beyond Water—Forming Lipid Vesicles and Vesicle-Gels in Polar Organic Solvents Faraz Burni, Srinivasa R. Raghavan and Niti Agrawal; University of Maryland, United States

Surfactants added at low concentrations can thicken or gel water by two routes. In one case, they can self-assemble into long, flexible chains called wormlike micelles. In a second case, surfactants can form vesicles, which can close-pack and fill the volume. Laundry products such as fabric softeners are known to contain close-packed vesicles. Vesicles are nanoscale containers where a bilayer of surfactants encloses an aqueous core. They are extensively used in drug delivery. While vesicles in water are well-known, there are *no reports of vesicles in polar organic solvents* like glycerol, formamide, or ethylene glycol (EG). Here, we demonstrate the formation of nanoscale vesicles in the above solvents using the common phospholipid lecithin (derived from soy). Our samples are mixtures of lecithin and the solvent with no additional cosurfactants or salt. Lecithin spontaneously gives rise to viscous fluids at low concentrations (~ 3%), with structures ~ 200 nm detected by dynamic light scattering. At higher concentrations (> 10%), lecithin forms clear gels that are strongly birefringent at rest. Dynamic rheology confirms the elastic response of the gels. Images from cryo-SEM indicate that the concentrated samples are **'vesicle-gels'**, with close-packed multilamellar vesicles. The discovery of vesicles and vesicle-gels in polar solvents widens the scope of systems that can be created by self-assembly. Interestingly, vesicles in polar solvents are stable indefinitely whereas in water, vesicles tend to aggregate or coalesce over time. The stability is attributed to refractive-index-matching between lipid bilayers and the solvents, i.e., these vesicles are relatively *invisible* and thus experience only weak attractions. The ability to use lipids (which are 'green' or eco-friendly molecules derived from renewable natural sources) to thicken and form gels in polar solvents could also prove useful in a variety of areas, including cosmetics, pharmaceuticals, and lubricants.

11:30 AM SF05.08.12
Secondary Self-Assembly Switches on Singlet Fission David J. Jones; University of Melbourne, Australia

Multiple exciton generation (MEG) through singlet fission (SF) is a spin allowed process whereby a singlet excited state is split into two triplet excitons. Inclusion of MEG chromophores into solar cells raises the maximum theoretical efficiency of a solar cell from the Shockly-Queisser limit of 33% to around 45% by effectively harvesting the energy from high energy photons. SF has been reported and extensively studied in crystalline acenes, and more recently acene dimers to better understand the fundamental photophysics and materials requirements for SF. Incorporation of these SF materials into functional solar cells, although demonstrating modest efficiency enhancements, has had limited success. In our efforts to produce higher efficiency printed organic solar cells we had the desire to incorporate solution processible SF materials in printed organic solar cells, however most of the reported SF materials are highly crystalline and either do not promote SF in the solid state or controlling crystallisation in the deposited films is difficult.
Singlet fission yields are stronly dependent on crystal packing with different polymorphs resulting in low or no singlet fission.The strong pi-pi interactions of a fluorenyl-substituted hexabenzocoronene (FHBC) donor, generate a hexagonally packed discotic liquid crystalline structure, with pendant triplet host chromophores (THCs). Through design of intra-molecular singlet fission materials, with a linker designed to promote secondary self-assembly, we have demonstrated the ability to enhance highly ordered thin films and high solid state singlet fission yields[1].
A number of promising SF chromophores do not support SF in the solid state, due to crystal packing that does not appropraite orbital overlap. Recently we have discovered that we can turn on singlet fission in these chromophores, when the THC is linked via a molecular core that promotes secondary self-assembly, for some chromophores that do not promote SF due to poor crystallisation.
In this talk I will discuss new systems being developed in my laboratory for siolid state SF, where the secondary self-assembly is key in generating high SF yields. The materials have been extensively studied in solution and in thin film by steady state and ultra-fast spectroscopy, both transient absorption, and GIWAX. for example, thin films of the discotic liquid crystalline FHBC(TDPP)$_2$ material forms hexagonally packed columns and has a singlet energy level of 2.00 eV. SF studies on FHBC(TDPP)$_2$ demonstrate a triplet yield of 150% in amorphous thin films, increasing to 170% in thermally annealed films.

[1] Masoomi-Godarzi, S.; Liu, M.; Tachibana, Y.; Mitchell, V. D.; Goerigk, L.; Ghiggino, K. P.; Smith, T. A.; Jones, D. J., "Liquid Crystallinity as a Self-Assembly Motif for High-Efficiency, Solution-Processed, Solid-State Singlet Fission Materials" *Adv. Energy Mater.* **2019,** *9* (31). **DOI**: 10.1002/aenm.201901069

11:45 AM SF05.08.13

Soft Capsules That Change Shape and Exhibit Structural Color Due to Nanoparticle Assembly in Their Cores Medha Rath, Taylor J. Woehl and Srinivasa R. Raghavan; University of Maryland, College Park, United States

Dyes and pigments are the primary source of color for most materials. However, they are susceptible to environmental (light, heat, etc.) or chemical damage and can easily fade over time causing the color to fade. Coloration that is resistant to damage and fading is desirable. For instance, structural color or iridescence is a phenomenon primarily observed in nature (butterflies, mollusks, birds, etc.) that shows brilliant colors due to the nanoscale morphology and structure of the material instead of chemical dyes. Structural color emerges due to the long-range ordered arrangement of non-absorbing nanostructured particles that diffract light at a particular wavelength corresponding to their size. Since structural color emerges from nanoscale morphology of the material, the colors are non-fading if the microstructure remains. Most natural and synthetic materials exhibit permanent structural color, while complex nanocomposites are required to generate materials that exhibit reconfigurable structural color.
Here we demonstrate a simple approach to obtain structural color within a millimeter sized hydrogel capsule. We fabricate a thin spherical polymer hydrogel shell of alginate surrounding an aqueous liquid core containing a concentrated dispersion of silica nanoparticles. The hydrogel shell acts as a selective permeation barrier, allowing water and small molecules to pass between the liquid core and surrounding fluid, but excluding large polymers and nanoparticles. Placing the capsule in a concentrated polymer solution (*e.g.*, polyacrylic acid, sodium alginate) induces a positive osmotic pressure gradient on the capsule that causes water to diffuse out of the capsule, causing it to collapse. Nanoparticles are entrained in the fluid flow out of the capsule and captured on the inner surface of the hydrogel shell. Electron microscopy and dark field optical microscopy show that the nanoparticles formed a conformal layer and colloidal crystal particles that were tens of microns in size on the inner hydrogel surface. Video rate fluorescence microscopy of fluorescent polystyrene tracer particles show there were recirculating fluid flows inside the capsule during osmotic pressure-induced collapse, which deposited the colloids onto the inner surface of the hydrogel shell. The final collapse step of the capsule, where the hydrogel shell with positive curvature buckled into a complex 3D shape with negative curvature, such as a bowl or folded shape, served to pack the colloids into ordered structures responsible for structural color. We demonstrate that this phenomenon is reversible and can be applied to a range of nanoparticle sizes. Interestingly, we find that the final shape and geometry of the collapsed capsule is dependent on the type and concentration of osmolyte used.

SESSION SF05.09: Application of Assembled Materials I

Session Chair: Shuai Zhang
Thursday Afternoon, April 13, 2023
Marriott Marquis, B2 Level, Golden Gate B

1:30 PM SF05.09.01
Optimal Binding Affinity for Sieving-Type Separation of Propylene from Propane in an Oxyfluoride Anion-Based Metal-Organic Framework Yi Xie; The University of Texas at San Antonio, United States

Highly efficient adsorptive separation of propylene from propane offers an ideal alternative method to replace the energy-intensive cryogenic distillation technology. Molecular sieving-type separation via high-performance adsorbents is targeted for the superior selectivity but the limit in adsorption capacity remains a great challenge. Here we report an oxyfluoride-based ultramicroporous metal-organic framework **UTSA-400**, [Ni(WO_2F_4)($pyz)_2$] (pyz = pyrazine), featuring one-dimensional pore channels that can accommodate the propylene molecules with optimal binding affinity while specifically exclude the propane molecules. The exposed oxide/fluoride pair sites in **UTSA-400** serve as strong functional sites for strengthened propylene-host interactions, resulting in a significantly enhanced adsorption uptake, while the propane molecules are excluded due to the regulated host dynamics. The strong propylene binding enables near saturation of propylene in the pore confinement at ambient conditions, leading to full utilization of pore space and superior packing density. Dispersion-corrected density functional theory calculations and *in situ* infrared spectroscopy clearly unveil the nature of boosted host-guest binding. Direct production of polymer-grade (>99.5%) propylene with remarkable dynamic productivity is demonstrated by column breakthrough experiments. This work presents a feasible strategy to break the trade-off in adsorptive separation through guest binding optimization in molecular sieve.

1:45 PM SF05.09.02
Self-Assembled Artificial Water Channels—Structural Determinants of for Enhanced Membranes Filtration Performances Mihail Barboiu; Institut Europeen des Membranes, France

Artificial water channels-AWC and their natural aquaporin counterparts are selectively transport water. They are a tremendous source of inspiration to construct biomimetic membrane technologies, including desalination. These biomimetic membranes contain variable nanochannel constructs with adaptative architectures and morphologies. Herein, we critically discuss the structural details that can impact on performances of biomimetic I-quartets AWCs obtained *via* adaptive self-assembly of alkylureido-ethyl-imidazoles **HC4-HC18** in bilayer or polymeric desalination membranes. We first revisit I-quartet performances and transport behaviors in bilayer membranes, identifying that hydrophobicity is an essential key parameter to increase water permeability. We compare various channel types with different hydrophobic tails (from **HC4** to **HC18**) and we found in particular that a huge increase in single channel water permeability from 10^4 to 10^7 water molecules/s/ channel is obtained by increasing the size of grafted alkyl tail. Quantitative assessment of biomimetic AWC-polyamide membranes formats show that pure water permeability increases from roughly 2.09 to 3.85 L m^{-2} h^{-1} bar^{-1}, for **HC4** and **HC6** membranes while maintaining higher salt rejection (99.25-99.51%) while the **HC8** loading induce a drop of performance reminiscent with a defective membrane formation. We show that the production of nanoscale defects can be obtained with insoluble low soluble and low dispersed particles of AWCs, explaining observed subpar performance. We conclude that optimal solubility enabling breakthrough performance, must be considered to maximize the inclusion and the stability in the bilayer membranes or to find an optimal homogeneous distribution of percolated particles that minimize the defects in hybrid polyamide membranes.

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[2] M. Di Vincenzo, et al. *Proc. Natl. Acad. Sci. USA,* **2021**, *118(37)*, e2022200118
[3] L.-B. Huang, M. Di Vincenzo, M. Göktuğ Ahunbay, A. van der Lee, D. Cot, S. Cerneaux, G. Maurin, and M. Barboiu, *J. Am. Chem. Soc.* 2021, *143*, 14386-14393.

2:00 PM SF05.09.03
Induced Fit of Adsorbates inside Nano-Sized Quantum Confinements Aisha Ahsan[1,2], Luiza Buimaga-Iarinca[3], Lutz A. Gade[4] and Thomas A. Jung[2,1]; [1]University of Basel, Switzerland; [2]Paul Scherrer Institute, Switzerland; [3]CETATEA, Romania; [4]Universität Heidelberg, Germany

Host-guest architectures provide ideal systems to investigate site-specific physical and chemical effects. Condensation events in nanometer sized confinements are particularly interesting for the investigation of inter-molecular and molecule-surface interactions. They may be accompanied by conformational adjustments representing induced fit packing patterns. Here, we report that the symmetry of small clusters formed upon condensation, their registry with the substrate, their lateral packing as well as their adsorption height is characteristically modified by the packing of cycloalkanes in confinements. While cyclopentane and cycloheptane display cooperativity upon filling of the hosting pores, cyclooctane and to a lesser degree cyclohexane diffusively re-distribute to more favoured adsorption sites. The dynamic behaviour of cyclooctane is surprising at 5K given the cycloalkane melting point above 0°C. The site-specific modification of the interaction and behaviour of adsorbates in confinements plays a crucial role in many applications of 3D porous materials as gas storage agents or catalysts/bio-catalysts.

2:15 PM SF05.09.04
Super Diffusive Self-Aligning Vertical and Lateral Interconnect Formation by Gas Phase Electrodeposition Leslie Schlag, Nishchay A. Isaac and Heiko O. Jacobs; TU Ilmenau FG Nanotechnologie, Germany

This presentaion reports self-aligning metallic vertical and lateral intterconnect formation by gas phase electrodeposition. Key operational parameters to fabricate vertical ruthenium and rhodium interconnects (via) with a diameter of 100 nm are discussed. Moreover, airgaps are implemented during the deposition process, which utilizes spark discharge to generate a flux of charged nanoparticles. An inert gas flow transports the nanoparticles through a reactor chamber close to the target substrate. As well, the talk will introduce a super diffusive approach for gas phase electrodeposition, which uses a substrate with pre-patterned resist openings to guide the nanoparticles in the self-assembling manner into the openings by an interplay of drag, Coulomb force, and Brownian motion. Five process parameters were identified, which impact the morphology and conductance of the resulting interconnects: spark discharge power, gas flow rate, micro lens via dimensions, substrate surface potential, and in-situ flash lamp power. This parameter set enables a controlled adjustment of the vertical and lateral interconnect morphology and its minimum feature size. Gas flow rate in combination with spark discharge power contribute significantly to the morphology of the interconnect. Spark power and micro lens via dimensions have the largest influence on the surface potential of the insulating resist cover, which enables a localized micro lensing gas phase electrodeposition of a via with a controlled ratio between conducting diameter and airgap. To get a better insight into the growth characteristics, a statistical model leads to a better understanding of gas phase electrodeposition. The model implements that added to usual standard diffusion with random walks in a certain direction, long flights occur to a particle as well, if there is an additional the electrical field. As a result, the diffusion factor D is not a constant anymore and follows the approach of super diffusion.

2:30 PM BREAK

3:30 PM SF05.09.05
Nucleation Enhancement Mechanism of Ruthenium Metals Thin Films by Atomic Layer Deposition Amnon Rothman, Dionysis Tsousis and Stacey F. Bent; Stanford University, United States

Noble metal thin films have attracted much attention due to their unique properties and structure, leading to a wide variety of applications in microelectronics, catalysis, energy and photovoltaics. Different parameters determine the metal properties for these applications, where an important one is the deposition process. One of the common deposition methods is atomic layer deposition (ALD), a surface-sensitive thin-film deposition technique. The self-limiting surface reactions during the ALD process promote the layer-by-layer growth mechanism, thus providing significant control over the film thickness and conformality. However, due to an island growth mechanism and nanoparticle formation, it can be difficult to achieve the formation of continuous and pinhole-free layers from noble metal ALD on oxide surfaces, leading to poor-quality films. These nonidealities are mainly due to a lack of nucleation sites for the noble metal ALD on oxide substrates and a poor wettability of these low-surface energy surfaces. In order to maximize the potential of ALD, it is important to fully understand the nucleation and growth mechanism of the ALD process. This work focuses on nucleation enhancement of ruthenium ALD as a model system. Ruthenium metal is a promising candidate in thin film technology because of its low bulk resistivity, high work function, thermal stability even at a higher temperature, low specific electrical resistivity even in its oxidized state, and low solid solubility with strong adhesion to copper. These properties make ruthenium an attractive barrier metal or seed layer for copper electroplating.
We study the nucleation enhancement of ALD ruthenium layers on silicon substrates by using single organometallic monolayers, with and without H_2O exposure, prior to deposition. The nucleation enhancement is demonstrated for ruthenium ALD using three different ALD precursors with different ligands. The results show that pretreatments with organometallic molecules (trimethylaluminum or diethylzinc, with and without H_2O, prior to deposition) reduce the nucleation delay of the ruthenium layer. The surface pretreatment strongly influences the ruthenium nucleation, yielding up to a 2.1-fold increase in surface coverage. The ruthenium ALD nucleation and growth mechanism are studied using scanning electron microscopy (SEM), ellipsometry and X-ray photoelectron spectroscopy (XPS) on the treated and untreated substrates. A theoretical model based on the Avrami nucleation model is developed and fitted to the experimental results, pointing to the possible growth enhancement mechanism, which we propose occurs by increasing the surface diffusion of nanoparticles/adatoms on the pretreated surface. Implications of the nucleation enhancement strategy applied to other metal ALD systems will be discussed.

3:45 PM SF05.09.06
Nanopore Wettability and Transport Laura Despot, Adnan Khalil and Annette Andrieu-Brunsen; TU Darmstadt, Germany

Porous inorganic-organic hybrid materials can be prepared using evaporation induced self-assembly (EISA) and they are of particular interest in the field of nanofluidics, as understanding and design of wetting-transport interplay as well as wettability-defined liquid infiltration into porous materials is not fully understood but important for improving transport-related applications. Here, we investigated the interplay of wetting and molecular transport in mesoporous silica layers. Via post-functionalization of mesoporous thin films with perfluorinated silanes or co condensation of tetraethoxysilane with methylated silanes mesoporous thin films with tuneable wettability were obtained. Wettability dependent water sorption, molecular transport and water imbibition were studied using ellipsometry and cyclic voltammetry as well as cameras and image analysis for fluid imbibition evaluation. Among others, we show the direct correlation between wetting properties of mesoporous silica thin films and ionic mesopore accessibility determining two different transport mechanisms. Furthermore, we show the influence of wettability on the imbibition area around a water droplet, deposited on the mesoporous surface. We show the importance of wettability dependent evaporation resulting in fluid front oscillations. The obtained results improve the understanding of solid-liquid interaction in nanopore confinement and help to improve nanopore transport-related applications such as nanofluidics.

4:00 PM SF05.09.07
Ultrasound-Assisted Directed Self-Assembly Digital Light 3D Printing of Composites Wei Zhai, Xinwei Li, Guanjin Li and Kian M. Lim; National University of Singapore, Singapore

The advent of advanced manufacturing technologies brings about the possibilities of novel materials with potentially unprecedented material properties. Through ultrasound-assisted directed self-assembly digital light processing, we present a novel class of composite – the discontinuous interpenetrating-phase com- posite (d-IPC) – where the cellular filler phase is based on lines of particle assemblies, as opposed to continuous materials. Through yttria particle doping, we fully illustrate the unique microstructural-specific mechanical properties of the d-IPC. Despite being fully bulk and having a similar density (1.18 g/cm3) and strength (68 MPa) as the matrix polymer, it presents an additional plateau-deformation behaviour under large compressive strains and hence a 218% increase in specific energy absorption up to 37 J/g. The enabling mechanism is derived from the peculiar discontinuous and macroscopically aligned particle-based struts which do not contribute to a notable diminution of strength but can yet modulate high-strain deformation via induction of progressive localized failures. The concept of d-IPC is also extendable to solid fillers of all materials, morphology, and reasonable sizes, allowing the d-IPC to be highly customizable with multifunctional potentials. Through this work, we also aim to demonstrate the potential of using advanced microstructural-controllable manufacturing techniques to achieve conceptually new and advanced composite materials.

4:15 PM SF05.09.08
Multifunctional Electroactive Foams within Flow Catalytic Reactions Jamie Mannering; University of Leeds, United Kingdom

Nanostructured carbon networks assembled into 3D macroscopic foams are exploited as a versatile heterogeneous support framework for flow-based catalytic reactions. The network composition which includes the type of building block (graphene or carbon nanotubes), interconnectivity, pore structure and pore volume fraction all influence the overall macroscopic properties of the foam (i.e. surface area, electrothermal conductivity and mechanical profile) enabling support frameworks that can influence reaction dynamics and provides new avenues of research within heterogeneous catalysis.[1] Here, I explore two distinct functional features of graphene-based macroscopic foams and highlight a burgeoning area of research that encapsulates a wide range of applications from energy storage and generation to (electro)chemical catalysis and environmental remediation.[2]
The first developments utilise graphene-based foams as electroactive sorbents for homogeneous molecular catalysts introducing a novel approach towards a controlled capture-release mechanism providing a modern alternative for a low-cost recyclable system addressing many of the challenges currently facing the pharmaceutical industry. As a consequence, we also reveal how this capture-release mechanism affords interesting opportunities for molecular functionalisation of carbon supports and a unique method of studying heterogeneous-homogeneous catalytic relationships.
Secondly, applying a rapid heating approach within electrothermally conducting ruthenium precursor functionalised graphene-based foams we explore a powerful and generalised tool for the rapid formation of catalytically active metallic nanoparticles that can be regenerated upon reaction deactivation. Moreover, control over the network structure within catalyst functionalised foams provides an interesting approach to explore reaction dynamics to gain an understanding of the implications of fluidic turbulence within a support-induced micromixing environment. Structure-function relationships are examined utilising a templating approach within model graphene-based foams creating different lamellar networks and combining experimental X-ray and electron tomographic data with computational fluid dynamics simulations to quantify the impact of foam structures on reaction output with broad scope implications for various applications.

1.) J. Mannering, R. Stones, D. Xia, D. Sykes, N. Hondow, E. Flahaut, T. W. Chamberlain, R. Brydson, G. A. Cairns and R. Menzel, **Adv. Mater.**, 2021, 33, 2008307.
2.) D. Xia, H. Li, J. Mannering, P. Huang, X. Zheng, A. Kulak, D. Baker, D. Iruretagoyena, R. Menzel, **Adv. Funct. Mater.**, 2020, 30, 2002788.

4:30 PM SF05.09.09
Tailoring Electrode Architectures via Self-Assembly for Scalable Energy Storage Systems Zhengyu Ju and Guihua Yu; The University of Texas at Austin, United States

Replacing fossil fuels-powered vehicles with electric ones is an indispensable part of achieving carbon neutrality in the near future. Although the past decade has witnessed the unprecedented growth of electric vehicle market, long endurance and fast-charging capacities are the two main challenges remained. This asks for lithium-ion batteries, the heart part of the electric vehicle, with both high energy/power and scalability. In this talk, I will present our recent research progress on understanding the underlying charge transport kinetics and designing tailorable electrode architectures via self-assembly enabling high-rate capabilities in scalable thick electrodes. First, electrode-scale alignment is achieved via assembling porous magnetite (Fe_3O_4) nanosheet building blocks under a controllable magnetic field. Electrode architecture-correlated electrochemical properties are quantitatively explored, revealing the merit of low tortuosity characteristics for rapid charge transport from the nano- to microscale. In addition, a high-density yet low-tortuosity electrode is fabricated by magnetic-assisted self-assembly and drying-induced densification of Fe_3O_4 nanoparticle-decorated graphene oxide building blocks. Vertically assembled channels ensure good electrolyte penetration and material utilization, enabling well-maintained charge storage capability when scaling up the electrode thickness. Besides, a universal bidirectional freeze casting methodology is also explored to artificially induce material assembly to form the densely-packed lamellar structure. Simultaneous high areal capacity and rate capability could be realized in various materials-based electrodes attributed to the efficient mass transport in the ordered assembled architecture. Coupled with advanced three-dimensional visualization techniques, our research provides an in-depth understanding of the spatial mass distribution effects on electrochemical properties in thick electrodes, which could offer multiscale design considerations for next-generation scalable energy storage systems.

4:45 PM SF05.09.10
Generalized 3D Microprinting of Functional Nanocrstal-Based Inorganic Aerogels Minju Song and Jae Sung Son; UNIST, Korea (the Republic of)

Aerogels are porous materials with low densities and exceptionally high surface areas made up of non-fluid colloidal nanoscale networks. Due to their distinctive properties, aerogels are excellent materials for a number of applications, such as thermal and acoustic insulation, energy storage, catalyst, adsorbents, filters, electrodes, and sensors. Numerous materials, including oxides, polymers, carbons, metals, and even semiconductors, have thus far been synthesized as aerogels using sol-gel chemistry techniques or by the gelation of clusters or nanocrystals. However, aerogels' inherent brittleness hinders their processability through subtractive processes like machining. For instance, using conventional subtractive manufacturing techniques, the precision micro-processing of aerogels has never been accomplished.
The development of additive manufacturing enabled the fabrication of a wide variety of materials into unique shapes and dimensions, which is regarded as a next-generation manufacturing technique. Furthermore, micro-stereolithography methods based on multiphoton absorption or using a projection lens, as well as direct ink writing with microneedles, enable the development of microscale 3D architectures that have the potential to revolutionize the production of microscale components for a variety of applications, including microelectronics, micro-electromechanical systems (MEMS), and biomedical systems. Recently, 3D-printed aerogels achieved by an extrusion process using viscoelastic inks containing active particles were reported. Although these reports describe the feasibility of 3D printing for aerogels comprised of some specific materials, such as graphene, silica, and cellulose, the methods described have low resolution and are limited to only a few printable materials. For example, the resolution of reported 3D-printed aerogels is generally in the scale of several hundreds of micrometers, and sub-100-micrometers have rarely been achieved. These reported strategies adhere to the common ink extrusion process that requires a viscoelastic formulation of inks to ensure printability. Particularly, the polymer-based viscosifiers used as additives in aerogel-based inks for inorganic materials deteriorate their intrinsic functionality.
Here, we demonstrate an inorganic ligands-capped nanocrystal ink being directly written in the gelation bath as a generalized approach of high-resolution wet 3D microprinting for inorganic aerogels. Our process was designed to immediately link the thiometallate-based inorganic ligands with the coordinating metal ion linkers in the bath, thereby generating multibranched gel networks of various inorganic materials, such as metals, semiconductors, magnets, and oxides, without any organic additives. This method is designed to produce 3D microarchitectures of purely inorganic aerogels while combining the many advantages of conventional nanocrystal-based aerogels, such as material diversity and integrity of crystalline nanostructures. The microscale aerogel

filaments are printed with precisely controlled dimensions from 7 µm to 44 µm. Complex 3D structures are achieved by layer-by-layer deposition of aerogel filaments with highly porous microstructures and high specific surface areas, comparable to those of traditional nanocrystal-based and silica aerogels. In addition, the functionality of primary nanocrystals, including the magnetic, electrical, and luminous properties, were well preserved in the printed aerogels. Additionally, our technology produced multi-material aerogels by sequentially printing each nanocrystal or mixing nanocrystal inks.

SESSION SF05.10: Poster Session II

Session Chairs: Sijie Chen and Xin Zhang
Thursday Afternoon, April 13, 2023
Moscone West, Level 1, Exhibit Hall

5:00 PM SF05.10.01
Submicron TiO_2-Polystyrene Hybrid Hollow Spheres from Pickering Emulsion Polymerization for Visible Light Scattering Liangdong Liu and To Ngai; The Chinese University of Hong Kong, Hong Kong

Opacity, or hiding power, is one of the most important parameters of white coatings. It is dominated by multiple scattering of visible light among pigment particles, which is determined by the light scattering efficiency of the pigments. With the same pigment material, the light scattering efficiency can be varied by adjusting the size of the pigments. However, it does have an upper limit, highest light scattering efficiency, positively related to the reflective index (RI) of the material.
The most widely used white pigment is titanium white (TiO_2) owing to its high RI (2.50-2.80), poor light absorbance in visible region, and high fastness. However, white coating development has been suppressed by the aggregation and sedimentation of TiO_2 pigments, which is caused by their high density (~4 g/cm^3).
To overcome the limitations, we presented a new method to prepare TiO_2-polystyrene hybrid hollow spheres. The hollow structure can not only reduce the density of pigments but also increase the light scattering efficiency. In detail, an organic acid-modified TiO_2 nanoparticle stabilized oil-in-water Pickering miniemulsion was prepared firstly as the template, in which the TiO_2 nanoparticles would be absorbed onto the oil/water interface. Then the droplets were further converted to hollow spheres by interfacial polymerization, which not only reinforced the interface but also bound the TiO_2 nanoparticles together. The hollow spheres can be used for visible light scattering in coatings and have high opacity and stability when compared to other white pigments contributing by their hollow structure. At the same time, a stronger combination between nanoparticles and polystyrene shell is achieved that can resist the shearing force during homogenization. Moreover, the production scale of the method can be further enlarged by using a high-pressure microjet homogenizer, which brings extensive industrial application prospects to the hollow spheres.

5:00 PM SF05.10.02
Tracking Directional Movement of Nanomotors with Liquid Cell Electron Microscopy Jiawei Wan[1,2], Qiubo Zhang[1], Jiayun Liang[2], Karen Bustillo[1], Zakaria Al Balushi[2], Mark Asta[1,2] and Haimei Zheng[1,2]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of California, Berkeley, United States

Liquid cell transmission electron microscopy (TEM) has become a powerful tool for the study of nanoparticle movement and self-assembly. By tracking the individual nanoparticle motion, mechanisms of the movement can be achieved. Extensive studies have demonstrated that various interaction forces contribute to the nanoparticle motion, which lead to the self-assembly of nanoparticles into one-dimensional chains, two-dimensional patterns, and three-dimensional architectures. Nanoparticle motion can be introduced predominantly by electron beam illumination, in which nanoparticles resemble the light-activated nanomotors. Herein, using cadmium chloride tetrahydrate ($CdCl_2·4H_2O$) nanomotor as an example, we studied the relationship between the configurational asymmetry and consequent motion of a nanomotor. Using in situ liquid cell TEM, we observed the directional motion of a $CdCl_2·4H_2O$ nanomotor under electron beam irradiation. The movement dynamics were regulated by the configurational asymmetry of the nanoparticles, which was caused by the difference in the reaction activity of various crystal facets. High resolution TEM images and numerical simulations showed a working mechanism that was related to the electric field generated around the nanomotor. This work points out the influence of asymmetry on the dynamics of nanomotors. Also, this study contributes to the understanding of mechanisms on nanoparticle movements and self-assembly, and suggests a new strategy for designing nanodevices for applications.

5:00 PM SF05.10.03
Exclusive Production of Icosahedral and Single-Crystalline Photonic Colloidal Clusters through Osmosis-Induced Consolidation of Emulsion Droplets Yehun Choi and Shin-Hyun Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Monodispersed colloids can spontaneously form crystalline lattices, which have been used as photonic materials with bandgap properties. Emulsion template provides spherical microparticles with colloidal crystals through a confining spherical geometry. The photonic microspheres have different photonic properties compared with film format as their varied crystalline structures. Therefore, the photonic microspheres have served differentiated applications with a bulk film format such as structural colorants, colorimetric microsensors, and optically-encoded microcarriers. In addition, the emulsion template provides a tool to study the crystallization behavior of colloids under confining spherical confinement. The microsphere composed of ih and fcc colloidal arrays has anisotropic optical properties as the orientation of the microsphere responsible for different crystalline faces. Therefore, the fcc and ih microspheres show various reflection colors and patterns as their rotate. These unique properties, distinguished from optically isotropic onion-like or polycrystalline microspheres, render the fcc and ih microspheres potentially appealing for advanced structural colorants and active color pixels.
To assemble colloids confined in droplets, the emulsions are usually exposed to air to let the dispersion medium of the droplet phase dissolves into and diffuses through the continuous phase and finally evaporate into the air. Although fcc structures and ih structures are more energetically stable than onion-like or polycrystalline structures in spherical confinement, these structures are only produced when the colloids are condensed slowly enough to arrange the colloids even after the nucleation from the droplet interface. Nevertheless, the fraction of fcc structures is not high because the evaporation rate of emulsion droplets varies depending on the position of droplets; the evaporation of medium is faster for the droplet closer to the emulsion-air interface due to the shorter diffusion length.
In this work, we suggest the osmotic extraction of water from particles-laden emulsion droplets using salt-dissolved droplets for the consolidation of colloidal particles at a consistent and controlled rate. Two different emulsion droplets containing polystyrene particles and salt are respectively prepared by a microfluidic device to have uniform size, which are randomly mixed to induce a water flux from the particles-laden droplets to salt-dissolved droplets. Therefore, the particle droplets gradually shrink whereas the salt droplets inflate. The rate of shrinkage is consistent as most particle droplets are subjected to a similar number of neighboring salt droplets for the random mixtures. Moreover, the narrow gap between two distinct droplets leads to fast water flux owing to a short diffusion length. Importantly, the rate of shrinkage is controllable in equal temperature conditions by adjusting the concentration of salt.

An optically-anisotropic fcc and ih structure is produced at a high fraction for slow consolidation with a low concentration of salt. It seems that the reduction of osmotic pressure difference and loosening of particle droplet-to-salt droplet contact in a course of the osmosis gradually slows down the shrinkage of droplets, which facilitates the particle rearrangement near the critical volume fraction responsible for spontaneous crystallization, enabling the production of fcc or ih structure even for a short overall consolidation time with high fraction. In addition, it is possible to produce an optically-isotropic polycrystalline structure for relatively fast consolidation with a high concentration of salt. This osmosis-induced consolidation protocol is applicable for polydisperse emulsion droplets produced by bulk emulsification, potentially providing a simple yet reliable means for the large-scale production of photonic microspheres.

5:00 PM SF05.10.04
Design and Assembly of Colloidal Quantum-Dot-Based Three-Dimensional Optical Nanostructures Geon Yeong Kim, Shinho Kim, Min Seok Jang and Yeon Sik Jung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

An optical nanostructure can be rationally designed in the way of desired light interactions. The coupling between nanostructure and electromagnetic wave enables manipulating a light traveling path, phase, and polarization state. Realizing high-performance optical components such as light sources, antennae, filters, and photodetectors has been focused on for decades. In particular, periodically arranged subwavelength optical nanostructures have been spotlighted owing to their excellent light controllability beyond conventional bulky optical components. 3D nanostructure, along with its 2D counterpart, has attracted significant interest in optics over decades due to the potential for omni-direction manipulation of electromagnetic waves. Various tools for the fabrication of artificial nanostructure have been demonstrated, including e-beam, focused ion beam, dip-pen, laser interference, nanosphere, and nanoimprint lithography. However, the inherent constraints of materials, complex and time-consuming fabrication, and limits in large-scale production have hindered the potential for high-performance 3D nanostructure. Above all, the fabrication of 3D structures with colloidal nanoparticles (cNPs) is yet considered to be challenging technically. Hence, for functional cNP-based optoelectronics, the developed fabrication method providing versatile platforms is necessary. Here, we report a new scheme of nano-transfer printing to build cNP-based 3D optical nanostructures. The transferred patterns feature outstanding pattern quality on a centimeter scale. A 3D structure can be formed with fully suspended multiple layers. The individual layer of a few hundred-nanometer thicknesses can be stacked with arbitrary angles, giving tunability in 3D structure symmetry, which is an essential requirement for high-performance 3D optical applications. Our strategy is adaptable for various nanoparticles covering all surface energies through controlling polymer brush and picking layer. Among potential applications of colloidal quantum dots (cQDs)-based optical nanostructures, two functional 3D optical nanostructures are demonstrated; emissive CdSe QDs for down-conversion QD film and absorptive PbS QDs for a circularly polarized light detector. Matching the absorbed energy of both devices to the resonance frequency of each nanostructure is crucial for substantial absorption efficiency. As the matched wavelength with the periodic structure results in optical resonance, this can increase light absorption into the incorporated QDs with more extended light-matter coupling. Consequently, a significant increase in photoluminescence in the CdSe structure and circular dichroism intensity in the PbS structure are achieved, both corresponding to high-performance devices.

5:00 PM SF05.10.05
Molecular Self-Assembly of Organic Semiconductors on Strained Graphene Jisang Park[1], Jinhyun Hwang[1], Hyo Chan Lee[2] and Kilwon Cho[1]; [1]Pohang University of Science and Technology, Korea (the Republic of); [2]Myongji University, Korea (the Republic of)

Graphene has been utilized as a growth template for self-assembly of organic semiconductor thin films (OSCs). Synthesis and transfer of graphene on a target substrate can cause a non-uniform strain field in the graphene, so morphology and crystallinity of the deposited OSC films can be altered. A strain field in graphene also introduces pseudo-electric field in graphene. The effects of strain in graphene template on graphene-organic molecule interactions during epitaxial growth of organic molecule have not been considered yet. Here, we investigated the effects of strain and strain-induced pseudo-electric field of graphene template on the self-assembly of organic molecules. We examined early stage of the growth and nucleation behavior of C60 thin films on the strained graphene. We propose that the strain-induced pseudo-electric field in graphene modulates the binding energy of organic molecules on the graphene. Our study on the growth of OSC thin films on strained graphene would lead to the understanding of the relation between the organic-graphene molecule interactions and the pseudo-electric field of graphene.

5:00 PM SF05.10.07
Confinement Driven Self-Assembled Fibrous Liquid Crystalline Polymer Jae Gyeong Lee[1], Jae Gwang Kim[2] and Jeong Jae Wie[1]; [1]Hanyang University, Korea (the Republic of); [2]Texas A&M University, United States

Liquid crystalline polymers have drawn a significant attention as a programmable material owing to their self-assembly capability with directed molecular orientation. In a hydrophilic media, liquid crystalline molecules, mainly consisting of hydrocarbon, construct spherical micelles to minimize the surface tension. Recent study reported formation of branched fibrous networks with liquid crystalline oligomers in an aqueous media, driven by molecular heterogeneity. Alteration of balance between interfacial energy and elastic energy generates the kinetic fluctuation during the construction of vesicles upon the oligomerization. In this study, we constructed fibrous liquid crystalline polymer with a high aspect ratio in a microchannel filled with aqueous media. The micro-channel induces confinement effects in liquid crystal oligomer droplets, providing the directional self-assembly. We will discuss analysis of fractal dimension and lacunarity to quantitatively demonstrate linearity of the liquid crystalline fiber.

5:00 PM SF05.10.08
Multi-Scale Investigation of Self-Assembly Induced by Capillary-Forces in Arrays of Carbon Nanotubes—From Density Functional Theory to Gecko's Effect Stefania Carapezzi[1], Aida Todri-Sanial[1,2] and Gabriele Boschetto[1]; [1]LIRMM, University of Montpellier, CNRS, France; [2]Eindhoven University of Technology, Netherlands

Self-assembly is a large ensemble of bio-mimicking strategies, where the organization of components into desired geometries is achieved without human intervention. This can be purposeful exploited to drive the fabrication of aggressively miniaturized devices, overcoming the material and engineering limitations of fabrication of non-planar 3D structures at such scales. However, self-assembly may have also a detrimental impact. This is the case with procedures involving wet etching or cleaning of vertically aligned nanostructures with high aspect ratio, such as nanowires and carbon nanotubes (CNTs). Then, the associated drying process involves a capillary menisci between adjacent nano-pillars, where the induced lateral forces may be strong enough to bend and finally assemble these nano-objects together. The consequent misalignment resulting from the processing of densely-packed arrays of 1D nanostructures affects negatively the physical properties associated to the preservation of their vertical direction.
The ability to engineer and control self-assembly is critical both to avoid undesired effects or, on the contrary, to exploit them smartly to build nanoarchitectured materials. In particular, the elasto-capillary driven self-assembly of arrays of 1D nano-structures is a complex phenomenon where different aspects play a role, such as the mechanical properties of the nano-structures, the geometrical properties of the array, and finally the evaporation rate and the surface tension of the fluid. In this work, we propose a multi-scale investigation of capillary-force-driven self-assembly of arrays of CNTs. In particular, density functional theory is used to predict the dependence from diameter and chirality of the relevant mechanical properties of CNTs: Young's modulus, Poisson's ratio, and surface energy. Then, we combine these physics-based parameters with a theoretical model describing the contact behavior

of fibrillar interfaces in lizards (Gecko's effect). Finally, we illustrate the inferences that our approach yields regarding the occurrence of self-assembly induced by capillary-forces in arrays of CNTs.

References

S. Carapezzi, G. Boschetto, A. Todri-Sanial, Nanoscale Advances, 4, 4131-4137, 2022. https://doi.org/10.1039/D2NA00295G

5:00 PM SF05.10.09
Bio-Engineered Polydopamine Nanoparticles for Biomedical Applications Swetha Lingamgunta; University of Cambridge, United Kingdom

Polydopamine (PDA) is a eumelanin-like biopolymer that is gaining popularity for various medical applications such as photothermal therapy, drug delivery and antimicrobial applications.[1] PDA can be synthesised through the oxidation of dopamine under basic conditions and utilised as nanoparticles, coatings and films.[2] Furthermore, PDA has remarkable adhesive properties which stem from various functional groups present within the structure of PDA (amino, imino, hydroxyl and catechols) and π-π interactions.[2] Its anti-oxidant pro-oxidant properties have also allowed it to be utilised by researches to enhance photodynamic anticancer therapy (PDT).[3] Functional groups present such as phenol groups, catechol, carboxy, o-quinone, amino, imine, which have a strong ability to combine with metals via chelation, π–π stacking interactions, electrostatic interaction, hydrogen bonding.[4] In this work, we utilise this characteristic of PDA for antimicrobial applications (e.g. we explore microwave enhanced PDA-silver nanoparticles) or to be used as a nanocarrier for radiolabels (e.g. chelator free labelling of many metals). In the context of drug delivery, plentiful aromatic rings in PDA makes it possible to load chemical drugs or dyes on their surface via π–π stacking and/or hydrophobic–hydrophobic interactions.[5,6] To enhance drug loading and delivery, we attempt to increase the PDA nanoparticle surface area and loading capabilities. In this work, we describe methods by which PDA NPs can be utilised to maximise drug delivery and radiolabelling for imaging.

5:00 PM SF05.10.10
Reconstruction Engineering of Oxygen-Deficient Metal-Oxide Nanoparticles Toward Effective Chemical Conversion and Energy Applications Mansu Kim[1], Jonghwan Park[2], Namgee Jung[3], Dongmok Whang[2] and Joseph T. Hupp[1]; [1]Northwestern University, United States; [2]Sungkyunkwan University, Korea (the Republic of); [3]Chungnam National University, Korea (the Republic of)

Metal-organic frameworks (MOFs) typically consist of coordinated metal ions or clusters and multitopic organic bridging ligands, utilized as precursors for metal oxide-based catalysts on 3D porous networks. Here, we report on the formation of well-dispersed ZrO_2 clusters with a size of less than 1 nm from atomic-level ordered MOFs in a perfectly controlled annealing environment. Heat treatment in a high temperature and inert environment forms oxygen defects in the ZrO_2 particles, which inhibits particle growth and increases the uniformity and formation of defective ZrO_2 nanoclusters. Also, MOFs containing various transition metal precursors show completely different trends after annealing in the same environment. In MOF, the Zr ion of Zr_6 node and metal precursor ions compete to occupy preferred oxygen in an oxygen-deficient environment, which affects the size and structure of ZrO_2 particles after the annealing process. Restructuring engineering of metal oxide nanoparticles opens up a wide range of applications and particle formation at very small levels that have not been approached by conventional methods.

5:00 PM SF05.10.11
Investigating Crystallization Pathway of DNA Voxel Assembly Katerina R. DeOlivares[1], Zohar A. Arnon[1], Daniel McKeen[1], Aaron Michelson[2,1], Brian Minevich[1] and Oleg Gang[1,2]; [1]Columbia University, United States; [2]Brookhaven National Laboratory, United States

The ability to design and engineer complex, functional and tunable nanoscale architectures remains a continual challenge in the field of nanotechnology. Currently, many conventional nanofabrication techniques lack the specificity and control required to develop precisely organized three-dimensional (3D) nanomaterials and are limited in their ability to incorporate nanoparticles. Self-assembly approaches offer a viable alternative, as such methods enable the integration of a diverse array of nanoparticles. Particularly, a DNA-based assembly approach leverages the specificity and programmability of Watson-Crick base-pairing to form designable organized architectures with high precision at the nanoscale. DNA can be folded into origami frames and integrated with nano-cargo, thus creating a unit block, or a so-called material voxel. Previous studies from our group have shown that these individual voxels can reversibly self-assemble into 3D crystal lattices through DNA-driven assembly and thermal annealing. While the structures of a variety of DNA voxel lattices have been extensively characterized, less is known about the mechanism of nucleation, crystal growth and disorder-to-order transition. Specifically, there is limited understanding of how the thermal protocols promote the transition from amorphous assembly to a crystalline lattice, and how the assembly pathway affects the formation of intrinsic defects and imperfections in the lattice. We utilized in-situ synchrotron-based small-angle X-ray scattering (SAXS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to gain insight into structural evolution during the assembly process and thermal annealing. In addition, we investigated the crystallization pathway with single nanoparticle resolution using x-ray nano-tomography to visualize 3D structure and occurring defects at different pathway stages. The presented work provides insight on structure and morphology of intermediate states during self-assembly, which is critical for minimizing defects. The established methodology will lead to improvements in the design of self-assembly pathways and the realization of more complex engineered nanomaterials.

5:00 PM SF05.10.12
Design of Nanoreactors—Role of Dimensionality on Thermodinamics and Kinetics of Reactions Cecile Malardier-Jugroot and Manish Jugroot; Royal Military College of Canada, Canada

From the medical field to new technologies, the potential applications of nanomaterials and their impact in the development of smart materials capable of reacting to their environment is thriving. The characterization of phenomena at the nanoscale has revealed novel properties for natural as well as synthetic materials and unveiled the complex nature of the interactions occurring at that scale requiring an interdisciplinary approach to successfully develop new and revolutionary applications. In particular, biomimetism has shown great promises in the development of sensors, nanocatalysts, green processes for the use of sustainable energy sources. Biomimetism is divided in two main research areas: reproducing structures of biological systems or mimicking its function and physical properties. The first approach often combines biological systems (like enzymes) to artificial systems to take advantage of the high efficiency of the biological system optimized for specific physiological conditions. However, due to the high sensitivity of biological systems to change in their environment, the efficiency of these structures can decrease significantly with small perturbations. The second method that will be detailed in the presentation, mimics the physical properties and enhanced reactivity of biosystems has the distinct advantage of allowing the development of tailored structures stable under various conditions retaining the very high efficiency of their biological counterparts. The presentation will highlight the crucial role of confinement in equilibrium interactions and rates of reaction, as well as the effect of dimensionality on the thermodynamics and kinetics of reactions within the nanoreactors. The design and characterization of the nanoreactors and metal catalysts (Pt and Au) combines molecular modelling, dynamic light scattering, quasi-elastic neutron scattering and UV-Vis. The insight gained on the development of nanoreactors has allowed the synthesis of highly catalytically active monoatomically thin Au layers, stable under normal temperature and pressure conditions.

5:00 PM SF05.10.14
One-Dimensional, Lepidocrocite-Based Nanofilaments and Their Self-Assembly Kaustubh Sudhakar, Michel Barsoum, Hussein Badr and Avishek

Karmakar; Drexel University, United States

Water stable, one dimensional, 1D, materials are few and far between and none are titania-based. Herein we react inexpensive, water insoluble titanium-based precursors - TiC, TiB_2 and TiN - with 25 wt. % tetramethyl ammonium hydroxide (TMAH) in water at 80°C, under ambient pressures to produce C-containing, 1D sub-nanometers lepidocrocite-based inorganic polymer chains that, depending on reaction times - varied between 2 and 5 days - and processing details self-assemble into a plethora of hierarchical microstructures that range from 2D flakes to 1D nanofilaments with subnanoscale cross-sections. Using X-ray diffraction, X-ray photoelectron, Raman, transmission and scanning electron micrographs, and selected area diffraction we determine that regardless of the experimental conditions, nanofilaments are omnipresent along with a relatively small fraction of nanoparticles. The cross-section of these nanofilaments is 5x5 $Å^2$ and can be microns long. In all cases, however, like in organic polymers, the 1D nature of the material is preserved.

The first-of-a-kind *dual bottom-up* strategy prompted nanoengineering of 2D materials could build up new roadmaps towards fabrication of functional materials for sustainable future.

5:00 PM SF05.10.15

Switching Lattice Parameters of 3D DNA Frameworks Dayoung G. Lee[1], Zohar Arnon[1], Brian Minevich[1], Daniel McKeen[1], Daniel C. Redeker[1] and Oleg Gang[1,2]; [1]Columbia University, United States; [2]Brookhaven National Laboratory, United States

Nanomaterials with switchable and stimuli-responsive properties, such as repairing, sensing, and reconfiguration, are of great interest for medical, optical, and energy applications. However, the challenge remains to implement such dynamic properties into nanomaterial systems. DNA has demonstrated the capability to self-assemble into nanostructures with well-defined geometries and nanoscale precision, due to its unique programmable properties based on complementary base pair binding. Recent advancements in DNA nanotechnology show that it is possible to design and generate diverse three-dimensional (3D) nanoscale polyhedral frames constructed from DNA with ability to carry a variety of nanoscale cargo. Individual 3D DNA frames have external complementary bonds, known as sticky-ends, that are responsible for inter-frame binding. These programmable interactions drive the assembly of the frames into well-ordered superlattices with different crystal symmetries and provide an opportunity to implement stimuli-responsive capabilities. Here, we present a switchable and reversible control over DNA framework lattices with a switchable motif integrated into inter-frame linkers. The length of the switchable linkers can be changed on demand in response to the DNA signals. This allows for changing lattice parameters of the 3D superlattice in a facile and rapid manner. Furthermore, we explored the differentiation and control of switchable linkers for different axis in response to specific signals to enable anisotropic responses. Small-angle X-ray scattering (SAXS) techniques and electron microscopy methods were applied to study the structure and reconfiguration of the discussed system.

5:00 PM SF05.10.16

Assembly of Donor-Acceptor Stenhouse Adducts onto Cotton Textiles via Two-Step Immobilization Approach Jennifer J. Leung and Juan Hinestroza; Cornell University, United States

Smart textiles are emerging innovations adding technology to the basic textiles known. Many industries require the use of textiles that can accommodate and support their niche functions and environmental demands. A subset of smart textiles includes photochromic textiles. Photochromic dye molecules are situated into textiles to create commonly done via microcapsules or implementing traditional dye methods. Once integrated and stimulated by a light source, the photofunctionality is induced in the polymer matrix and can also be reversed. This reversibility can occur through heat activation or light irradiation, classifying the photochromic molecules as either T-Type or P-Type, respectively. Donor-Acceptor-Stenhouse-Adducts (DASAs) are a recent discovery of photochromic photoswitches that can be integrated in a variety of materials to advance the efficacy of smart textiles. Compared to other photoswitching molecules, DASAs offer advantages such as easier synthesis, hydrophilic-hydrophobic molecular micelle stability, high yield, fatigue resistance, and fine tunability. The simplified mechanism of DASAs isomerizes a colored, hydrophobic linear molecule into a colorless, hydrophilic cyclic version via visible light irradiation. Heat can then be applied to induce the cyclic to linear DASA reversibility of the T-type photochromic molecule. Upon its discovery, DASAs have been studied into generations to better understand its utilities, improve their limitations, and extend their capabilities. DASAs offer a platform of photoswitching capabilities that can be integrated in a variety of materials to advance the efficacy of smart textiles. In first generation DASAs, the donor-acceptor structure is composed of an alkyl amine with typically either a Meldrum's acid or barbituric acid. Successful and effective self-assembly and reversibility for first generation DASAs are reliant on solvent choice. Different solvents can either drive or inhibit the mechanisms at which the DASA enters a phase change in the photoswitching process. DASA photoswitching has been successfully demonstrated on polymers and surfaces from DASA modified polydopamine coated silica micro/nanoparticles on glass substrates to DASA-azobenzene-polystyrene mix on glass substrate to DASAs onto TiO_2 anatase surfaces but not on textiles. First generation DASAs are integrated on cotton for the first time via a two-step assembly approach. Cotton fabric is amine functionalized via the attachment of N, N-methyl(2-bromo-ethyl) ammonium bromide, creating secondary amines on the cotton samples. Then, the DASA compounds, 5-(furan-2-ylmethlene)-2,2-dimethyl-1,3-dioxane-4,6-dione, are self-assembled onto the cotton fabric. DASAs aggregate and stabilize themselves onto the cotton samples. Environmental stimuli such as visible light irradiation, water, and heat were induced onto the DASA-modified samples to understand the photochromic intensities and reversibility in unique situations. The confirmation of successful DASA attachment was confirmed through characterization and measurements including H-NMR and C-NMR spectroscopy, FTIR, and CIELAB Color Space (L*a*b). The characterizations and measurements displayed successful immobilization of first generation DASAs onto cotton. The stimuli induced onto the modified cotton gave insights into how DASAs on cotton could respond on a larger scale in various environments.

5:00 PM SF05.10.17

The Influence of the Roundness of Polymer-Grafted Nanocubes on Their Self-Assembly Behavior Priscilla F. Pieters[1], Emma Vargo[1], Yiwen Qian[1], A. Paul Alivisatos[1,2] and Ting Xu[1,1]; [1]University of California, Berkeley, United States; [2]The University of Chicago, United States

Polymer-grafted nanoparticles (PGNPs), which consist of an inorganic core and a polymer shell, offer many possibilities to build advanced materials. Expanding our materials library from spherical particles to faceted particles opens up a whole new space of self-assembled materials that can exhibit emergent properties, with self-assembly driving forces unique to their shape and the polymer conformation on the surface. This work aims to understand the self-assembly behavior of faceted PGNPs, by investigating the interplay of the nanoparticle geometry and contributions from the surface ligands on the self-assembly of nanocubes, including the structural and orientational order of the superlattices.

Monodisperse and shape-pure iron oxide nanocubes were self-assembled at the air-liquid interface, and their superlattice structure was studied with TEM and scattering experiments. In the absence of a polymer shell, the superlattice structure is predominantly determined by the shape parameter of the nanocubes, which we can consider as the *hard* roundness of the particles. This *hard* roundness does not alter the orientational order of the superlattice, and therefore all the nanocubes are aligned inside the superlattice. Hower, when introducing a polymeric ligand onto the surface of the particles, we alter the *soft* roundness of the particles. This influences the superlattice structure similarly to the *hard* roundness, however it also alters the orientational order between the particles, where increasing the *soft* roundness decreases the lateral orientational order in the nanocube superlattice. We demonstrate that this separate control of nanoparticle shape and polymeric ligand can be utilized to achieve control of the structural and orientational order of the nanocubes.

Our research shows that small changes can be used to guide the self-assembly of faceted particles, opening up avenues for the design of new advanced materials. Additionally, the structure and orientation dependent properties of these materials can be studied.

5:00 PM SF05.10.18
Revealing the Relationships Between System Design and Imperfections in DNA-Assembled Nanoparticle Lattices Eric Shen and Aaron Michelson; Columbia University, United States

A defining quality of nanoscale materials is the ability to fine-tune their properties by adjusting the system architecture and constituent elements. DNA origami – customizable wire-frame voxels – afford us a bottom-up fabrication platform with a high degree of control over the self-assembly of nanoscale crystalline frameworks and the organization of cargo such as nanoparticles and proteins within those assemblies. This methodology lets us fabricate complex, multifunctional lattices with varying symmetries. One of the core challenges is the development of methods to understand the relationships between prescribed structures and the resultant properties of nanomaterials.

In studying the defects and imperfections in engineered nanoscale systems, we can probe the average for a population of assemblies or the intricacies of a single sample. Small angle x-ray scattering (SAXS) and x-ray tomography correspondingly examine these two modes of nanoscale lattices. We used hard x-ray nanoprobe (HXN) tomography to investigate the 3D organization of nanoparticle superlattices supported by inorganically templated DNA-voxel frameworks. We simultaneously collected transmission ptychography data and fluorescence data to reconstruct a volumetric map of individual gold nanoparticles throughout a nanoscale lattice with 7-nanometer resolution. In addition, this allowed us to pinpoint and detail the presence of point vacancies and interstices, screw dislocations, and grain boundaries. Because the presented approach is non-destructive, we coupled it with synchrotron-based small angle x-ray scattering (SAXS) on the same sample to gain insight into the ordering and structure of the global population of nanoparticle lattices. Together, these methods explain the role system design parameters, such as frame geometry and bond design, have on the defects and imperfections found in engineered nanoscale lattices.

Author list and reference: Aaron Michelson, Brian Minevich, Shih-Ting (Christine) Wang, Hanfei Yan, Chonghang Zhao, Yong Chu, Xiaojing Huang, Oleg Gang

5:00 PM SF05.10.19
Kinetically Controlled Phases in Complexed Block Copolymers Boyce Chang; Iowa State University, United States

Block copolymers (BCPs) are macromolecules with well-defined architecture and can self-assemble into intricate nanostructures. Feature sizes of BCPs are molecularly defined and could range from optical wavelengths down to sub-10nm. Thus, they have been utilized for the fabrication of photonic crystals, selective membranes, and semiconductor patterning. The nanostructure formed by BCPs depend on its molecular weight and fraction of each block. More recently, it has been shown that BCP morphology can be similarly altered using selective continuous flow solvent vapor annealing (SVA) (Figure 1). Here, we demonstrate the effect of SVA conditions on the morphology of thin film complexed BCP. Solvent activity, quenching and affinity are systematically investigated through a flow controlled system.

5:00 PM SF05.10.21
Unassisted Hydrogen Peroxide Production via Buckypaper-Integrated Perovskite Photocathode—Passivation Strategy for Stable Aqueous Electrolysis Dongrak Oh, Rashmi Mehrotra and Ji-Wook Jang; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Hydrogen peroxide (H_2O_2), one of top 100 chemicals, is a representative eco-friendly oxidizing agent serving as wide range of applications such as wastewater treatment, the paper industry, and pulp bleaching etc. In addition, H_2O_2 is a promising eco-friendly energy carrier together with H_2, because it possesses similar energy density (3.0 MJ L^{-1} at 60%) to compressed H_2 (2.8 MJ L^{-1} at 35 MPa), and ease to store and transport as it is liquid phase unlike gas phase of H_2. On the other hand, currently more than 95% of H_2O_2 is industrially produced by the anthraquinone oxidation process, which requires complicated multi-step, hazardous organic chemicals consuming much fossil fuels and producing large amount of CO_2. Thus, development eco-friendly technology for H_2O_2 production is very essential.

In this point, solar H_2O_2 production via the single-step $2e^-$ oxygen reduction reaction (ORR) offers a simple, safe, and sustainable way. Current solar H_2O_2 production applications, however, only utilize inorganic-based photoelectrodes. Such electrodes intrinsically show poor charge transfer characteristics and thus result in low performances. On the other hand, perovskite (PSK) photoabsorbers offer many benefits over inorganic-based photoelectrodes such as a longer charge carrier diffusion, band tunability, and an excellent light absorption coefficient. However, despite of these better features, PSK materials have not attracted much attention because of their poor stability in aqueous solution.

Herein, we introduce an unassisted hydrogen peroxide production system in an aqueous electrolyte with oxidized buckypaper (O-BP)-integrated perovskite photocathode. The technical strategy building proper junction between active surface catalyst and photoabsorber serves as critical role to enhance the stability of perovskite electrode. First, O-BP which is self-cross-linked by oxidized carbon nanotubes is fabricated for the efficient $2e^-$ ORR. Experimental measurements demostrates conspicuous advantages of such sheet type carbon compared to powder in terms of physical stability on photoelectrode, while it still shows 100% of Fradaic efficiency and excellent stability. Next, highly efficient inorganic–organic methylammonium lead triiodide ($MAPbI_3$)-based photocathode is synthesized to utilize solar energy. Finally, Field's metal (FM) is used as interlayer between O-BP surface catalyst and perovskite photoabsorber. FM melts at ~65 °C and solidifies at ambient temperature, which easily control their state and thus results in formation of tight attachment facilitating charge transfer and perfect protection from aqueous electrolyte invasion when it's liquid and solid, respectively. From the fusion of three part technically, the stable O-BP-integrated pervoskite photocathode shows better stability (for 45 h) compared to that of the non-passivated PSK layer (for few minutes) in no external bias system with famous a-$NiFeO_x$ oxygen evolution electrode. Moreover, a H_2O_2 production rate of ~0.751 μmol min^{-1} cm^{-2} and ~1.463% of solar-to-chemical conversion efficiency (SCC) was achieved. This work presents importance of engineering skill by utilizing only well-known catalysts and photoabsorber, demonstrating significant increase of SCC compared to previous works.

5:00 PM SF05.10.22
Electrophoretic Formation of Colloidal Crystals and Their Inverse Opals in Large Areas Shun-Yu Tsai, Yun-Cheng Huang, Wai-Hong Cheang and Puwei Wu; National Yang Ming Chiao Tung University, Taiwan

We demonstrate the use of a variety of electrophoresis techniques to fabricate colloidal crystals (polystyrene microspheres, SiO2 microspheres, core-shell microspheres) and their relevant inverse opaline structures. The electrophoresis involves the suspension of those microspheres and the imposition of electrical fields to direct their packing into ordered structures in large-area. An example of our recent work is the formation of monolayered polystyrene microspheres on a two-inch GaN wafer, with a half-layered ZnO occupying the interstitial voids among the neighboring polystyrene microspheres. This structure serves as the gradient refractive index layer that faciliates the transmission of light from the GaN. Lastly, we will discuss the possibility of combining dielectrophoresis and electrophoresis for assemblying microspheres.

5:00 PM SF05.10.23
Evaluation of Strength of Sintered Porous Titanium Containing Biodegradable Polymer Chuen Kum Lee[1], Naritoshi Aoyagi[2] and Mari Miyata[2]; [1]Nanyang Polytechnic, Singapore; [2]Nagaoka College NIT, Japan

Introduction: Ti6Al4V alloy is widely used as a biomedical material due to its excellentcorrosion resistance and mechanical properties. On the other hand, bio-based polymers have an excellentbiocompatibility and biodegradability. By impregnating a bio-based polymer into a porous titanium surface, it may be applicable as a new biomedical material with excellent mechanical properties and biocompatibility. In this study, four types of bio-based polymers were used: cellulose derivative (hereinafter, BP1), PLA (BP2),chitosan (BP3), and chitosan derivative (BP4). The purpose of this study is to clarify the structure, compressive strength and bending characteristics of porous titanium materials and its composites.
Methods: Commercial Ti6Al4V powder with 45μm was used as raw material for porous titanium. Porous titanium was produced by spark plasma sintering method at 30MPa pressure with a temperature of 750degree. It has 20mm diameter and 10mm height with a porosity of 27%. After polishing the surface to 0.1μm,compression test specimens were obtained by wire cutting. These specimens are 5mm in diameter and 10mm height. These specimens were impregnated with four types of bio-based polymers. Firstly, these bio-based polymers were dissolved in chloroform, and then soaked in the solution for 2 hours, degassed for 1 hour and impregnated. Microstructures and sintered surface morphology were observed with a scanning electronmicroscope (SEM). Compression tests were performed at a compression rate of 1mm/min, with no lubrication.Compressive proof stress was obtained from stress-strain curves. Three-point bending strength was also measured for porous titanium by ASTM standard. These are 25mm in length, 12.5 mm width and 6 mm thickness.
Results: SEM images were taken at the cross sections of porous titanium and its composites. Polymer impregnation was confirmed by these surface observation and elemental analysis. Compressive proof stress and standard deviation were also obtained.
Proof stress of BP1 composites has 258 MPa. This is lower than porous titanium, 291MPa. Other proof stresses of composites with BP2, BP3 or BP4 showed 345, 348 and 346MPa respectively.
Discussions and conclusions: Composites proof stress is higher than human bone. Standard deviation results show that scattering in stress values tend to be suppressed when polymer was impregnated. Fracture occurs by cracking and propagation. It is considered that cracks firstly initiate into polymer. These cracks are connected with increasing stress. The Gibson-Ashby equation of the form $(\sigma/\sigma_s) = A(\rho/\rho_s)^B$
was used to model the compression stress for this type of open cell material. The parameters σ and σ_s
refer to the compressive stresses of the titanium composites and the theoretical compressive stress of zero porosity titanium respectively. Similarly, the parameters ρ and ρ_s refer to the densities of the titanium composites and zero porosity titanium respectively The coefficients A and B were calculated and will be presented in this work.

5:00 PM SF05.10.24
Logarithmic Correlation and Dispersion of Surfactant-Capped WC/Co Nanoparticle Measured by Atomic Force Microscopy and Dynamic Light Scattering Chengmin Zhang and Byung Yang Lee; Korea University, Korea (the Republic of)

This work reveals a logarithmic correlation between AFM and DLS measured mean particle size according to the relative standard deviation (RSD) using surfactant-modified WC/Co nanoparticles. The ratio of AFM and DLS measurement results is 1 with a 0.07 RSD according to nonlinear regression analysis. The aggregation of WC/Co nanoparticles in aqueous media is a serious problem during the sintering process, which reduces their mechanical properties due to local overheating. Here, cationic, anionic, and nonionic surfactants with different concentrations are added into WC/Co NPs suspension. Mean diameter and particle size distribution reported by DLS and AFM indicate that 20 mg/L concentration hexadecyltrimethylammonium bromide (CTAB) supplies an optimum dispersion effect due to the electrostatic and steric repulsion force. The zeta-potential, FT-IR, and XRD were carried out to investigate the capping behavior of CTAB on WC/Co nanoparticle surfaces. We hope this report could help to solve the aggregation phenomenon that exists in industry products based on WC/Co nanoparticles and supply a comparison protocol between AFM and DLS on polydisperse nanoparticle size characterization.

5:00 PM
Versatile Metal Organic Frameworks-Based Chitosan Air Filters for Efficient NO and Particular Matter Removal Jooran Kim; Korea Institute of Industrial Technology, Korea (the Republic of)

Chitosan, a naturally abundant and sustainable organic biopolymer, is a linear polysaccharide composed of β-(1–4) glucosamine and *N*-acetyl glucosamine. It is the second most plentiful polysaccharide after cellulose and is useful for an extensive range of applications because of its abundance, low cost, excellent biodegradability, and renewability. Many researchers have successfully synthesized numerous metal organic frameworks (MOFs) and demonstrated their gas adsorption ability, MOFs are difficult to use because of their fragility, nanoscale size, and handling problems. To solve these problems, the *in situ* growth of MOFs on fibers is the most favorable method for the development of air filters, and it can lead to good gas adsorption performances. However, research on chitosan-based MOF filters for NO gas adsorption is very limited. In this study, MOFs (CuBTC or ZIF67) were grown on the chitosan fibers *in situ,* and NO gas adsorption performance was investigated using a real-time gas monitoring system. Further, the PMs filtration efficiency and antibacterial properties of the fabricated materials against *E. coli* and *S. epidermidis* were examined.
ZIF67- or CuBTC-based chitosan fibers grown *in situ* on fibers can be used in the development of effective air filters. In this context, metal–organic frameworks (ZIF67 or CuBTC) are grown *in situ* on chitosan fibers (denoted as C-ZIF67 or C-CuBTC), and the NO gas adsorption performance, particular matter filtration efficiency, and antibacterial properties of the fabricated materials against *E. coli* and *S. epidermidis* are investigated. The specific surface areas of C-ZIF67 and C-CuBTC are 311.9 and 140.1 $m^2\,g^{-1}$, respectively, whereas that of the untreated chitosan fibers is 0.1 $m^2\,g^{-1}$. For C-ZIF67, the NO adsorption efficiency rapidly increases up to 78%; specifically, 70% adsorption is maintained for 65 min. For C-CuBTC, the NO adsorption efficiency rapidly increases up to 54% initially and substantially decreases to 41% after 10 min. Furthermore, C-ZIF67 exhibits a 3.4 times higher NO adsorption capacity than that of C-CuBTC. For C-ZIF67 and C-CuBTC, the filtration efficiencies against PMs were higher than 99%. However, C-CuBTC shows a higher antibacterial activity (99.99%) against *E. coli* and *S. epidermidis* compared to C-ZIF67. The C-ZIF67 and C-CuBTC, derived from renewable resources, can be good alternatives for commercial synthetic air filters because they are biodegradable, cost-effective, and environment-friendly.

SESSION SF05.11: Application of Assembled Materials II
Session Chairs: Biao Jin and Shuai Zhang
Friday Morning, April 14, 2023
Marriott Marquis, B2 Level, Golden Gate B

8:30 AM SF05.11.01
Ultrahigh Porous Aramid Nanofiber Separators by Phase Separation–Controlled Self-Assembly for High-Speed Lithium-Metal Batteries Bongjun Yeom[1], Arum Jung[1] and Jeong Gon Son[2]; [1]Hanyang University, Korea (the Republic of); [2]Korea Institute of Science and Technology, Korea (the Republic of)

Aramid nanofibrils (ANFs) prepared from poly(*p*-phenylene terephthalamide) fibers have showed excellent mechanical properties and electrochemical stabilities with nanoporous structures, that can be promising candidates as advanced separators for Li-metal batteries. However, the ANFs exhibited limited performances in the electrochemical properties and battery performances due to limits in control of porous structures. Herein, we report hierarchically porous aramid nanofiber separators with maximized porosities >95%, that are capable of effectively suppressing the Li dendrite growth while maintaining highly stable cycle performances at high charge/discharge rates. A two-step solvent exchange process combined with reprotonation-mediated self-assembly is utilized to control the bimodal porous structure of the separators. The first solvent exchange step has a critical role in determination of degree of partial assembly of the aramid nanoseed sols into fibrillar forms. pKa-dependent partial assembly of the aramids results in formations of macroporous structures with a few micron diameters inside the separators. Nanofibrillar assembly are completed at the second stage of the solvent exchange with water. Resultant films show hierarchical porous structures containing nanopores in macroporous polymer frameworks to yield a mechanically stable membrane with high porosity of 95% or more. The optimized samples exhibit high ionic conductivities of 1.9–4.0 mS cm^{-1} and high Li-ion transference numbers of around 0.8 because of the ultrahigh porosity and selective affinity to anions. Formation of Li dendrites are effectively suppressed via fast ionic transports and delocalized distributions of Li ions that can be attributed to marcropores and nanopores, respectively. In addition, the $LiFePO_4$/Li full cell retains around 80% of its capacity after 1000 cycles at charge rates of >10 C. The design and control of porous structures at the micro and nanoscales can be an ideal and promising approach for application as separators in Li-metal batteries to achieve excellent cycling performance at high charge/discharge rates.

8:45 AM SF05.11.02
Self-Healing Advanced Microvascular Diaphragms in Gas Transmission Md Mahfujjul H. Khan and Michael Keller; The University of Tulsa, United States

Using a microvascular approach, this study analyzes polymer-based diaphragm materials for their self-healing characteristics. A self-healing diaphragm system was manufactured using Silicone rubber or Polyurethane that can be installed in a commercially available pneumatic controller in gas transmission. Pressure differential tests are conducted up to 25 psi for the manufactured QM280 PDMS lab-scale membrane materials incorporated with self-healing microvascular channels. The Diaphragm performed well up to 15 psi and failed around 25 psi. A fabric reinforcement was designed to improve the performance. FEA study by ANSYS 2021 R2 with Endurica plugin revealed the stress concentration and fatigue life analysis. Three different orientations for microvascular 1 mm diameter channels were considered: Radially oriented 24 and 52 channels and Spirally oriented channels. Diaphragm experiences minimum deformation at the peripheral surface due to the fixed support boundary condition for all cases. Conversely, Maximum deformation occurred at the center for Radially oriented channels Diaphragm. It is worth noting that in the spiral channels diaphragm, the maximum deformation occurs slightly off-center with an indication of bending in one direction. This phenomenon is attributed to the highest density of spiral channels on that side of the Diaphragm. A variable stress field was observed between the sharp joint of the Diaphragm and the stainless-steel plate assembly. The equivalent Von-Mises stress was the maximum of 27.49 MPa for the Radial 24 channels diaphragm, while 48.63 MPa for the Radial 52 channels and 29.28 MPa for Spiral in the TPU-Plate assembly. The variable through-thickness stress experienced by the Diaphragm is attributed to the presence of the stress riser zones around the 1 mm channels. The principal elastic strains obtained from Ansys static structural results were used as the input for the fatigue analysis with Neo Hookean elasticity stress-strain behavior and the simplest Thomas fatigue model. The results revealed minimum fatigue life for Spiral Diaphragm whereas a maximum for the Radial 52 channel. The predicted minimum fatigue life portrayed the edge of the Diaphragm as the weakest zone subjected to fatigue loading. It was evident that the Spiral channel diaphragm sustained 50% reduced fatigue life compared to the radial channel diaphragm. This reduced fatigue life is attributed to the bending stress generation in spirally oriented channels Diaphragm.

9:00 AM SF05.11.03
Self-Assembled Inverse Opal Photonic Crystals as Diagnostic Sensors Natalie Nicolas; Harvard University, United States

Inverse opals are self-assembled porous 3D photonic crystals whose geometry can be controlled by the size of colloidal particles and concentration of ceramic precursor used during deposition. These structures have a unique potential for colorimetric diagnostic sensing of both soluble biomarkers and viral particles. Changes their structural color due to the selective wetting of pores and subsequent change in effective refractive index can be used to distinguish between fluids with different physical properties, which can be indicative of disease states, or to determine the presence of bound particles. The colorimetric differentiation of fluids with nanomolar to micromolar concentrations of surfactants including bile salts is made possible by patterning the surface chemistry of an inverse opal with a self-assembled monolayer of silanes with several different hydrophobicities. The label-free detection of viruses with an optical microscope has been enabled by observing the change in the wetting of a test solution into the inverse opal due to the binding of a virus to the pore wall. By understanding how to better control pore geometry and surface chemistry and their contributions to the interactions between inverse opals and fluids, we can more effectively utilize these structured materials for diagnostic sensing.

9:15 AM SF05.11.04
Metal-Organic Framework-Based Composite Materials for Chemical Sensor Applications Joon-Seok Lee, Seung-Ho Choi, Won-Jun Choi and Seon-Jin Choi; Hanyang University, Korea (the Republic of)

Metal-organic frameworks (MOFs) consisting of metal ions and organic linkers are promising materials considering their large surface area and high porosity for applications in filtration and sensors. So far, various MOFs have been synthesized and demonstrated as chemical sensing layers.[1-4] Nevertheless, the insulative properties of conventional 3D MOFs limit their applications in electrochemical sensing materials. To address these issues, MOFs were incorporated with conductive materials such as carbon nanotubes (CNTs) and graphene and demonstrated in electrochemical sensing layers for gas and ion detections.

In this presentation, we present the electrochemical sensing properties of MOF-based composites. To obtain electrical conductivity, carbon nanotubes (CNTs) were incorporated with MOFs (e.g., MOF-8 and UiO-66) by in-situ growth on the defective surface of CNTs. The chemical sensing properties of the composite materials were investigated by two different types of transduction techniques; i) chemiresistive-type and ii) cyclic voltammetry-type. In terms of chemiresistive-type sensors, we investigated the role of metal nodes and organic linkers in MOFs upon the injection of reactive gas species such as H_2S by spectroscopy analysis. In the case of the cyclic voltammetry sensor, the detection capability of various heavy metal ions such as Hg^{2+}, Cd^{2+}, and Pb^{2+} was investigated using CNT-ZIF-8 composite via redox reactions. The chemiresistive sensor was integrated with a wireless sensing module for application in real-time wireless detection of chemical species. The proposed MOF-based composites as sensing layers can be applied in various fields such as environmental monitoring and healthcare.

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9:30 AM SF05.11.06
Formation of Pseudo-Facets on Polymer Grafted Nanoparticles Induced by Low Surface Curvature Tiffany Chen, Emma Vargo, Junpyo Kwon, Yiwen Qian and Ting Xu; University Of California Berkeley, United States

Polymer chain conformation on polymer grafted nanoparticles (PGNPs) is a versatile handle to modulate PGNP assembly and properties of single component composites (SCCs). Despite the obvious effect of curvature on chain conformation, interfacial width, and particle assembly, only the two extremes have been explored—flat and highly curved surfaces. How polymer chains behave on a lowly curved surface (i.e. large particle), neither faceted nor highly curved, is not extensively studied. This leads to the question of to what extent (e,g, distance from core, surface curvature and grafting density) will the behavior of polymer on lowly curved surface be influenced by neighboring molecules and nanoparticles. It remains unknown whether the polymer chains will behave like on a curved surface or on a flat surface, or they will have emerging behavior of the two systems.

As the surface transition from a small nanoparticle to a flat surface, we hypothesize that the grafted polymer chains may locally organize in the lateral direction. In the size regime where the ratio of particle diameter to polymer radius of gyration is one to two orders of magnitude, polymer brush on nanoparticle can locally rearrange to form faceted polymer grafted nanoparticles that have similar organization as those on faceted particles. Here we tested the hypothesis using polystyrene grafted silica particles, with the particle core size of 100, 150 and 380 nm, polymer molecular weight ranges from 40k to 100k g/mol and grafting density of 0.1 – 0.2 chains/nm^2. Image analysis showed increasing interparticle distance with increasing polymer chain length and 60° interparticle angle of the self-assembled 2D monolayer film, confirming hexagonal packing. Deformations of 2D PGNP monolayer reveals uneven mechanical strength around the core, suggesting different types of chain interactions. Polymer brush form aligned nanofibrils and generate voids in between the particles, while polymer brush at the interstitial sites are intact and less resistant to deformation. We speculate the polymer brush are mobile and can locally rearrange to form pseudo-facets during self-assembly, resulting in weaker mechanical response due to chain interdigitation instead of chain entanglement between the neighboring particles. The width of the voids corresponds to the size of facet, which is consistent with 30° degree vector. Despite the isotropic spherical core, polymer brush can adopt anisotropic organizations. This work utilizes qualitative information to elucidate how energy is absorbed and dissipated across the PGNP system to understand polymer chain conformation. This study also introduces a new parameter of lateral heterogeneity in chain conformation on nanoparticles, subsequently, modulating how PGNPs assemble and the properties of PGNP-based SCCs.

9:45 AM BREAK

10:15 AM SF05.11.07
Structuring Liquids With Chemically Fueled Interfacial Assemblies Sarah Gleeson[1], Paul Ashby[1], Thomas Russell[2,1,3] and Brett A. Helms[1]; [1]Lawrence Berkeley National Laboratory, United States; [2]University of Massachusetts Amherst, United States; [3]World Premier Institute–Advanced Institute for Materials Research, Tohoku University, Japan

Nature uses molecular aggregation to spatiotemporally organize compartments, resulting in precise control over liquid-phase chemistries. Structured liquids are able to partially replicate this natural behavior, using particle and molecular assembly at interfaces to lock unique liquid geometries in place. By adding an internal clock to structured liquids, the ability to control chemical systems in both space and time will enable life-like behavior in liquid materials. Currently, jammed interfaces are energetically trapped into their assembled state and require a stimulus to disrupt their binding to allow for reconfiguration. Here, we show that interfacial assemblies can be transiently energized into an out-of-equilibrium assembly, allowing for a structured liquid interface with a pre-programmed lifetime. We add chemical fuel to convert hydrophilic moieties on a water-soluble polymer into hydrophobic anhydrides, driving the formation of colloidal aggregates in solution and leading to polymer adsorption at an oil-water interface. While the fuel is present, the liquid interface is stabilized by a solid-like film, but over time the fuel is depleted, leading to anhydride hydrolysis and desorption of material from the interface. The result is a transient structured liquid: non-equilibrium liquid compartmentalized geometries that are locked in place for a predetermined amount of time before weakening of the interfacial assembly leads to unjamming and spatial reconfiguration. This provides unprecedented temporal control over structured liquids and a means to design all-liquid chemical systems that autonomously change over time, opening the door to future advances in chemical reactors, timed release, and adaptive membranes.

10:30 AM SF05.11.09
Spontaneous Mirror Symmetry Broken Patterns for Physically Unclonable Anti-Counterfeiting Labels Geonhyeong Park[1], Hyewon Park[1], Joanna M. Wolska[2], Jesse G. Park[1] and Dong Ki Yoon[1]; [1]KAIST, Korea (the Republic of); [2]University of Warsaw, Poland

Advances in technology improve our daily lives. At the same time, however, evolving counterfeit technologies bring enormous challenges. Accordingly, the demand for security systems to protect personal information has been increased. Anti-counterfeiting labels based on physical unclonable function (PUF) are in the spotlight because of their natural randomness, making them difficult to forge. Here, a new concept of PUF is introduced using spontaneous mirror- symmetry breaking facilitated by directed self-assembly of achiral bent-shaped molecules. Statistical analysis of the chiroptical responses shows that this PUF with mirror-symmetry breaking have excellent performances such as uniqueness, reproducibility, stability, and reconfigurability. Furthermore, high-level security tags that embed chiral random patterns in deterministic codes can be fabricated with selective light exposure. Our strategy of incorporating the randomness of nature into artificial devices is expected to serve as a cornerstone for applying various natural phenomena to high-level security systems.

10:45 AM SF05.11.11
3D Printing of Structurally-Colored Architectures Using Bingham Colloidal Inks Jong Bin Kim[1], Su Yeon Lee[2] and Shin-Hyun Kim[1]; [1]Korea Advanced Institute of Science and Technology, Korea (the Republic of); [2]Korea Research Institute of Chemical Technology, Korea (the Republic of)

Nature has adopted spectacular nanoscience in exhibiting structural colors on epidermal skins of organisms or gems. Researchers have endeavored to fabricate artificial structural colors, which are non-toxic, nonfading, and stimulus-responsive. There has been a recent surge of interest in the 3D printing of nanomaterials to form smart interfaces or functional devices. However, nanomaterials with structural colors have rarely been 3D-printed as they should accompany the periodicity in the colloidal arrangement as well as the structural fixation in a three-dimensional space. Recently, 3D printing of colloidal crystals was reported using digital light processing (DLP), but direct writing is still required for more time-efficient and colloid-saving strategies. There are previous studies in direct-writing of colloidal crystals and glasses, but the well-controlled evaporation of the solvent is necessitated so that structural shrinkage occurs and the process is time-consuming.

Here, we fabricated Bingham fluid using the particle aggregation in the repulsive colloidal system, which does not accompany any structural shrinkage after crosslinking and coloration. A novel idea has been applied to make Bingham colloidal inks; hydrophilic nanoparticles dispersed in hydrophobic resin by forming hydrogen bonds are repulsive by steric hindrance, but become linked after the enforced dispersion of hydrophilic solvent which destroys the solvation layer around nanoparticles. Furthermore, the optimal composition has been uncovered by using both the cosolvent which dissolves particles and resin together, and the specific solvent which selectively dissolves into nanoparticles. Both kinds of solvents are found to be crucial in terms of the high modulus of the Bingham ink and ink extrudability without nozzle blockage. In addition, coloration by the well-defined periodicity in a short-range order is adjusted by the mixing ratio of the solvent.

The ink system is composed of silica particles dispersed in urethane acrylate, where the hydrogen bonds between the two form so-called solvation layers around particles where their overlap brings about interparticle repulsion, inducing colloidal crystallization. The linkage between particles occurs after the dispersion of ethanol due to the destruction of solvation layers. Ethanol is penetrated into the voids of particles and refractive indices are matched, hence making the ink transparent. The index match impedes the formation of large aggregations on the ground of minimized van der Waals force. The particle linkage occurs in nanoscale so that the printing resolution is not compromised with Bingham property. The additional dispersion of water more selectively binds the colloidal linkage, resulting in higher modulus and yield stress of the ink. The values are among the highest in the previous reports.

The high modulus and yield stress enable the printing of a sphere, upright tower, tilted tower, and even buildings or insects. UV crosslinking fixes the structures right after the extrusion without any shrinkage from solvent evaporation, where the evaporation only endows them with structural colors by increasing the index contrast. Ethanol dispersion renders the interparticle distance to decrease as it dismantles the solvation layers around particles. Interestingly, water dispersion further decreases the gap between particles as it is selectively dispersed into nanoparticles, thus breaking down the solvation layer further. The optical properties resultingly show the blueshift of the photonic bandgap. The optimal range of mixture dispersion is explored as an excess amount of solvent impairs even the periodicity in a short-range order. This strategy successfully prints customizable 3D objects with structural colors in terms of colors, design, and high-resolution printing. It will open a new avenue in the 3D printing of soft robots and sensors with nonfading and stimulus-responsive structural colors.

SESSION SF05.12: Building Advanced Materials via Aggregation and Self-assembly
Session Chair: Shuai Zhang
Friday Afternoon, April 14, 2023
Marriott Marquis, B2 Level, Golden Gate B

1:30 PM SF05.12.02
New Avenues for Anticounterfeiting by Phase Selection and Plasmonic Shifts in Binary Plasmonic Alloy Nanoclusters Stephan V. Roth[1,2], Matthias Schwartzkopf[1], Niko Carstens[3], Thomas Strunskus[3], Peter Muller-Buschbaum[4] and Franz Faupel[3]; [1]Deutsches Elektronen-Synchrotron DESY, Germany; [2]KTH Royal Institute of Technology, Sweden; [3]Christian Albrechts-Universität zu Kiel, Germany; [4]Technical University of Munich, Germany

Anticounterfeiting decisively relies on tailoring structural colors based on plasmon resonances. The structural color is uniquely determined by the plasmon resonances' spectral shape and position [1]. For the first time, we are able to directly observe in situ and quantify the onset of different phases and compositional changes in binary alloy plasmon-active silver (Ag)-copper (Cu) nanoclusters due to spinodal decomposition [2]. We are able to tune and establish an advanced Cu-rich core and Ag-rich shell morphology for the alloy clusters in a high-density nanocluster plasmonic multilayer device during sputter deposition of the alloy. In this ground-breaking study we are able to quantify effective diffusion coefficients and to clearly corroborate theoretical assumptions on the phase separation process on the nanoscale in complex alloy self-assembled nanocluster devices: With Cu being the structure-defining component and Ag predominantly in the shell, our findings offer the potential to partially decouple structural (distance) effects and size- and composition-related influences on the plasmon resonance in directly deposited, high-density, organic shell-free cluster layers. With scale effects coming into play, we are thus able to uniquely correlate cluster morphology and composition with the changing optoelectronic properties. Such tunable, plasmon resonance-based structural color paves an unprecedented way for advanced for high-density nanocluster-based anti-counterfeiting.

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1:45 PM SF05.12.03
Multifunctional Materials by Self-Assembly of Perovskite Nanocrystals Alberto Sanzde leon, Miriam Herrera and Sergio I. Molina; Universidad de Cádiz, Spain

Metal halide perovskite nanocrystals (NCs) have gained much attention in the last years due to their unique optical properties. In particular, cesium lead halide NCs ($CsPbX_3$, X = Br, Cl and I) present excellent photoluminescence quantum yields and narrow emission line widths. However, $CsPbX_3$ tend to be unstable under environmental conditions (humidity, UV radiation, water, oxygen, heat, polar solvents...), which limits their viability in long-term applications on an industrial scale. Embedding the $CsPbX_3$ NCs in a polymer matrix improves their stability while maintaining their optoelectronic properties. In addition, the possibility of creating a micropattern with the polymer matrix allows the development of multifunctional materials, expanding the number of potential applications.[1,2]

In this context, breath figures (BF) is a bioinspired, bottom-up approach that allows the creation of honeycomb-patterned porous surfaces with controlled topography and composition in one single step by solvent casting. The surfaces are formed by condensation of micron-sized water droplets and self-assembly of amphiphilic compounds (e.g. block copolymers or surfactants), which migrate towards the interface between the water droplets and the organic polymeric solution. When the experimental conditions are optimized, the surface porosity after the BF approach also provides self-cleaning properties to the material, in agreement with the Cassie-Baxter model.[3,4]

We report on the development of a method to prepare nanocomposites by embedding $CsPbBr_3$ NCs in a polystyrene matrix by BF. As a result, a hierarchically structured, hybrid film with double functionality is obtained in one single step within few seconds: the formation of a well-arranged, honeycomb-patterned porous structure confers the hybrid film with self-cleaning properties while the $CsPbBr_3$ NCs keep their luminescent behavior within the polymer. This allows to have a film with controlled composition and topography, being an interesting alternative to top-down techniques as lithography, which are more time consuming and require expensive equipment.

This approach has also been applied onto LED lenses demonstrating its applicability in real-life applications. The strategy herein proposed can potentially be extended to other perovskite NCs and other nanomaterials in order to obtain new hybrid coatings with different functionalities, paving the way to multifunctional materials with self-cleaning properties with potential applications in optoelectronics or photovoltaics.

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2:00 PM SF05.12.04
Multiscale Structural Control of Thiostannate Chalcogels with Two-Dimensional Crystalline Constituents Heehyeon Lee[1,2], Thanh Duy C. Ha[3], Youngtak Oh[1] and Myung-Gil Kim[3]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Korea University, Korea (the Republic of); [3]Sungkyunkwan University, Korea (the Republic of)

Chalcogenide aerogels (chalcogels) are amorphous structures widely known for their lack of localized structural control. This study, however, demonstrates a precise multiscale structural control through a thiostannate motif ($[Sn_2S_6]^{4-}$)-transformation-induced self-assembly, yielding Na-Mn-Sn-S, Na-Mg-Sn-S, and Na-Sn(II)-Sn(IV)-S aerogels. The aerogels exhibited $[Sn_2S_6]^{4-}$:Mn^{2+} stoichiometric-variation-induced-control of average specific surface areas (95–226 $m^2\ g^{-1}$), thiostannate coordination networks (octahedral to tetrahedral), phase crystallinity (crystalline to amorphous), and hierarchical porous structures (micropore-intensive to mixed-pore state). In addition, these chalcogels successfully adopted the structural motifs and ion-exchange principles of two-dimensional layered metal sulfides ($K_{2x}Mn_xSn_{3-x}S_6$, KMS-1), featuring a layer-by-layer stacking structure and effective radionuclide (Cs^+, Sr^{2+})-control functionality. The thiostannate cluster-based gelation principle can be extended to afford Na-Mg-Sn-S and Na-Sn(II)-Sn(IV)-S chalcogels with the same structural features as the Na-Mn-Sn-S chalcogels (NMSCs). The study of NMSCs and their chalcogel family proves that the self-assembly principle of twodimensional chalcogenide clusters can be used to design unique chalcogels with unprecedented structural hierarchy.

2:15 PM SF05.12.05
Rising From the Flatland—A Strategy to Achieve Solid-State Emission and Circularly Polarized Luminescence Zijie Qiu; The Chinese University of Hong Kong, China

Aggregation-induced emission (AIE) describes a photophysical phenomenon in which molecular aggregates exhibit stronger emission than single molecules, thus the AIE luminogens (AIEgens) are promising solid-state emitters. One of the common features of AIEgens is the non-planar molecular structure, which prevents severe π-π interactions in the aggregated and solid states. Rising from the flatland is therefore a general strategy to achieve solid-state emission for various high-tech applications. Chirality and circularly polarized luminescence can also be obtained from non-planar structures. In this talk, I will present several works about the precise synthesis, amplified properties, as well as high-tech applications of organic functional materials with non-planar molecular structures.

2:30 PM SF05.12.06
Surface Assembly of Ionic Liquid Functionalities on Mesoporous Silica to Enhance Paraffin Affinity and Induce Reverse Selectivity for Ethane/Ethylene Separation Fahmi Anwar[1,1], K Suresh Kumar Reddy[1,1], Anish M. Varghese[1,1], Maryam Khaleel[1,1,1], Kean Wang[1,1] and Georgios Karanikolos[1,1,2]; [1]Khalifa University of Science and Technology, United Arab Emirates; [2]University of Patras, Greece

Low molecular weight olefins, such as ethylene, constitute an important feedstock not only in polymer production but also as reactants for the synthesis of several compounds, with a global production rate of over 200 million tons per year. Ethylene is mainly produced by steam cracking of naphtha, and, depending on its final application, it can be obtained in different grades. For example, a high-purity grade (>99.5%) is required for polymer production. To obtain polymer-grade olefins, it is imperative to separate light olefins from paraffins. The state-of-the-art technology for light olefin/paraffin separation is cryogenic distillation, yet because of the similar sizes and close volatilities of the C_2H_4/C_2H_6 molecules, the process is energy-intensive, such that even subtle improvements in the quality of separation can significantly affect the operating cost.
Adsorptive separations based on porous adsorbents exhibit high potential for light-olefin/paraffin separation. As the industrial feed is rich in olefins, developing a paraffin-selective adsorbent is energetically favorable. In this study, we developed surface-functionalized silica-based adsorbents for C_2H_4/C_2H_6 separation which selectively take up ethane because of their enhanced van der Waal's interactions with ethane molecules. Fluorine-containing anions for instance, have been reported to have stronger interactions with C_2H_6 molecules, attributed to the C–H—F van der Waal's forces between the six hydrogen atoms of the C_2H_6 molecule and the fluorine atoms. Therefore, in our work, a fluorine-based ionic liquid (IL) with longer alkyl chains, 1-propyl-3-methyl-imidazolium bis(tri-fluoro-methyl-sulfonyl) imide was selected as the primary IL for grafting on MCM-41 surface *via* silanization to develop a reverse-selective adsorbent.
To study the effect of the type of anion and cation on adsorbent performance, anions such as dicyanamide and stearate were also investigated by switching the anions of the primary IL. In addition, the effect of the cation on the selectivity was investigated by swapping the imidazolium-based cation with a phosphonium-based cation. These novel functionalized adsorbents were observed to switch selectivity after IL modification and exhibited reverse selectivity. The developed adsorbents exhibited also low enthalpies of adsorption, i.e., 12 kJ/mol and 9 kJ/mol for C_2H_6 and C_2H_4, respectively, which implies facile regeneration with reduced energy consumption.

2:45 PM BREAK

3:00 PM SF05.12.07
Growth of Mesoscale Ordered Two-Dimensional Hydrogen-Bond Organic Framework with the Observation of Flat Band Feng Liu[1], Minghu Pan[2] and Fangsen Li[3]; [1]University of Utah, United States; [2]Shaanxi Normal University, China; [3]Chinese Academy of Sciences, China

Flat bands (FBs), presenting a strongly interacting quantum system, have drawn increasing interest recently. However, experimental growth and synthesis of FB materials have been challenging and remained elusive for the ideal form of monolayer materials where the FB arises from destructive quantum interference as predicted in 2D lattice models. Here, we report surface growth of self-assembled monolayer of 2D hydrogen-bond (H-bond) organic frameworks (HOFs) of 1,3,5-tris(4-hydroxyphenyl)benzene (THPB) on Au(111) substrate and the observation of FB. High-resolution scanning tunneling microscopy/spectroscopy (STM/STS) shows mesoscale, highly-ordered and uniform THPB-HOF domains, while angle-resolved photoemission spectroscopy (ARPES) highlights a FB over the whole Brillouin zone (BZ). Density-functional-theory (DFT) calculations and analyses reveal that the observed topological FB arises from a hidden *electronic* breathing-Kagome lattice without *atomically* breathing bonds. Our findings demonstrate that self-assembly of HOFs provides a viable approach for synthesis of 2D organic topological materials, paving the way to explore many-body quantum states of topological FBs.

3:15 PM SF05.12.08
Self-Assembled Magnetic-Fluorescent Nanocluster for Highly Sensitive Rotavirus Detection Hong En Fu and Young Keun Kim; Korea University, Korea (the Republic of)

Rotaviruses are well-known pathogenic agents of severe gastroenteritis responsible for acute diarrhea and vomiting, leading to dehydration and death in young children. The appropriate treatment can avoid the death of patients; however, due to late diagnosis, morbidity is still increasing. Point-of-care testing, especially lateral flow assay (LFA), has received much attention because of its rapid, simple, and inexpensive detection method [1]. Unfortunately, the present LFA kits have poor sensitivities and specificities compared to other immunoassay methods. Recently, magnetic antigen enrichment incorporating both magnetic and fluorescent nanoparticles has dramatically enhanced the sensitivity of the target antigens [2]. However, a significant challenge is the creation of a magnetic-fluorescent nanoconstruct with high magnetic responsivity, strong light emission, and structural uniformity [3]. Here, we developed a facile strategy to synthesize magnetic-fluorescent CdSe-CdS/Fe_3O_4 nanoclusters (CFNCs) for highly sensitive and specific rotavirus detection. The interparticle distance between nanoclusters can be enlarged by regulating solvent polarity, allowing other nanoparticles to penetrate the nanoclusters. We coupled quantum dots to as-synthesized Fe_3O_4 nanoclusters by the above method. Massive CdSe-CdS integration allows for reducing the fluorescent quenching effect. Furthermore, we functionalized CFNCs with biocompatible poly(acrylate sodium salt) on the surface to improve water dispersity and facilitate antibody conjugation. Finally, we evaluated the CFNCs-based LFA performance by detecting the rotavirus as a target antigen, comparing the unconcentrated condition and the magnetic enrichment in fluorescence intensity and detection limit.

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3:30 PM SF05.12.10
Physical Supercritical Fluid Deposition—A Scalable Process for Controlling Polymer Self-Assembly on Surfaces Loren G. Kaake; Simon Fraser University, Canada

Controlling materials self-assembly over a wide range of length scales is vital to advanced applications in a wide variety of fields. The key challenge in developing a fabrication technique is not only to form nanoscale structures reproducibly and robustly, but to direct their placement to form mesoscale and even macroscale structures. To this end, we are investigating self-assembly processes in supercritical fluids. In a correctly chosen solvent system, a solute can exhibit a peak in its saturation solubility with respect to temperature. By holding the solvent at the temperature of the peak and heating the substrate, the solute can be precipitated from the supercritical solvent onto the substrate. The location of the deposition can be controlled by locally heating the substrate, for example, by passing current through lithographically patterned conductive traces. This coupling of solution phase self-assembly and photolithography gives physical supercritical fluid deposition the potential to control material deposition at all length scales. The unique deposition conditions also provide additional means of controlling the nanoscale structure of materials resulting in uncommon morphologies for polymer semiconductors. The self-assembly process takes place in several steps including a solution phase pre-aggregation step that is sensitive to the Rayleigh number of the solution. Following deposition onto the substrate, the presence of solvent additives can facilitate the formation of larger scale structures by increasing the surface mobility of the deposited material.

3:45 PM SF05.12.11
Effective and Sustainable Cs^+ Remediation via Exchangeable Sodium-Ion Sites in Graphene Oxide Fibers Youngtak Oh[1] and Heehyeon Lee[1,2]; [1]Korea Institute of Science and Technology, Korea (the Republic of); [2]Korea University, Korea (the Republic of)

The uncontrolled release of radionuclides following the Fukusima incident has prompted the need for rapid, stable, and sustainable radionuclide-capturing materials. If the intrinsic problems related to the slow adsorption, low capacity, and complexity of surface modulation methods are solved, graphene oxide (GO) structures can be utilized for effective cesium (Cs^+) remediation. This study presents sodium-infused GO fibers with a highly efficient Cs^+ capture ability (150–220 mg g^{-1} capacity within a 30-min saturation time) and consistent regeneration ability. The crucial role of sodium in GO colloid assemblies and the highly efficient and sustainable Cs^+ remediation functionality is investigated.

4:00 PM SF05.12.12
Reformulated FeOOH Acetate Nanoplatelet for Heavy Metal Immobilization DaeBeom Lee, Yun-Sik Lee, Bum Chul Park, Kijong Cho and Young Keun Kim; Korea University, Korea (the Republic of)

Arsenic is a heavy metal that contaminates the ecosystem and originates global damage to a sustainable environment.[1] The attempt to immobilize arsenic using neither nanostructure-engineered material nor natural nanomaterials is suggested due to its productivity and potential to harm the ecosystem in the soil.[2]

Here, we suggest a method to enhance the arsenic immobilization via using sustainable nanomaterial amendment, reformulated FeOOH-acetate nanoplatelets (FAN). Iron oxyhydroxide is a clay mineral that is abundant in the earth's crust and is a sustainable natural material.[3] FAN is synthesized either by reformulating the natural iron oxyhydroxide form or by the particle attachment-based synthesis, both in an expandable scale. In the crystallization process of FAN, acetate anions are coordinated to the iron atom with bidentate bridging, inducing a stacking of FeO_6 octahedron layers with a large spacing. It has an inorganic-organic hybrid structure with an extended lepidocrocite layered structure with a basal spacing of 1.14 nm. FAN immobilizes arsenic by two mechanisms, electrostatic intercalation with a large interlayer spacing and chemical adsorption on the surface of layers. This synergetic adsorption mechanism enables FAN to enhance the adsorption capacity of arsenic species acting as sustainable engineered nano-amendments. The ability to immobilize the bioavailable arsenic is confirmed with the bioassay of collembolan and plant reproduction, and arsenic adsorption results in arsenic-contaminated artificial soil and mine soil. This research will be the basis for crystallization-based engineering of natural materials for a sustainable environment.

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[2] Titirici, M. et al. The sustainable materials roadmap. *J. Phys. Mater.* **5**, 032001 (2022).
[3] R. B. Frankel, Iron Oxides: From Nature to Applications, 1st edition (Wiley-VCH, 2016)

4:15 PM SF05.12.13
Polymerized Ionic Liquid-Enabled Heterostructured Carbon MesoNetworks by Electrospinning Qi Li[1], Feng Yan[1] and John Texter[1,2,3]; [1]Soochow University, China; [2]Eastern Michigan University, United States; [3]Strider Research Corporation, United States

This paper illustrates symmetry-breaking heterostructured network coatings prepared by electrospinning using (1) graphene and (2) MWCNT building blocks. Aqueous thermodynamically-stable dispersions of carbon nanotubes and graphene, respectively, at 6-17% by weight, are prepared liquid phase exfoliation using polymerized (surfactant) ionic liquid stabilizers. These dispersions provide ultra-high thermal conductivity and heterostructured and high specific surface area coatings. Such advanced coatings enable development of a platform for catalytic membranes and electrocatalytic electrodes derived by electrospinning (ES) and further extend the utility and potential of 2D materials and advanced composites based on 2D materials. We demonstrate how networks made by ES can be grown beyond inherent 1D fibers to provide 2D-heterostructured networks as supports and electrodes. Two classes of such networks are presented: (1) randomly oriented graphene flakes connected by nanofibers; (2) 2D-microscale membranes composing mesoscale networks of MWCNTs connected by nanofibers. These MWCNT mesoscale networks exhibit a 0D+1D=2D self-assembly phenomenon that appears driven by (a) polymer bead-necklace connectivity and (b) capillary-force-driven 2D assembly of MWCNT out of a highly electrically polarized columnar fluid stream. **These free-standing 2D heterostructured micro-films have no 2D constituents.** Morphology tuning and densification, and modulation of ionic and electrical conductivities by chemical doping, chemical deposition, and anion exchange are described. Applications of such coatings to catalysis, electrocatalysis, and energy devices (batteries, fuel cells, and dye-sensitized solar cells) are discussed.

SESSION SF05.13: Virtual Session: Building Advanced Materials via Aggregation and Self-Assembly
Session Chairs: Sijie Chen and Xin Zhang
Tuesday Morning, April 25, 2023
SF05-virtual

9:00 AM *SF05.13.01
Tetraphenylbenzene-Based AIEgens—Preparation and OLED Application Anjun Qin; South China University of Technology, China

Aggregation-induced emitting (AIE), a scientific concept coined by Tang et al. in 2001, refers to a unique phenomenon that molecules that emit weakly or non-luminously in solutions are induced to emit intensely in the aggregate and solid states. Currently, the AIE luminogens (AIEgens) have been widely applied in diverse areas, and advantages over traditaional fluorophores have been well demonstrated. To further expand the research fields of AIE, more AIE cores besides tetraphenylethene, silole, and 9,10-distyrylanthrance, need to be designed and synthesized.
In this talk, I will report our recent efforts on development of tetraphenylbenzene-based AIEgens under the guidance of restrictiction of intramolecular rotation. At the same time, the application of them in blue/deep blue nondoped OLED will be discussed.

9:30 AM *SF05.13.02
Redox-Based Study Opportunities with AIEgens Towards Microalgae-Derived Health Supplements Youhong Tang; Flinders University, Australia

Reactive oxygen species (ROS) are oxygen derivatives comprised of hydrogen peroxide (H_2O_2), hydroxyl ions (OH^-), superoxide anions (O_2^-), and their secondary reaction products, produced by the metabolic redox reactions in living cells. ROS can be produced in chloroplasts, mitochondria, and several other subcellular compartments in photosynthetic organisms. Among the photosynthetic organisms, microalgae are a large group of unicellular organisms in marine and freshwater environments. These organisms possess a wide range of polysaccharides, lipids, proteins, antioxidants, vitamins, and pigments that could be exploited as sustainable nutritional and therapeutic supplements. These biomolecules synthesizing machineries could be triggered by altering the environmental conditions, such as nutrients or stress conditions. ROS formation often accompanies the stress-based strategies as an essential cellular component of responding to stress factors. In order to upstream the yield of the beneficiary biomolecules from microalgae, a further realization of the ROS interventions during their bioaccumulation processes could radically improve the production of these health supplements.
Recent advancements of aggregation-induced emission luminogens (AIEgens) offer remunerative sensing applications with strong photo-bleaching resistance, high signal-to-noise ratio, and large Stokes' shift. The photophysical properties of these AIEgens could be utilized in algal research for growth induction and essential biomolecules production through altering the ROS signalling pathways and light wavelength in favourable regime to improve their association in the biological application and health supplements from microalgae. However, photosynthetic organisms contain different biomolecules with their autofluorescence properties, selecting appropriate probes for the studies is very challenging and in demand. This could lead to the optical engineering of suitable photosensitizers to maximize the availability of the essential biomolecules in microalgae. Thus, utilizing organic luminogenic aggregates could provide us with a promising opportunity to develop algal technology for more significant health benefits.

10:00 AM *SF05.13.03
The Assembly of Inorganic Ionic Oligomers for Advanced Material Preparation Zhaoming Liu and Ruikang Tang; Zhejiang University, China

Polymerization and crosslinking of organic monomers or oligomers have made diverse bulk polymeric materials with advanced functions. Yet, it is hardly been achieved on inorganic ionic species for bulk materials preparation due to the different behavior of covalent and ionic bonds. Our recent works revealed that the inorganic ions can be assembled into inorganic ionic oligomers, which could act as precursors for bulk material synthesis *via* inorganic ionic polymerization and crosslinking. (Nature, 2019, 574, 394). In this way, the inorganic bulks could be moldable constructed as we making organic polymers. The inorganic ionic polymerization and crosslinking enabled multiple advanced structures preparation, such as biomimetic continuous amorphous-crystalline interface, biomimetic flexible mineral phase, biomimetic organic-inorganic interface, periodic mineral defects etc.. Based on such structures, we realized the moldable construction of hard minerals by particle fusion (Science, 2021, 372, 1466), regrowth of tooth enamel (Sci. Adv., 2019, 5, eaaw9569), fast (within 5 min) remineralization of human dentin (Adv. Healthc. Mater., 2022, 2201161), production of biomimetic unltra-tough materials (Angew. Chem. Int. Ed., 2020, 59, 2071; ACS Nano, 2022, 16, 7926), biomimetic humidity sensor (Adv. Funct. Mater., 2021, 2101291) and hybrid minerals as a new plastic substitute (Adv. Mater. 2022, 34, 2107523). Our works present the inorganic ionic oligomers as new precursors for advanced material preparation, shedding light on an alternative strategy to make marvelous inorganic and hybrid materials. It also emphasizes the unique and important role of making materials by aggregation and assembly of clusters through non-classical crystallization pathway.

10:30 AM SF05.13.04
Programmable Patterning of Cholesteric Liquid Crystals by Self-Assembly Lang Qin and Yanlei Yu; Fudan University, China

Responsive photonic crystals are widely employed to construct rewritable paper, where patterns are written and erased repeatedly via color switching. The working principle mainly lies in the changes on the lattice constant of periodic structures, which, however, restricts the localized color tuning of the recorded patterns and thus limits multicolor information transfer. Herein, a novel strategy is reported to write, erase, and importantly to tune the colors by developing unique light-driven cholesteric liquid crystals (CLCs) that possess self-organized helical superstructures with two structural elements of pitch lengths (lattice constant) and helical axes (reconfiguration). Reconfiguration of the helical axes provides two high-contrast optical states for writing and erasing by pressure and electricity, whereas precise photocontrol of the pitch lengths contributes to localized color tuning. These features primarily capitalize on the light-driven CLC with diverse photostationary colors, which is induced by a newly designed binary chiral system and confined in the polymer dispersed liquid crystal layer. Distinct multicolor patterns are mechanically written, optically tuned, and electrically erased on the rewritable photonic paper in a programmable manner. Such photonic paper has potential to record, program, and remember optically addressed images in visualized color information and user-interactive display technologies.

10:45 AM SF05.13.05
One Step Method to Simultaneously Growth TiO_2 Compact and Porous Layers for DSSC Photoelectrodes Arturo I. Espinoza[1], Ana L. Leal[2], Alicia Vera[2], Carlos Zúñiga[1] and Josue Aguilar[3]; [1]Instituto Nacional de Astrofísica, Óptica y Electrónica, Mexico; [2]Universidad de Sonora, Mexico; [3]Universidad Autónoma de Nuevo León, Mexico

Titanium dioxide (TiO_2) interest has increased considerably in recent years, owing to its exceptional optoelectronic properties and potential applications in electronic devices, such as photodetectors and DSSCs. In DSSCs, photoelectrodes play an important role. Typically, photoelectrodes must have a blocking and a porous layer of oxides to avoid electron leakage and to improve conversión efficiency. Typically, those layers are fabricated through different techniques or processes. In the present work, a one-step method for simultaneous fabrication of TiO_2 blocking and porous layers at relatively low temperatures is presented. In addition, samples with TiO_2 blocking and porous layers were characterized by FESEM/EDS, XRD, and UV-visible spectroscopy techniques with the purpose of determining their structural characteristics, morphology, optical behavior, and bandgap. As result, crystalline TiO_2 blocking and porous layers were successfully obtained and tested as photoelectrodes for DSSCs. The best oxide materials obtained by the developed process correspond to the Anatase phase, which is formed by a TiO_2 compact layer and a porous layer of particles of 100-200 nm, the optical band gap of 3.30 eV, and optical bandwidth comprises the visible range with applications in DSSC photoelectrodes.

SESSION SF05.14: Virtual Session II: Building Advanced Materials via Aggregation and Self-Assembly
Session Chairs: Shuai Zhang and Xin Zhang
Wednesday Morning, April 26, 2023
SF05-virtual

10:30 AM SF05.14.01
Lightweight High-Strength Nano-Architecture Silica Templated from 3D DNA Frameworks Aaron N. Michelson[1], Tyler Flanagan[2], Seok-Woo Lee[2] and Oleg Gang[3,1]; [1]Brookhaven National Laboratory, United States; [2]University of Connecticut, United States; [3]Columbia University, United States

Nanolattices are an emerging class of mechanical metamaterials highly attractive due to their superior strength-to-weight ratios which originate from their complex spatial architectures and the nanoscale-sized elements that usually possess near-theoretical strength. Despite much interest, rational design and fabrication of nanolattices remains challenging, particularly when the dimension of element is less than 50 nm, because it is extremely difficult to arrange such small elements into complexly designed three-dimensional structures. In this study, we solved this problem and successfully fabricated silica nanolattices with ~4-20nm thick elements using self-assembly and silica templating of DNA origami ordered frameworks. In-situ micro-compression testing was performed to examine the mechanical properties. We observed the strong effects of lattice dimensions on yield strength and failure mode. Nonetheless, all silica nanolattices were found to exhibit yield strengths much higher than those of any known engineering materials with the similar mass density. The robust octahedron coordination of the extremely thin silica elements with ultrahigh strength leads to the excellent combination of light-weight and high-strength. Our results show that DNA-based self-assembly offer an effective approach for a fabrication nano-architectured lattices with superior mechanical properties.

10:45 AM SF05.14.02
Thermal-Responsive Poly (N-isopropyl acrylamide)/Divalent Cation Alginate Hydrogels Chenyan Zhao, Jiusi Chen and Zhaowei Yuan; National University of Singapore, Singapore

Temperature-responsive hydrogels with enhanced mechanical properties are desirable in intelligent device area including artificial electronic skin and soft robotics. In this contribution, poly(N-isopropyl acrylamide)/sodium alginate (PNIPAM/Ca-alginate) and PNIPAM/Fe^{2+}-alginate hydrogels were prepared by a two-step strategy, obtaining hydrogels with two kinds of cross-linking: chemical cross-linking and ionic cross-linking. Maintaining the excellent water harvesting ability, the hydrogels exhibited improved mechanical properties compared with that of the PNIPAM/Alg hydrogel and the compressive strength of 2 hydrogels depended significantly on the cross-linking density. Meanwhile, compared with the traditional single network, the ‘egg-box’ structure of these hydrogels performed better stability with the formation of channels from which water diffuses easily during swelling and deswelling.

10:50 AM *SF05.14.05
Luminescent Aggregate Materials Based on Excited-State Molecular Motion Regulation Zheng Zhao; The Chinese University of Hong Kong, Shenzhen, China

Aggregates include powder, nanoparticles and film serve as a particularly useful form of materials that often display new properties compared to their molecular components. Aggregation-induced emission is one of the most representative examples of aggregate materials. In the following presentation, we will introduce our research development in regulating excited molecular motion of AIE materials and our exploration in utilizing excited state molecular motion regulation to achieve addition function of AIE materials besides luminescent property. The involve contents include luminescence mechanism study, new structure design and application exploration. What we want to claim is that molecular structure design is much significant for materials science, however, from molecules to solid state materials, a lot of things happen during the aggregation process, which may endow molecules with many new properties and functions. Elucidating the new emerging properties and the underlying mechanism is of great significance. We have coined this as aggregate science

11:20 AM SF05.14.06
Magnesium Hydroxy Carbonate Hydrates—Nature-Inspired Water Filters for Heavy Metal Sequestration Anton Sednev-Lugovets[1], Yang Lu[1], Ørnulv Vistad[2], Håkon Austrheim[1], Henrik Friis[1], Patricia Carvalho[2] and Matylda Guzik[1]; [1]University of Oslo, Norway; [2]SINTEF Industry, Norway

The climate change, growing world population, together with a widespread use of chemicals in industry and our everyday life, are projected to reduce water availability in sufficient quantity and quality. Heavy metal contaminations have a seriously damaging impact on the quality of water bodies, imposing a great burden on downstream users and ecosystems. Although, natural materials, such as charcoal, sand and diatomaceous earth, have been already incorporated into modern water filtration systems (1), there is still a great need for highly efficient and environmentally sustainable sorbents.

Motivated by this challenge, we focus our research on investigation of nature-inspired sustainable functional materials and their application in water filter technologies.

Magnesium hydroxy carbonate hydrates are a relatively small group of naturally formed minerals that have been widely investigated for large-scale CO_2 sequestration. However, our recent study has shown that these compounds can also effectively remove heavy metals (e.g., Cr, Cd, Cu, Pb, Ni (2)) from water and act as water filters (3,4). Two members of this mineral family: ***1)*** dypingite (named in ’70s by Gunnar Raade, after the Dypingdal serpentine-magnesite deposit in Norway), and yet ***2)*** unnamed compound (hereafter referred to as UPh, a new crystalline phase identified by us while studying dypingite samples), deserve particular attention due to their unique desert rose morphology. The term “desert rose” designates self-assembled microstructures with clusters organized into fanning platelets. These 3D configurations exhibit hierarchical features that span across multiple length scales and present high specific surface area, which are crucial for many applications including sorption. Despite the remarkable sorption performance, information about the dypingite and UPh structural properties is surprisingly limited. Even though, the naturally occurring dypingite was a subject of several investigations (5,6), the available data on the material chemical composition, in particular

water content, and structural features are inconsistent. The synthetic dypingite minerals has also been obtained but none of the applied approaches resulted in the formation of desert rose-like microstructures, occurring exclusively in naturally formed compounds. For better understanding of phenomena behind the physical & chemical performance of both minerals, the systematic and detailed material analysis is indispensable.

To partly fill this gap, we have been performing comprehensive structural, microstructural and functional studies on natural and synthetic samples of both minerals that allow us: ***i)*** to define optimum synthesis conditions for the formation of materials with desert rose morphologies, ***ii)*** to determine relationship between the material structural/microstructural characteristics and its heavy metal sorption capacity, ***iii)*** to define the compound stability range, and ***iv)*** to identify unique powder X-ray diffraction patterns of both phases, in order to solve their crystal structures.

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